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On behalf of the organizing committee, we are pleased to announce that the 3th International Conference on Environmental Science and Technology (ICOEST-2017) is held from October 19 to 23, 2017 in Budapest. ICOEST 2017 provides an ideal academic platform for researchers to present the latest research findings and describe emerging technologies, and directions in Environmental Science and Technology. The conference seeks to contribute to presenting novel research results in all aspects of Environmental Science and Technology. The conference aims to bring together leading academic scientists, researchers and research scholars to exchange and share their experiences and research results about all aspects of Environmental Science and Technology. It also provides the premier interdisciplinary forum for scientists, engineers, and practitioners to present their latest research results, ideas, developments, and applications in al lareas of Environmental Science and Technology. The conference will bring together leading academic scientists, researchers and scholars in the domain of interest from around the world. ICOEST 2017 is the oncoming event of the successful conference series focusing on Environmental Science and Technology. The scientific program focuses on current advances in th eresearch, production and use of Environmental Engineering and Sciences with particular focus on their role in maintaining academic level in Science and Technology and elevating the science level such as: Water and waste water treatment, sludge handling and management, Solid waste and management, Surface water quality monitoring, Noise pollution and control, Air pollution and control, Ecology and ecosystem management, Environmental data analysis and modeling, Environmental education, Environmental planning, management and policies for cities and regions, Green energy and sustainability, Water resources and river basin management. The conference's goals are to provide a scientific forum for all international prestige scholars around the world and enable the interactive exchange of state-of-the-art knowledge. The conference will focus on evidence-based benefits proven in environmental science and engineering experiments.

Best regards,

Prof. Dr.Özer ÇINAR

CONTENT	PAGE

Cost Evaluation of Aqueous Solutions Containing of Anionic Surfactant by US Process Treatability

Eylem TOPKAYA[1], Ayla ARSLAN[1], Sevil VELI[1]*

Abstract

In this study, treatability of LINEAR alkyl benzene sulphonic acid (LABSA) from anionic surfactants were made by ultrasound method from advanced oxidation processes and cost analysis. Treatment of LABSA were evaluated by detergent removals. The removal efficiency and cost effects were investigated for concentration (5-20 mg/L), pH (5-10), reaction time (0-120 min), amplitude (Am=60-80%) and energy consumption parameters. The highest removal efficiency was found 76% for 20 mg/L LABSA concentration, pH=5.5, 90 min reaction time, 80% amplitude and consumption of 0.105 kWh energy. As a result of the cost analysis; in the same experiment conditions for 60 min reaction duration time by 0.065 kWh energy consumption 75% recovery yield was obtained and the unit cost of the treatment was determined as 0.168 Euro/gLABSA.

Keywords: *Anionic surfactant, Cost, Treatment, Ultrasound method.*

1. INTRODUCTION

Surfactans are come from two groups of molecules as hydrophobic and hydrophilic and grouped taking into account the chemical structure of the hydrophilic group contains [1]. They are separated to 4 groups as anionic, cationic, non-ionic and amphoteric according to the hydrophilic part load. Surfactants are a wide group of chemicals that play an important and a big role in different applications as cleaning, food, textile, metallurgy, pharmacy, medicine, painting and polishing, mining and many more [2].

Anionic surfactants are known as products containing of one or more functional groups ionized in water to produce organic ions. Linear alkyl benzene sulphonic acid (LABSA) is the most commonly used anionic surfactant. Many detergents are contain large amounts of anionic surfactants. LABSA is the most important raw materials using in detergent manufacturing industries [2].

Due to the production volume, these substances enter high correlating group of chemicals with the environment [2]. These substances have limited biological treatability in domestic and industrial wastewater treatment plants and they reach the receiving environments by abandoning the conventional wastewater treatment plants without structural modification [3]. They have shown accumulation at different concentrations in the surface waters, bottom sediments and soil and composed of a hazard in terms of health and environment. For this reason, wastewater containing these substances needs to be treatment efficiently before being delivered to receiving media [4], [5]. Advanced oxidation processes (AOPs) as alternative chemical treatment technologies for these pollutant treatments are envisaged and given weight to work this direction in recent times [6]- [9].

* [1]*Corresponding author: Kocaeli University, Department of Environmental Engineering, 41380, Izmit/ Kocaeli, Turkey.* *eylem.topkaya@kocaeli.edu.tr*

[1] *Kocaeli University, Department of Environmental Engineering, ataberk@kocaeli.edu.tr ; sevilv@kocaeli.edu.tr*

Advanced Oxidation Processes (AOPs) are based on the free radicals reaction, primarily the hydroxyl radical (HO•) which is usually very high oxidation potential for difficult decomposition, inert or toxic pollutants [6], [10]. In these methods, the toxicity of the target pollutant is eliminated with partial oxidation and/or the pollutant is converted into biologically more easily decomposable oxidation intermediates, in some cases the pollutant is oxidized up to oxidation end products such as CO_2 and H_2O [7], [11], [12]. Recently, ultrasonic (US) processes and applicability of AOP methods have begun to gain importance [13]-[16].

The ultrasound process is a chemical oxidation method provided by ultrasonic waves. The reactions performed by US processes are sonochemical reactions. This process is used electric energy generating devices to spread the sound waves to the environment. Ultrasound waves spreading in the medium they give rise to cavitation in water while moving. Cavitation is an event of bubbels build, grow and burst by energizing very large quantities, due to the pressure changes in the liquid medium

formed by sound waves [17], [18]. In the ultrasound process, the sound waves given to aquatic environment at a suitable temperature and pressure are caused formation of radicals such as H•, HO•, HO_2•, H_2O_2 in the liquid by changing the physical and chemical composition of water. These radicals provide to converting into such as CO_2, N_2, NO_3, COOH stable end products or less harmful compounds of the toxic and organic compounds in wastewater [19], [20]. Although chemicals are not used in these processes, these are preferred because of they are efficient.

In this experimental study, works were made for determining the best treatment and cost under different conditions by using US process which is sonochemical AOP for aqueous solutions containing of LABSA from anionic surfactants. The efficiency of the processes were determined by observing the change of the detergent concentration parameter.

2. MATERIALS AND METHODS

2.1.Materials and samples

The raw material of LABSA ($CH_3(CH_2)_{11}C_6H_4SO_3H$) was supplied from a detergent factory. The pH of the solution was adjusted using 1N NaOH or 1N H_2SO_4, other the experiments were carried out as such at the original solution pH.

2.2.US System

SONOPULS HD 3400 model (brand of BANDELIN) probe type ultrasonic device was used for ultrasonic process (frequency of 20 kHz, maximum power of 400 W). US device probe (VS200T probe), which is 25 mm in diameter, 130 mm in length, 82 µm in amplitude and 20 kHz in frequency, is a titanium probe. The capacity of the device is 100-2500 mL. The probe of the ultrasonic device was immersed into the water as it would be exactly in the middle of the reactor and 3 cm from the bottom of the reactor. The lateral wall of the reactor was filled with cooling water in order to keep the solution temperature at (25±2)^{o}C. The system was established into the sound-proof cabinet partly preventive to the noises.

2.3. Analysis

US experiments were performed with 1L LABSA solution. A digital pH-meter (HACH, HQd) was also used for pH measurement and 1N H_2SO_4 or 1N NaOH were used to adjust the pH. Concentration of surfactant was measured by using the methylene blue anionic surfactant (MBAS) analysis, according to the standard methods for the examination of water and wastewater [21]. Concentration of LABSA was calculated from the absorbance read at 652 nm. In US probe applications, the experiments were made pulse off application for preventing temperature control and probe heating.

3. RESULTS and DISCUSSION

3.1. The Effect of pH on Yields

In this study, LABSA which is an anionic surfactant was examined with treatment by US process from over the detergent removal efficiency for different concentartion 10-20 mg/L and different range of pH (5-10) (Figure1).

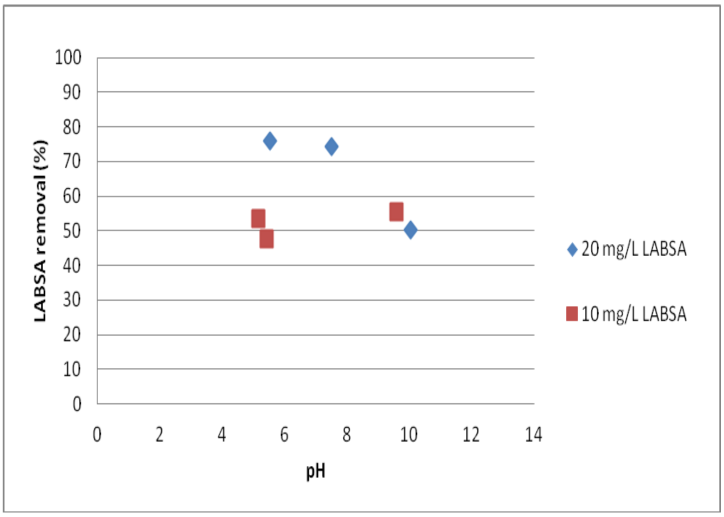

Figure 1. Effect of pH on LABSA removal efficiency (t= 90 min)

According to Figure 1; a yield of 76% was obtained at pH = 5.5, 20 mg / L LABSA concentration and 90 min reaction time. The LABSA removal yield was remained between 50-55 % at alkaline conditions above pH =7.5. LABSA removal efficiencies were found to be better at acidic pH. The maximum removal efficiency has been seen generally under acidic conditions at the US processes working in the literature [13], [22].

3.2. Effect of Anionic Surfactant Concentration on Yields

The experiments were made at 5-10-20 mg/L concentration range, at different pH(5-10) and 90 min reaction time to determine the effect of LABSA concentration on yield (Figure 2).

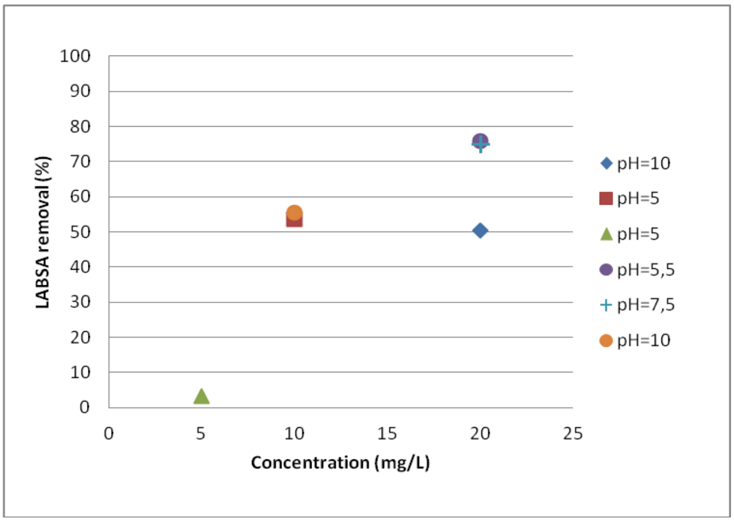

Figure 2. Effect of initial LABSA concentration on yield (t=90 min)

As can seen from Figure 2, when the amount of concentration was decrease, removal efficiency was decreased too. According to the best removal efficiency (76%), initial LABSA concentration was determined to 20 mg/L.

3.3. Effect of the Reaction Time on Yields

After the initial LABSA concentration was determined to 20 mg/L, studies were made under 30-120 min reaction conditions to determine the effect of time (Figure 3).

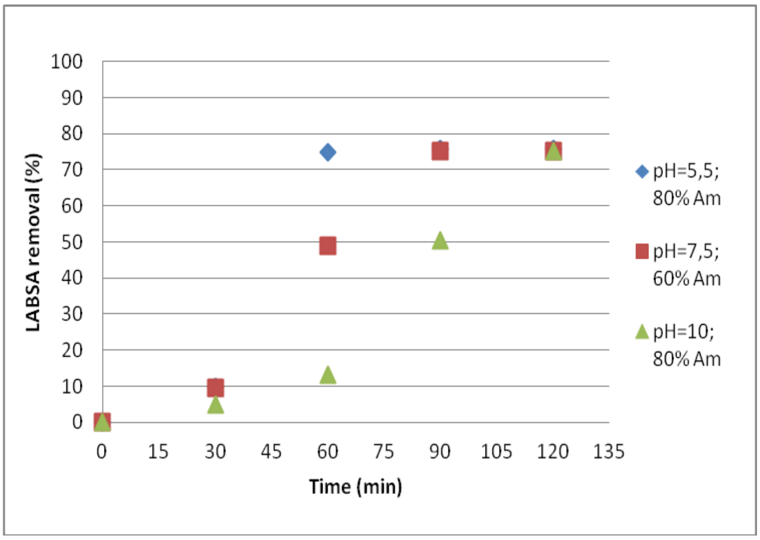

Figure 3. Effect of reaction time on LABSA removal efficiency (Co= 20 mg/L LABSA)

According to Figure 3, after from 60 min at pH = 5.5 at 20 mg / L LABSA concentration, there was no increase or decrease in recovery efficiency, but the yield was fixed at 75-76%. At pH = 7.5 the yield was increased when the reaction time increased to 90 min, and after 90 min the removal efficiency was fixed at 75%. At pH = 10, when the yield increased the reaction time increased too.

3.4. Effect of the Amplitude (Am) on Yields

LABSA removal efficiencies were investigated at different ultrasonic amplitudes (Am=60-80%) with the ultrasound process, when the amplitude amount increased the removal efficiencies also increased and the removal efficiency was maximum in less time for 80% amplitude. The solution environment was mixed in a good way with increasing the amplitude value of the US instrument, and contributed to the acceleration of the sono-sorption process. The effects of amplitude on LABSA removal efficiency was shown in Figure 4.

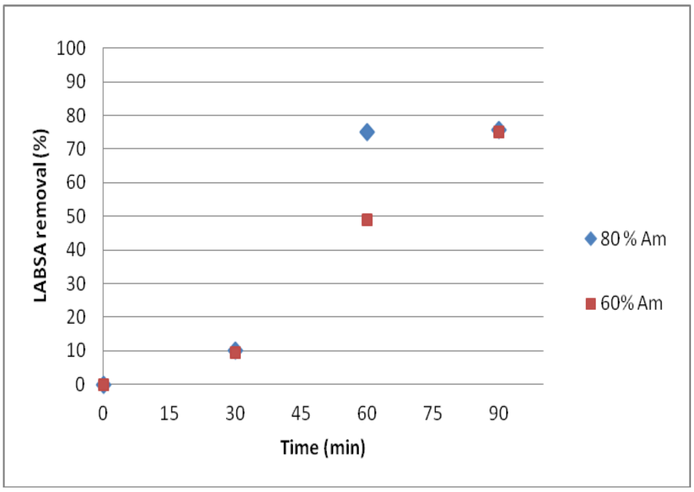

Figure 4. Effects of amplitude on LABSA removal efficiency (C_0=20 mg/L LABSA, pH=5,5)

As seen in Figure 4, when the amplitude value was 80 %, LABSA removal efficiency was determined as 75 % in the 60th minute. When the Amplitude value was 60%, removal efficiency 75% was reached at the longer reactions time (90 min).

In similar studies with US processes show that, the removal efficiencies also increased when the amplitudes increased [23], [24].

3.5.Effect of Energy Consumption the US Process

Energy consumption becomes for operation of the US process. The energy consumption reading from device is in kJ units. The effect of consumed energy on yield is indicated in Figure 5, according to the study results doing the 90 min reaction time, at 10-20 mg/L LABSA concentration, 60-80% Am values and range of pH=5-6.

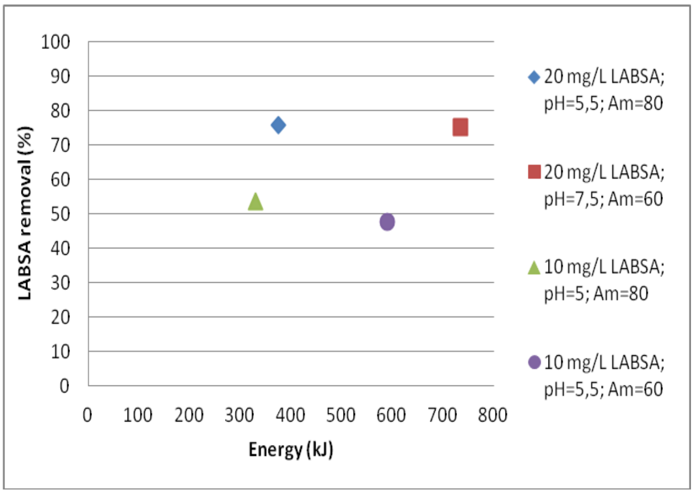

Figure 5. Effect of energy consumption on LABSA removal efficiency (t=90 min)

According to Figure 5; more recovery efficiencies have been achieved by consuming less energy at high (20 mg / L LABSA) and low concentration (10 mg / L LABSA) and high Am (80%) values, 375,997 kJ (76% removal yield) and 331,121 kJ (54% removal yield), respectively.

3.6. Evaluation in Terms of Cost

In this work, studies were made for the purification of LABSA with US process experiments to do at different concentrations, pHs, amplitudes and reaction times. Calculations have been made to according to the US process consumed energy (kJ) in kWh and to the amount of consumed chemical for pH adjustment. The unit cost of the treatment is calculated in Table 1 to determine the suitability of the results of these studies in terms of cost.

Table 1. US process operating costs calculated for different experimental conditions

LABSA conc. (mg/L)	pH	Am (%)	Time (min)	LABSA removal (%)	US Energy consumption (kJ)	US Energy consumption (kWh)	US Energy consumption (Euro)	pH adjustment (Euro)	Total (Euro)	Euro / g LABSA
20	5.5	80	30	10	179.627	0.04994	0.0026	0	0.0026	0.130
20	5.5	80	60	75	232.047	0.06451	0.0034	0	0.0034	0.168
20	5.5	80	60	75	240.050	0.06673	0.0035	0	0.0035	0.173
20	5.5	80	90	76	375.997	0.10453	0.0054	0	0.0054	0.272
20	5.5	80	120	76	484.912	0.13481	0.0070	0	0.0070	0.350
20	10	80	60	13	281.086	0.07814	0.0041	0.000259	0.0043	0.216
20	10	80	90	50	441.474	0.12273	0.0064	0	0.0064	0.319
20	10	80	120	75	569.649	0.15836	0.0082	0	0.0082	0.411
5	5	80	90	3	344.191	0.09569	0.0050	0	0.0050	0.994
10	5	80	60	51	216.119	0.06008	0.0031	0	0.0031	0.312
10	5	80	90	54	331.121	0.09205	0.0048	0	0.0048	0.478
10	5.5	60	30	8	239.579	0.06660	0.0035	0.000037	0.0035	0.350
10	5.5	60	60	11	448.761	0.12476	0.0065	0	0.0065	0.648
10	5.5	60	90	48	590.689	0.16421	0.0085	0	0.0085	0.853
10	10	60	30	34	227.599	0.06327	0.0033	0.000603	0.0039	0.389
10	10	60	60	37	525.873	0.14619	0.0076	0	0.0076	0.760
10	10	60	90	55	784.46	0.21808	0.0113	0	0.0113	1.133
20	7.5	60	60	74	605.956	0.16846	0.0088	0.000076	0.0088	0.441
20	7.5	60	90	74	918.891	0.25545	0.0133	0	0.0133	0.664
20	5	60	30	10	214.302	0.05958	0.0031	0.000051	0.0031	0.157
20	5	60	60	49	424.45	0.11800	0.0061	0	0.0061	0.307
20	5	60	90	75	733.936	0.20403	0.0106	0	0.0106	0.530
20	5	60	120	75	1116.203	0.31030	0.0161	0	0.0161	0.806

According to Table 1, the highest LABSA removal efficiency was determined to 76% with asidic conditions, at 20 mg/L LABSA concentration, 80% Am, 90 min recation time and 0.105 kWh energy consumption. The unit cost of this study was calculated as 0.272 Euro/g LABSA.

In the same conditions as 60 min reaction time removal efficieny was obtained to 75% by consuming 0.065 kWh energy. The unit treatment cost was calculated as 0.168 Euro/g LABSA. According to these results, the optimum treatment cost for this study was determined as 0.168 Euro/g LABSA because of the duration of the reaction prolongation didn't seriously changed of the yield and caused more energy consumption.

4. CONCLUSION

In this study, Treatability of water containing anionic surfactant by US advanced oxidation process was investigated in detergent removal efficiency and evaluated in terms of cost. In experiments of the 1L LABSA aqueous solution at different concentrations and different US amplitudes; the highest LABSA removal efficiency was obtained to 76% at Am= 80%, 20 mg/L concentration of LABSA and 90 min reaction time. As the prolongation of treatment times increases energy consumption, this situation affects the cost values negatively. For this reason, 60 min reaction time removal efficiency was obtained to 75% for in the same condition, this treatment was evaluated in terms of cost and the unit cost value was determined as 0.168 Euro/g LABSA. In this context, it can be said that the US process method is a feasible method for the treatment of detergent raw material and also in terms of cost.

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BIOGRAPHY

Eylem TOPKAYA; completed her undergraduate degree in 2004-2009 at Uludag University, Department of Environmental Engineering. She completed her master's degree in 2011-2014 at Gebze High Institute of Technology (GYTE), Institute of Natural and Applied Sciences, Department of Environmental Engineering. She has started her PhD education in 2014 at Kocaeli University, Institute of Natural and Applied Sciences, Department of Environmental Engineering and she is still in progress.

The effects of cadmium doses on plant characteristics of CAB-6P (*Prunus cerasus* L.)

Murat SAHIN[1], Lutfi PIRLAK[2], Ahmet ESITKEN[3], Fatma Nur DEVECI[4]

Abstract

Cadmium (Cd) is among the rare elements found in nature that are not necessary for plants. Cd is considered to be an important contaminant because its half-life is long and it is toxic at very low doses. Cadmium is found in all agricultural soils, with varying amounts (mostly in low quantities). However, uptake of Cd is easier by plants in low pH soils.

The study was carried out in the growing room and greenhouse in 2016 and CAB-6P (Prunus cerasus L.) cherry rootstock was used as plant material. Plants produced with seed were kept in a growth chamber until 50 cm length was reached. As a growing medium, a mixture of peat/perlite (2/1 v/v) was used. Plants reaching 50 cm were transferred to the greenhouse in 5 liter pots. As from June 25, 150, 300, 450 and 600 µM cadmium have been applied to each plant once a month. The study design was planned as 3 replications and each repetition had one plant. As of November the plants have been dismantled. The data obtained were assessed at the $P \leq 0.05$ level in the IBM SPSS (20.0) package statistical program with one-way variance analysis (ANOVA) and subjected to the Duncan Multiple Comparison Test.

The treatments that have the greatest negative effect on plant characteristics are as follows: trunk diameter (450 µM: 9.29 mm), root collar diameter (600 µM: 10.59 mm), plant height (600 µM: 64.67 cm), stem fresh weight (600 µM: 64.20 g), stem dry weight (600 µM: 17.73 g), root length (600 µM: 28.00 cm), root volume (600 µM: 83.00 cm^3), root fresh weight (600 µM: 78.28 g), root dry weight (600 µM: 25.25 g), leaf area (600 µM: 25.48 cm^2), leaf-relative water content (600 µM: 76.14 %), stomatal conductance (600 µM: 207.43 mol $m^{-2}s^{-1}$) and chlorophyll content (600 µM: 53.52 µg/cm^2).

According to the results obtained from recent study, Cd treatments reduced plant growth. Even the lowest cadmium dose has significant negative effects on plant characteristics.

Key Words: *Cadmium, cherry rootstock, heavy metal, plant characteristics.*

1.INTRODUCTION

The elements are divided into two main groups, metal and non-metals [1]. The main difference between metal and non-metals is the difference in electron acceptance requirements in the reactions they enter. While metals tend to give electrons in reactions, non-metals tend to get nonetheless.

In the case of negative effects of metals on plants, 'heavy metal' phrase is used. The main reason for this is that metals (the density is over 5 grams) such as zinc [Zn (7.1 g/cm^3)], chromium [Cr (7.2 g/cm^3)], cadmium [Cd (8.6 g/cm^3)], nickel [Ni (8.7 g/cm^3)], copper [Cu (8.9 g/cm^3)], lead [Pb (11.4 g/cm^3)] and mercury [Hg (13.5 g/cm^3)] are harmful for plants. However, it can also show similar damages by metals such as aluminium [Al (2.75 g/cm^3)]. Some metals such as copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni) and cobalt (Co) are micronutrient elements necessary for plant and animal development. Whether or not a micro-nutrient is present, a certain amount of all metals are harmful for living beings [2].

In order to prevent heavy metal welded soil pollution; pollutants such as city and industrial wastes must be mixed into the soil after purification. Besides, precautions such as planting of the plants that store heavy metals in the areas where the pollutants are concentrated and contaminated soils are the foreground. However, in areas where heavy metals are contaminated or are in danger of contamination, it is necessary to select species and varieties with high resistance to heavy metals in such areas in order to be able to do agriculture [2].

The uptake of the metal can vary depending on the plant species and cultivar. Properties such as root cation exchange capacity and root surface area of plants can affect metal uptake. Plants can affect metal uptake by changing the pH of the rhizosphere with the substances secreted from their roots (malat, citrat, musilaj) ([3], [4], [5]). It is assumed that Cd^{2+} ions enter plant roots through Ca^{2+} channels via Fe^{2+}, Zn^{2+} and Mn^{2+} transporters [6]. This idea is derived from the fact that an Arabidopsis mutant, which cannot express the IRT1 gene that provides Fe^{2+} ion transport, cannot accumulate Mn^{2+}, Zn^{2+}, and Cd^{2+} ions in the low iron conditions ([7], [8]). In addition, high amounts of zinc and cadmium in the roots of mutants with this gene overexpression support this idea [9]. There is also evidence that plants receive Cd2 + from their roots via NRAMP pumps [10] and their leaves via stomata [11].

The plants carry the metals they receive with their roots to trunk and leaves by xylems. However, the transport differs according to plant species and metals. Although cadmium is transported in the xylem in ionic form [12], there are ideas that organic acids also play a role in transport [13]. Cadmium is deposited in the vacuoles of the stem cells after entering the plant roots and charged in xylem with binders such as phytocelatins, glutathione and sulfur donor ligands. After that, the cadmium ion is stored in different parts of the plants (seeds, mesophyll tissues, cell wall etc.) in varying amounts depending on the cadmium tolerance ([14], [15]). Studies on the presence of metal transport in the phloem have shown that Cd has a partial transport in the applied leaves [16]. However, studies carried out with Cd, Cu and Zn have indicated that the transport does not extend from the leaves to the roots. This is attributed to the fact that living cells that constitute the phloem prevent metal transport through ions and molecules that can bind metals [13].

In higher plants, Glutathione [17], Selenium Binding Protein [18], Ergotoine [19], Phytocelatins [20], Metalothioneins [21], Ko-Enzyme-M, Tripanotiones and Mythiols [6] are cadmium binders. It has been reported that these bind the cadmium ions to cell structures more or less. In addition, it should also be noted that some physiological events involving these substances that bind cadmium are affected adversely [6]. Studies have shown that plants accumulate these metals in extracellular carbohydrates and cell walls when exposed to high concentrations of metals (Cr, Co, Ni, Zn, Cu, Mo, Cd and Pb) ([22], [23]).

Excessive exposure to metals causes many changes in plants. Some of the damage caused by these changes is visible and measurable (morphological changes), while the detection of the majority requires complex biochemical analyzes. The first and most obvious effect of metal damage is found in the roots because of the metal-containing environment ([24], [25]). Roots exposed to excessive metal doses may be seen to be shorter than normal plant roots, decrease in the number of hairy root, increase or decrease in the number of side roots. In addition, lignification in roots and some structural changes in epidermis and hypodermis have been identified. As the plant continues to be exposed to excess metal doses, the effect begins to show up in the tree trunk and the plant height is also affected. At the same time, fresh and dry weight reduction is observed in plants and plant growth slows down ([26], [24], [27]). In addition, depending on the type and density of the metal, changes in leaf formations, area reduction in leaves, clorosis and necrotic spot formation can be seen [2]. The reduction of water and ion uptake by plants under cadmium stress is the most important cause to prevent root growth and development. In addition, due to the closure of stomata in plants under cadmium stress, transpiration reduces water loss and prevents cadmium uptake and transport [28].

2.MATHERIALS and METHODS

The study was carried out in the growing room and greenhouse belonging to the Department of Horticulture of the Faculty of Agriculture of the Selcuk University in 2016. In this study effects of cadmium treatments on CAB-6P (*Prunus cerasus* L.) cherry rootstocks were investigated. As from June 25 cadmium have been applied to each plant once a month. The study design was planned as 3 replications and each repetition had one plant. The treatments are; control, 150 µM Cd, 300 µM Cd, 450 µM Cd and 600 µM Cd doses.

Plants produced with seed were kept in a 2 liter pots at a temperature of 27,5ºC / 22,5ºC (day/night) and 14/10 (day/night) day length in a growth chamber until a certain length (50 cm) was reached. As a growing medium, a mixture of peat/perlite (2/1 v/v) was used. When plants reach 50 cm length, they were transferred to the greenhouse in 9-liter pots and necessary cultural processes were carried out during the adaptation period. As of November the plants have been dismantled. Plant trunk diameter (5 cm above ground), root collar diameter (just above first lateral root), plant height (from ground to top), stem fresh and dry weight (just above first lateral branch to top), root length (from first lateral root to tip of longest root), root volume (all of root from first lateral root), root fresh and dry weight (all of root from first lateral root), leaf area (surface of leaf), leaf-relative water content (difference of fresh and dry leaf weight), leaf chlorophyll amount (measured with Konica-minolta chlorophyll meter spad- 502 plus) and stomatal conductance (measured with SC-1 leaf porometer) were investigated. The data obtained were assessed at the $P \leq 0.05$ level in the IBM SPSS (20.0) package statistical program with one-way variance analysis (ANOVA) and subjected to the Duncan Multiple Comparison Test.

3.RESULT AND DISCUSSION

3.1. Trunk (TD; mm) and Root Collar Diameter (RCD; mm)

Plant trunk diameter (TD) and root collar diameter (RCD) are severely affected by the environmental factors to which the plant is exposed. Although TD and RCD are not the first affected plant parts, they are severely affected by long-term factors (positive or negative). Cd is also one of the factors that adversely affect TD and RCD in the long-term. In the study conducted, although TD and RCD were affected in the negative way by cadmium, the effect on the TD in particular is not significant in terms of statistical significance. The effect of Cd treatment on the trunk diameter was negative in parallel with the dose increase. However, the effect on the trunk diameter of Cd treatments was limited due to the low doses and the limited period. As expected, the maximum loss was seen in 600 µM Cd treatment. In a study done by Elobeid et al. [25] (0 and 50 µM Cd treatment, with nutrient solution), TD began to decrease 15th day after Cd treatment. After the 20th day the difference was obviously increased and TD of the plants to which Cd was applied decreased. The results obtained from the recent study are similar to those obtained from the above study.

Considering the RCD, the negative effect of Cd treatments is more apparent than TD. This may be cause the root collar is in contact with the soil containing Cd. The most damaging treatment, as in TD, is 600 µM Cd treatment. However, 450 and 300 µM Cd treatments take place same statistic group with 600 µM Cd treatment. The RCD of *Achnatherum inebrians* plants grown in silt-clay soils applied with 0, 50, 100 and 200 µM Cd by watering with Hoagland solution (1 month) was significantly reduced [29]. In addition, the RCD of Radish (*Raphanus sativus* L.) plants grown at 0, 100 and 150 mg kg^{-1} Cd applied to the soil decreased in two growing season [27]. The results of these two studies are similar to results of the current study. As can be seen, according to the current study with previous studies, Cd treatments reduce RCD of plants. It is noted in previous studies that the causes of TD and RCD reductions are Cd treatments. According to this, Cd: 1. reduces synthesis of cell-wall components and changes the polysaccharide metabolism [30], 2. interfere water and nutrient uptake and photosynthesis [31] and 3. decrease cell turgor potential and cell wall elasticity that lead to formation of small cells and intercellular space areas [32].

Table 1. Effects of Cadmium treatments on Trunk Diameter (TD), Root Collar Diameter (RCD), Plant Height (PH), Stem Fresh Weight (SFW) and Stem Dry Weight (SDW).

	TD (mm)	RCD (mm)	PH (cm)	SFW (g)	SDW (g)
Control	9,81^{a}	12,96^{a}	80,67^{a}	84,22^{a}	30,90^{a}
150 µM Cd	9,80^{a}	12,71^{a}	77,67^{b}	79,98^{b}	28,41^{b}
300 µM Cd	9,69^{a}	11,17^{b}	71,33^{c}	76,87^{c}	23,29^{c}
450 µM Cd	9,29^{a}	10,64^{b}	66,17^{d}	70,89^{d}	19,35^{d}
600 µM Cd	9,52^{a}	10,59^{b}	64,67^{d}	64,20^{e}	17,73^{e}

3.2. Plant Height (PH; cm)

The plant height is at the top of the properties that are affected positively or negatively by environmental factors. In particular, stress factors that damage plants such as heavy metals have a negative effect on plant height. In the present study, the plant height was shortened in parallel with the increasing Cd doses. Plants applied 150 µM Cd were found 3 cm shorter than control, whereas plants applied 600 µM Cd were found 16 cm shorter than control. This reduction is considerably higher for 300, 450, and 600 µM Cd treatments when the reduction in PH is limited in 150 µM Cd treatments. When previous studies were examined, it was seen that Cd treatments decreased plant height. In some studies, the results were examined on a daily basis at the end of the treatment and changes in plant height were observed with time. According a study done in the sunflower by Azevedo et al. [24], on 3rd day after Cd supplementation, all treatments (0, 5, 50, and 500 µM) were equal in length, but on 8th day differences began. On the 8th and 15th days of the 500 µM Cd treatment, the plant size remained the same and on the 21st day the plants died. In another study, the difference between Cd treatments (0 and 50 µM) began to appear on day 7th, became more pronounced on 12th, and doubled on 24th day [25]. The studies done in the hydroponic environment, the results were obtained as end of the experiment and similar results were obtained with the above studies. According to Ouzounidou et al. [33] (0, 265, 530 and 1000 µM Cd), 265 µM Cd was significantly reduced plant height compared to the control. In other treatments, despite the reduction in plant height, the greatest difference was observed between control and 265 µM Cd doses. Farooqi et al. [34] conducted 6 different (0, 10, 30, 50, 70 and 90 µmol/L) Cd treatments in *Abizia lebbeck* (L.) Benth. According to the study, the most severe reduction was observed in the treatment of 90 µmol/L although the plant length shortened from 10 µmol/L Cd treatment. As can see above, the current study is compatible with previous studies. According to the results obtained from experiments carried out in different growing environments, Cd treatments have negative effects on plant height. However, the growth media can affect the minimum Cd dose that causes damage.

3.3. Stem Fresh (SFW; g) and Dry Weight (SDW; g)

The leaves of plants are organs most affected by environmental factors due to their high water content and susceptibility. The first effects of the factors on the plants are usually seen on the leaves. Changes in weights of leaves and fresh shoots cause changes in SFW and SDW. Heavy metals such as Cd slow down the growth of plants (leaves and fresh shoots in short-term and trunk in long-term) by preventing water and mineral intake from the soil. In the current study, this negative effect of Cd doses is obvious.

When the effects of Cd treatments on SFW are examined, the negative effects of all Cd treatments are clearly visible. As doses of Cd increase, SFW's decrease. SFW value of plants treated with 600 µM Cd was 64.20 g, while the value of the control plants was 84.22 g. In a study of the effects of Cd treatments on SFW, 0, 5, 50 and 500 µM Cd were applied to the plants. The results were examined on the 3rd, 8th, 15th and 21st days and the SFW's of the plants on the 3rd day were similar. On the 8th day, the fresh weights of the control and 5 µM treatments were greatly increased, whereas the fresh weights of the 50 and 500 µM treatments did not increase much. On the 15th day, the change was similar, and plants that eventually underwent 500 µM Cd at 21st day died [24]. Caffei et al. [35] used 0, 5, 10, 20 and 50 µM Cd doses in a study conducted on tomato. While the fresh weights of the control plants were above 3 g, they fell below 2.5 g at 5 µM Cd dose and below 1 g at 50 µM Cd dose. Farouk et al. [27] used 0, 100, and 150 µM Cd doses in a study on Radish plant. The experiment was repeated for 2 years and the SFW obtained from 150 µM Cd treatment in the first year was below the control and above the 100 µM Cd dose. However, in the second year the highest value was obtained from control and the lowest value was obtained in the 150 µM Cd treatment.

When SDW is examined, Cd treatments are seen to lead to a dry matter reduction of up to 50%. In particular, the reduction in the amount of dry matter in 300 and 450 µM Cd treatments is noteworthy. Compared to other treatments, the amount of dry matter is proportionally reduced by 300 and 450 µM Cd treatments a considerable amount. At the same time, the proportional decrease in 600 µM Cd treatment is relatively low. When considered together with the leaf area in Table 3, it can be assumed that the cause of this decrease is caused by the decrease in leaf size and number. The effects of CD treatments on SDW were investigated by Azevedo et al. [24]. The negative effect of the treatment of 500 µM Cd from the 3rd day has begun to appear. Over the following days the negative effects of 50 µM and finally 5 µM Cd treatment were well established. On the 21st day, 500 µM Cd applied plants died. Similarly, SDW, in the study conducted by Caffei et al. [35], which is above 0.25 g in control plants, fell below 0.2 g in 5 µM Cd treatment. For 10 and 20 µM Cd treatments, the SDW decreased to 0.1 g, while for the 50 µM Cd treatment it decreased to under 0.1 g. In another study conducted by Farouk et al. [27] on radish plant (2-year experiment), SDW decreased significantly in 100 and 150 µM Cd treatments. 150 µM Cd treatment reduced SDW by almost 50%. Cd treatments have negative effects on dry weight as well as fresh weight. In fact, the negative effect on dry weight is more than fresh weight. Azevedo et al. [24], Zhang et al. [29], Farouk et al. [27] and the results obtained from the current study support this idea, but Rai et al. [36] do not support.

3.4. Root length (RL; cm)

Because the roots are in the soil, they are face-to-face with soil stress factors. Since it is also in the soil, Cd damages to the roots firstly. After Cd damage, because the roots are less able to be produced and functioned, other parts of the plants cannot grow and develop sufficiently. In the present study, average plant root lengths as a result of Cd treatments decreased as expected. The root lengths of the control plants are 35 cm while the root lengths are lower in Cd treatments. However, although the root length decreased significantly in 150 µM Cd treatment, the decrease in 300 and 450 µM Cd treatments was slower. In 600 µM Cd treatment, root length was 28 cm. According to these results, even low cadmium doses can cause considerable damage to plant roots. Considering only the root length, the effect of high cadmium doses may be considered to be low. However, taking into account the other root characteristics in Table 2, it is understood that increasing doses cause significant damage. Rai et al. [36] conducted experiment using 0, 20, 50 and 100 ppm Cd on *Phyllanthus amarus* Schum. and Thonn. seedlings of the plant were used. Researchers reported that 20 ppm Cd (5.12 cm) dose resulted in decrease in root length, but 50 ppm Cd (3.99 cm) treatment to cause the most decrease (control: 5.51 cm) comparatively. At the same time, 100 ppm Cd treatment (3.48 cm) has provided the lowest root length value. Zhang et al. [29], 0, 50, 100 and 200 µM Cd doses were used on *Achnatherum inebrians* plant. Accordingly, 50 µM Cd treatment caused a slight increase in root length compared to control. However, in 100 µM Cd treatment root length decreased by almost 50%. In the case of 200 µM Cd, root length decreased to less than 50% of control. Farooqi et al. [27] used 0, 10, 30, 50, 70 and 90 µmol/L Cd doses in a study of *Albizia lebbeck* (L.) Benth. According to the study, the statistically significant difference in root length was observed from 10 µmol/L Cd treatment. Treatment of 30, 50 and 70 µmol/L Cd continued to reduce root length. In 90 µmol/L Cd treatment, the root length decreased dramatically. As seen in the results of previous studies, Cd treatments have a negative effect on root length. However, low doses of Cd may increase root length. From this aspect, the results of the present study and the results of the previous studies support each other.

3.5. Root Volume (RV; cm^3)

Cd has also adverse effect on root volume as well as root length. It leads to decrease of root mass as an obstacle to root length and lateral root growth. In the study done, the adverse effect of Cd treatments on root volume is clearly visible. The root volume of the control plants was 128.67 cm^3 while the root volume was found to be 119.00 cm^3 in 150 µM Cd treatment. However, the greatest volume reduction occurred between 150 µM (119.00 cm^3) and 300 µM (99.33 cm^3) Cd treatments. While there is no statistically difference in the root lengths of these treatments at this level, the difference in root volume may be related to the amount or length of lateral root. Finally, root volume reduction caused by 450 (93.67 cm^3) and 600 µM (83.00 cm^3) Cd treatments remained relatively low. As seen above, RV is susceptible to Cd like other root features. In parallel with the dose increase, RV decreases.

Table 2. Effects of Cadmium treatments on Root Length (RL), Root Volume (RV), Root Fresh Weight (RFW) and Root Dry Weight (RDW).

	RL (cm)	RV (cm^3)	RFW (g)	RDW (g)
Control	35,00^a	128,67^a	153,61^a	48,45^a
150 µM Cd	29,83^b	119,00^b	121,17^b	37,30^b
300 µM Cd	29,33^b	99,33^c	103,40^c	32,81^c
450 µM Cd	29,17^{bc}	93,67^d	80,49^d	25,41^d
600 µM Cd	28,00^c	83,00^e	78,28^d	25,25^d

3.6. Root Fresh (RFW; g) and Root Dry Weight (RDW; g)

RFW and RDW are susceptible to Cd stress like other root features. This is due to the decrease in root growth with the increase in the amount of Cd. Accordingly, the root fresh weight is decreasing in weight, parallel to the dose increase. According to the data obtained from the present study, increasing doses of Cd decrease the RFW. The most dramatic decrease is seen in 150 µM

(121.17 g) Cd treatment. With increasing doses, the rate of decrease in RFW is decreasing. Ultimately, the reduction in RFW with 600 µM Cd treatment is quite low. 450 (80.49 g) and 600 µM (78.28 g) Cd treatments are statistically in the same group. **Azevedo et al. [24],** 50 µM Cd is statistically insignificant although RFW is increased on 3rd day after treatment. Cd treatments caused RFW decline on the 8th and 15th days. On the 21st day, 500 µM Cd applied plants were completely dead. The RFW of 50 µM Cd applied plants were less than 50% of the control treatment. Caffei et al. [35] reported that 5 µM Cd treatment increased RFW in a study conducted on tomato. However, 10 and 20 µM Cd treatments were found to cause a slight decrease. In addition, RFW of plants treated with 50 µM Cd decreased by almost 40%.

According to the results obtained from recent study, both characteristics were similarly affected by Cd treatments. However, the treatment of 600 µM Cd in particular has more influence on RFW. Accordingly, the mean root dry weight of the control plants was 48.45 g, whereas at 150 µM Cd treatment the RDW decreased to 37.30 g. The most weight loss occurred with treatment of 150 µM Cd. While the weight loss caused by 300 (32.81 g) and 450 µM (25.41 g) Cd treatments was lower, the weight loss of the 600 µM (25.25 g) Cd treatment was similar to the 450 µM Cd treatment. According to these results, it can be said that the effects of 450 µM to 600 µM Cd treatments on root dry weight are similar. According to Azevedo et al. [24], Cd treatments cause reductions in RDW as well as in RFW. However, 5 µM Cd treatment was similar to control (8th day) and close results (15th day) unlike the effect in RFW. Similarly, Caffei et al. [35] also obtained similar results with RFW and the declining graph drawn by 10, 20 and 50 µM Cd treatments was linear. As can be seen, Cd treatments lead to reduced root fresh and dry weight. Similar results with previous and recent studies suggest that Cd has negative effects on root characteristics. However, it has been reported by researchers that low Cd doses have positive effects on roots.

3.7. Leaf Area (LA; cm^2)

The leaf area, which differs according to the plant species and cultivars, is one of the plant parts (another one is roots) which first affected by the factors harmful to the plants. Also in the present study, leaf area decreased by increasing doses of Cd. Decrease in leaf area reduced in a balanced manner parallel to the increase of Cd doses. The mean leaf area was 40.73 cm^2 in control plants, while this average was 25.48 cm^2 in 600 µM Cd treatment. According to a study on tomato done by Chaffei et al. [35], high Cd doses reduced leaf surface area while lower doses were increased. This positive effect of 5 µM Cd was very limited. LA of 10 µM Cd treatment was less than 70% compared to the control. Ultimately, the LA obtained from 50 µM Cd treatment was almost 40% of control LA. Haag-Kerwer et al. [37] conducted a study on *Brassica juncea* in which 2 different Cd doses (0 and 25 µM) were used. Leaf areas were measured at 0, 24, 48, 72 and 96 hours. Accordingly, plants treated with 25 µM Cd after 48 hours showed a significant decrease in LA. At the end of 72 and 96 hours, the LA of 25 µM Cd treatment was lower than the control. As seen in previous studies, higher cadmium doses reduce LA while lower doses increase. The high doses of Cd used in the present study have reduced LA's of plants.

3.8. Leaf-Relative Water Content (L-RWC; %)

Reducing the water content of the leaves is one of the obvious effect of stress factors. This effect may be caused by environmental stress factors such as drought, heat, as well as by soil stress factors affecting root development and function. Cd is among the stress factors that inhibit the transpiration of water to the leaves by reducing root development and preventing roots from functioning. The above-mentioned effects are also seen in the present study. The mean L-RWC of the control plants was 90.44%, while these ratios decreased with increasing Cd doses. So, it decreased to 84.08% at 150 µM Cd treatment. Along with the dose increase, the water content of the leaves has also decreased. However, L-RWC was similar in 300 (82.87%) and 450 µM (82.00%) Cd treatments, and these two treatments were statistically in the same group. In contrast to this, L-RWC was significantly reduced at 600 µM Cd and was 66.14%. Zhang et al. [38] reported that Cd treatment decreased L-RWC in a study conducted by applying 0, 50, 100 and 200 µM $CdCl_2$ for 4 weeks on *Achnatherum inebrians*. Accordingly, L-RWC reduction from 50 µM Cd treatment began and L-RWC fell below 80% in 200 µM Cd treatment. Farouk et al. [27] conducted a two-year study in the Radish plant, Cd treatments (0, 100 and 150 mg/kg soil DW) reduced L-RWC both years. While, the L-RWC ratios of control plants were higher than 80% in both years, L-RWC ratios of 100 (first year: 71.85%, second year: 75.61%) and 150 (first year: 66.12%, second year: 66.36%) mg/kg Cd treatments were significantly reduced. It has also been determined in the present study that Cd treatments reduce L-RWC. In this respect, there is no contradiction between the previous studies and the present study.

Table 3. Effects of Cadmium treatments on Leaf Area (LA), Leaf-Relative Water Content (L-RWC), Stomatal Conductance (SC) and Leaf Chlorophyll Content (Chl-C)

	LA (cm^2)	L-RWC (%)	SC (mmol m^{-2}s^{-1})	LCC (µg/cm^2)
Control	40,73^a	90,44^a	243,20^a	59,39^a
150 µM Cd	36,86^b	84,08^b	243,93^a	56,49^b
300 µM Cd	32,87^c	82,87^c	239,81^a	56,72^b
450 µM Cd	29,15^d	82,00^d	224,35^b	54,82^c
600 µM Cd	25,48^e	76,14^e	207,43^c	53,52^d

3.9. Stomatal Conductance (SC; mol $m^{-2}s^{-1}$)

Stomatal conductivity is high under optimum conditions, while under other conditions it is low. Stomatal conductance is reduced when the air temperature increases, water is reduced in the soil, or roots fail to function. This is also the case for heavy metal stresses such as Cd. Cd reduces stoma conduction by preventing root growth and functioning of roots. This is similar to the study done. However, with the 150 (243.93 mmol $m^{-2}s^{-1}$) and 300 µM (239.81 mmol $m^{-2}s^{-1}$) Cd treatments, the results obtained from the control treatment are similar. The results are statistically similar, although these doses of Cd have reduced stomatal conductance. However, the average stomatal conductance obtained from the control plants is 243.20 mmol $m^{-2}s^{-1}$, while the stomatal conductance is low at 450 µM (224.35 mmol $m^{-2}s^{-1}$) and 600 µM (207.43 mmol $m^{-2}s^{-1}$) Cd treatments. Haag-Kerver et al. [37] conducted a study in *Brassica juncea* using 25 µM $CdNO_3$. According to the researchers, although the transpiration rates were similar after 5 hours of treatment, the transpiration rates of Cd applied plants reduced when measurements were made after 48 and 96 hours. On the other hand, in a study conducted by Chaffei et al. [35], 0, 5, 10, 20 and 50 µM Cd doses were used. Accordingly, from 5 µM Cd treatment, transpiration was reduced (almost 30%). However, there was a partial increase in 10 µM Cd treatment compared to 5 µM Cd treatment. Subsequently, in 20 and 50 µM Cd treatments, transpiration decreased below 60% relative to the control. According to another study which conducted by Sandalio et al. [39] used 0, 10, 20, 30, 40 and 50 µM Cd doses in a study on pea plant. According to the researchers, statistically significant reduction was observed in 10 µM Cd (2.14 mM H_2O $m^{-2}s^{-1}$) treatment compared to the control (2.52 mM H_2O $m^{-2}s^{-1}$). In 50 µM Cd treatment, the transpiration was significantly reduced with 1.42 mM H_2O $m^{-2}s^{-1}$. The results obtained from the current study (even though the Cd doses are higher) are higher than the above studies. This may be due to the fact that the above studies have been carried out in the hydroponic, although the recent study has been carried out in the peat and perlite mixture.

3.10. Leaf Chlorophyll Content (LCC; µg/cm^2)

Chlorophyll is a molecule that allows plants to photosynthesize and is produced as a result of a synthesis where Iron (Fe) joined. In the case of iron deficiency, chlorophyll production slows down. As mentioned above, increasing the amount of Cd in the soil reduces the Fe content. Leaf chlorophyll content obtained from the study done supports this idea. The LCC obtained from the Cd treatments are lower than the control treatment. Furthermore, as the doses of Cd increase, the decrease in chlorophyll content is exacerbated. The mean LCC of control plants was 59.39 µg/cm^2, while at 150 mM Cd treatment the LCC decreased to 56.49 µg/cm^2. In 300 mm (56.72 µg/cm^2) Cd treatment, LCC is in the same statistical group with 150 mm Cd treatment. However, it was higher than the LLC 150 mm Cd treatment in the 300 mm Cd treatment. At 450 mm (54.82 µg/cm^2) Cd treatment, LCC continued to decrease and eventually reached the lowest level at 600 mm (53.52 µg/cm^2) Cd treatment. Sandolio et al. [39] used 0, 10, 20, 30, 40 and 50 µM $CdCl_2$ doses in the study of *Pisum sativum* L.. According to the data obtained from study, the LCC of the control plants was thereabout 110 µg.mg^{-1}. This value decreased with 10 µM Cd treatment and decreased to about 60 µg.mg^{-1} at 50 µM Cd treatment. In a study conducted by Ewais [26] on *Cyperus difformis*, *Chenopodium ambrosiodies* and *Digitaria sanguinolis* species, cadmium was used in doses of 0, 5, 10 and 20 mg.kg^{-1}. In all three species, LCC values began to decrease after 5 mg.kg^{-1} Cd treatment. In the case of 20 mg.kg^{-1} Cd, the decline in all three species was close to 30%. Farouk et al. [27] investigated chlorophyll content in the study of Cd (0, 100 and 150 mg.kg^{-1} soil DW) in Radish plant. The chlorophyll amounts were also reduced in all three species during both experiment years. However, the reduction rate in the second experiment year is lower than the first year. In 150 mg.kg^{-1} Cd treatment, LCC loss approached 30% in both years. As can be seen in previous studies, low cadmium doses caused high loss of LCC may be related to the age of the plants used and the growing medium used. The fact that the plants used in this study are older and the media used is different may explain low LCC loss.

4. CONCLUSION

In this study, the effects of 5 different Cd doses (0, 150, 300, 450 and 600 µM) on CAB-6P cherry rootstocks were investigated. According to the results obtained, Cd damages especially roots and leaves from low doses. Damage of Cd on relatively stronger trunk and tap-root are less. According to previous studies, Cd caused significant losses from low doses. At the same time, at very low doses, Cd has a positive effect on certain plant characteristics. However, the fact that these studies were usually carried out in hydroponic media may have caused Cd to be damaged at low doses. In plant growing medias such as soil, the minimum amount required for the occurrence of Cd damage may increase. The reason for this is the buffering feature of medias such as soil. As a result, Cd is among the heavy metals that can cause considerable damage to plants. It would be useful to select the species and varieties that are resistant to Cd containing soil.

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Removal of Linear Alkyl Benzene Sulphonic Acid by Sonication Process

Ayla ARSLAN[1], Eylem TOPKAYA[1], Sevil VELI[1], Deniz BINGOL[2]*

Abstract

In this study, treatability of linear alkyl benzene sulphonic acid (LABSA) from aqueous solutions were investigated by sonication process. The effects of initial LABSA concentration, pH and reaction time which are process independent variables were investigated on the yield. Removal of LABSA was followed by absorbance analysis. The system optimization was made with experimental design by using the surface response method in this study. It was determined that the independent variable that most affects LABSA removal was the reaction time. The reaction time and initial pH value of the solution showed a positive effect on the removal yield. The initial LABSA concentration had a negative effect, and as the concentration increased, the yield decreased. The predicted maximum absorbance removal was 68% at the optimum conditions of pH 9.6, initial LABSA concentration of 10 mg/L and reaction time of 78 min. Only 11% of total variability can't be explained by this model.

Keywords: *Anionic surfactant, Linear alkyl benzene sulphonic acid, Optimization, Response surface methodology, Ultrasonic degradation.*

1.INTRODUCTION

Linear AlkylBenzene Sulphonic Acid (LABSA) is an anionic surfactant. LABSA is one of the most important raw materials used in the detergent industry. It is used as the main surfactant in production processes like washing and dishwashers' powder detergents, detergent gels, liquid soaps, cleaning powders, liquid and oily soaps etc. today as well as dishwashing detergents [1].

Biological treatability of surfactants and degradation products are limited in domestic and industrial wastewater treatment plants. Moreover, the degradation products are become partly more toxic and refractory qualified from themselves [2]. These substances are shown accumulation at different concentrations in shallow water, bottom sediments and soil [3]. This accumulations are creating a growing danger in terms of health and environment, the wastewater of containing these substances must be treated effectively before being delivered to the receiving medium [4]. In the treatment of these pollutants, advanced oxidation processes (AOP) are anticipated as alternative chemical treatment technologies [5]-[8].

AOP is a method based on the formation of hydroxyl radicals (OH•), which can convert toxic and persistent organic substances into harmless end products such as CO_2 and H_2O [9]. OH• radicals are strong, non-selective chemical oxidants and can be produced by photochemical and chemical means [7].

* [1]*Corresponding author: Kocaeli University, Department of Environmental Engineering, 41380, Izmit/ Kocaeli, Turkey. eylem.topkaya@kocaeli.edu.tr*

[1] *Kocaeli University, Department of Environmental Engineering; ataberk@kocaeli.edu.tr ; sevilv@kocaeli.edu.tr*

[2] *Kocaeli University, Department of Chemistry; deniz.bingol@kocaeli.edu.tr*

The sonication process is improved chemical oxidation processes with supported by sound. In this process; creating of hydroxyl radicals are intended by ultrasonic waves cavitation effect. In this process microbubbles are formed, grew and then disappeared. Reactive free radicals are consisted of during the extinction phase. These radicals are provided conversion of toxic and organic compounds in wastewaters to stable final products or less harmful compounds [10]-[13]. Ultrasonic (US) method is preferred in recent times due to its simplicity in application and its not forming unwanted by-products (toxic etc.) [14]-[16].

In this study, sonication process was used to investigate the treatability of linear alkyl benzene sulphonic acid (LABSA) through the absorbance parameter and optimized by the surface response method.

2. MATERIALS and METHOD

2.1. Materials

The Linear Alkyl Benzene Sulphonic Acid (LABSA-$C_{18}H_{29}SO_2OH$) used in the study was obtained from HAYAT Chemical Company. The chemical formula of the LABSA used is given in Figure 1. LABSA aqueous solutions were used in the experiments. 1N H_2SO_4 or 1N NaOH solutions were used to adjust the pH.

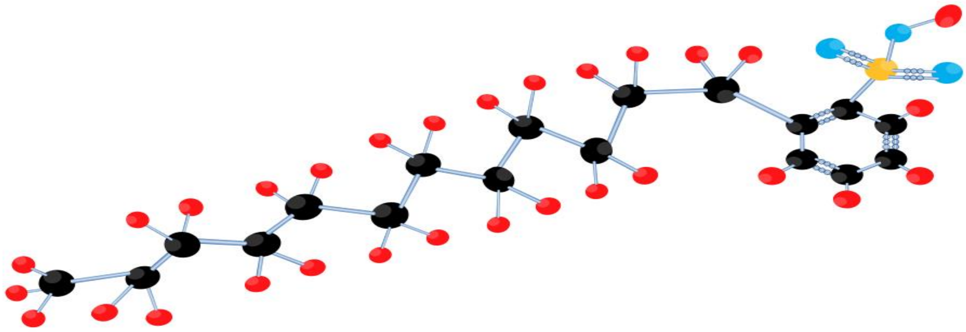
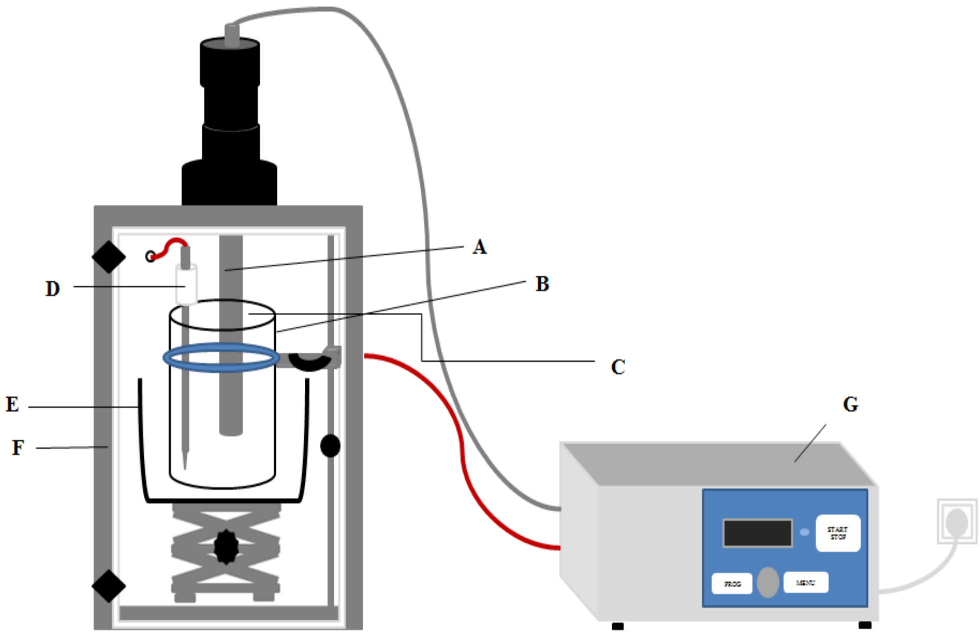


Figure 1. LABSA chemical formula

2.2. US System

The probe type ultrasonic device was used for oxidation studies by SONOPULS HD 3400 model (BANDELIN brand), 20 kHz frekans, 400 W maximum power. The ultrasonic probe is where ultrasound energy is converted to electrical energy or vice versa. The capacity of the US device is 100-2500 mL. The temperature was kept constant (25 ± 2 ° C) with cooling water during the experiment. The US device was established in a noise-proof partly preventive cabinet. The US device is as shown in Figure 2.



A: Ultarsonic probe nib; **B:** Glass reactor; **C:** Sampling point; **D:** Temperature meter; **E:** Cold water container; **F:**Sound holding cabin; **G:** Ultrasonicator monitor.

Figure 2. Ultrasonic System

2.3. Analysis

The experiments were performed with 1 L LABSA solution. HACH, HQd brand digital pH-meter was used for pH measurement. HACH DR 5000 spectrophotometer was used to measure the absorbance by scanning in the wavelength range of 200 to 700 nm. The absorbance of LABSA was measured at λmax=278 nm. All experiments were made in pulse off application to preventing temperature control and probe heating in US probe applications.

2.4. Experimental Design Technique

Response Surface Methodology (RSM), is an empirical modeling technique, designed to graphically evaluate the relationship between different experimental variables and the responses. The most commonly used designs to determine response surfaces are the full and fractional factorial designs and the more complex central composite, Box–Behnken, Doehlert and mixture designs. Central composite designs (CCD) presented by Box and Wilson are a second-order multivariate design technique based on three-level factorial design used for evaluation of a dependent variable as functions of independent variables. It allows the determination of both linear and quadratic models. The CCD is a better alternative to the full factorial three-level design since it demands a smaller number of experiments while providing comparable results [17], [18]. For the RSM, a second–order polynomial model (Eq. (1)) is usually performed to estimate the effects of various factors on a response based on experimental results from CCD.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{1 \le i \le j}^{k} \beta_{ij}\, x_i x_j + \varepsilon \qquad (1)$$

where y is the predicted response, xi is a coded variable, and the β_0 is the constant, the βi is linear coefficient, the βii is quadratic coefficient and the βij is the interactive coefficient [19].

3. RESULTS and DISCUSSION

In the studies carried out by the sonication process, the system efficiency was evaluated by observing absorbance removals. The maximum absorbance was observed at 278 nm in an absorbance spectral scan. Degradation of the LABSA was followed by checking its absorbance value at 278 nm. Response Surface Methodology was optimized based on the central composite design. The data used in experimental design:

Variables:

pH (4-11)

The reaction time (30-90 min)

The initial LABSA concentration (8-20 mg / L)

Outputs:

Percent of Absorbance Removal

3.1. Experimental

The conditions for 20 experiments containing different combinations of factors and the average results obtained are given in Table 1.

Table 1. Central composite designs matrix

Run	pH	LABSA (mg/L)	t (min)	Absorbance Removal (%)
1	5.4	10	42	32
2	9.6	10	42	42
3	5.4	18	42	8
4	9.6	18	42	11
5	5.4	10	78	64
6	9.6	10	78	68
7	5.4	18	78	14
8	9.6	18	78	13
9	4	14	60	18

10	11	14	60	34
11	7.5	8	60	47
12	7.5	20	60	32
13	7.5	14	30	12
14	7.5	14	90	32
15	7.5	14	60	22
16	7.5	14	60	33
17	7.5	14	60	18
18	7.5	14	60	20
19	7.5	14	60	21
20	7.5	14	60	22

The ANOVA table of the model obtained from the central composite design is given in Table 2.

Table 2. ANOVA for Absorbance Removal (%)

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	4317.65	479.74	4.82	0.011
Linear	3	3373.94	1124.65	11.30	0.001
pH	1	134.82	134.82	1.36	0.271
LABSA	1	2512.22	2512.22	25.25	0.001
t	1	726.91	726.91	7.31	0.022
Square	3	600.71	200.24	2.01	0.176
pH*pH	1	36.33	36.33	0.37	**0.559**
LABSA*LABSA	1	583.05	583.05	5.86	0.036
t*t	1	0.43	0.43	0.00	**0.949**
2-Way Interaction	3	343.00	114.33	1.15	**0.376**
pH*LABSA	1	18.00	18.00	0.18	**0.680**
pH*t	1	12.50	12.50	0.13	**0.730**
LABSA*t	1	312.50	312.50	3.14	**0.107**
Error	10	994.90	99.49		
Lack-of-Fit	5	855.56	171.11	6.14	0.034
Pure Error	5	139.33	27.87		
Total	19	5312.55			

Almost all major factors with a probability of less than 0.05 and their interactions are significant at 95% confidence level.

Since P> 0.05, the effects on the system at 95% confidence level of these interactions are statistically insignificant. For this reason, these interactions must be removed from the model.

Standard deviation and determination coefficients of the reduced model obtained with significant coefficients are as follows:

S= 5.0288 **R-sq=** 91.21% **R-sq(adj)=** 88.87% **R-sq(pred)=** 83.23%

Only 11% of total variability cannot be explained by this model.

The regression equation of the model obtained with the coded coefficients is given in the following equation:

Absorbance removal (%) = 23.92 + 3.14 pH − 13.56 LABSA + 7.30 t + 6.20 LABSA*LABSA

According to the above equation, the initial LABSA concentration had the greatest but negative effect on LABSA removal, followed by reaction time. Removal performance was least affected by pH.

Response surfaces are used to determine an optimum. In addition, it is a good way to graphically illustrate the relation between different experimental variables and the responses. To be able to determine an optimum it is necessary that the polynomial function contains quadratic terms. The three-dimensional response surface plots and contour plots are shown in Figure 3 and Figure 4, respectively.

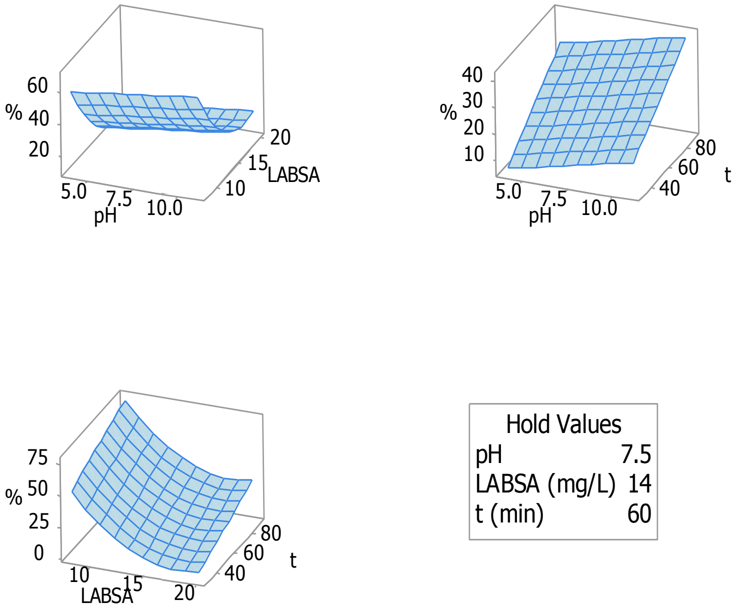


Figure 3. Response surface plots for the absorbance removal

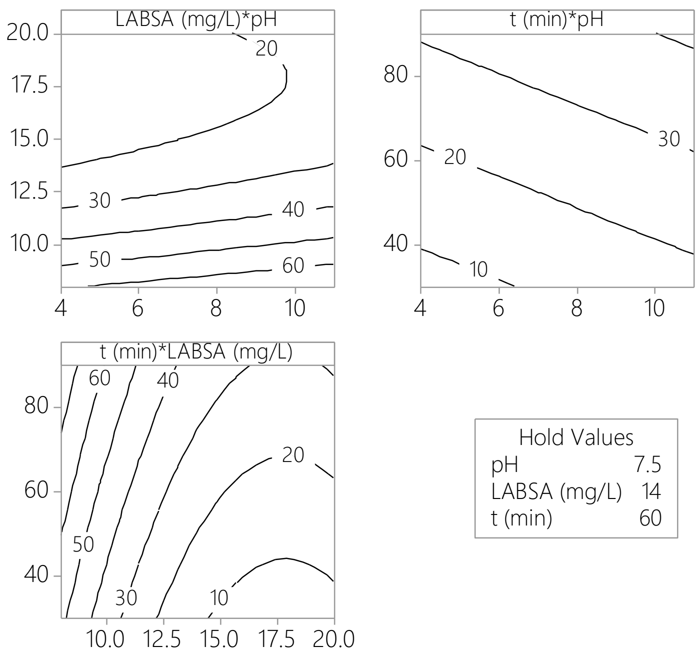


Figure 4. Contour plots for the absorbance removal

3.2. Application of the RSM results to the real wastewater

In this study, wastewater sample was taken from the detergent plant where LABSA was supplied. pH value of wastewater was 9.6; the maximum absorbance value was measured as 3.725 at 366 nm wavelength. The effects of process components were revealed by RSM in LABSA degradation. Taking these results into consideration, sonication treatment was applied to wastewater at three different pH values. The results of experiments carried out with wastewater are as indicated in Table 3.

Table 3. Results of wastewater studies

pH	**Time (min)**	**Absorbance values after sonication (abs) (366 nm)**	**Absorbance Removal (%)**
5.3	0	3.386	-
	30	2.961	13
	60	2.134	37
	90	2.278	33
7.5	0	3.377	-
	30	2.819	17
	60	2.818	17
	90	2.821	16
9.6	0	3.725	-
	30	3.089	17
	60	2.992	20
	90	2.078	44

According to Table 3; The US process was more effective under basic conditions for industrial wastewater and the absorbance removal was achieved up to 44%. Treatment of sonication process will be more economical at the original pH value of the wastewater.

4. CONCLUSION

LABSA removal was investigated by sonication process from aqueous solutions. In the experimentals design, the system optimization was made of using the surface response method. The initial LABSA concentration, pH and reaction time, which were process independent variables, effects on the removal efficiency were investigated.

In the study carried out with the sonication process; a maximum absorbance removal of 68% was achieved at pH of 9.6, initial LABSA concentration of 10 mg / L and reaction time of 78 min.

When LABSA removal was followed by the absorbance parameter, it was determined that the independent variable most affecting the yield was the reaction time. The reaction time and the solution initial pH value were showed a positive effect on the recovery efficiency. The initial LABSA concentration had a negative effect. As the initial LABSA concentration increased, the yield decreased. According to the model; for pH 9.6, initial LABSA concentration 10 mg / L, and reaction time of 78 min the maximum absorbance removal was estimated to be 68%. Only 11% of total variability can't be explained by this model.

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Eylem TOPKAYA; completed her undergraduate degree in 2004-2009 at Uludag University, Department of Environmental Engineering. She completed her master's degree in 2011-2014 at Gebze High Institute of Technology (GYTE), Institute of Natural and Applied Sciences, Department of Environmental Engineering. She has started her PhD education in 2014 at Kocaeli University, Institute of Natural and Applied Sciences, Department of Environmental Engineering and she is still in progress.

Biodiesel Production from Microalgae

Veli Gokhan DEMIR[1], Hakan Serhad SOYHAN[1]*

Abstract

Depletion of fossil fuel reserves, increasing energy demand and serious environmental concerns makes renewable energy such as biofuels more importance. In recent years, biodiesel, the methyl or ethyl esters of fatty acids, gained a significant position as an environmentally friendly substitute of conventional diesel fuel. Generally, biodiesel is produced through transesterification method between vegetable oil and alcohol in the presence of catalyst efficiently. However, the major obstacle of large-scale commercialization of biodiesel production is its high cost related to high feedstock prices especially in the countries that import most of the consuming food-grade oils such as Turkey. On the other hand, microalgae have gained attention as an alternative biodiesel feedstock because of their fast growing nature and high adaptability to the existing environment. The aim of this study is to investigate "microalgae" as an alternative biodiesel feedstock to vegetable oils. In this regard, the processes and used technologies existing in from microalgae to biodiesel formation; including microalgae production, harvesting, and conversion methods, are reviewed. It is found that using microalgae in biodiesel production in Turkey can be helpful to make it self-sufficient for energy demands.

Keywords: *Biodiesel, Feedstock, Microalgae, Transesterification.*

1.INTRODUCTION

The world energy consumption has increased rapidly and will continue to increase due to an annual projected population increase of about 1%. Fluctuations of oil prices have worsen the situation and further decreased oil supply due to political pressure. It is estimated that the seriousness of the depletion of oil and other fossil fuels along with the climate change effects will be felt by the beginning of 2030–2050 [1], stressing the need for alternative fuels. As a result, a large amount of money is being invested on the research and development of alternate energy resources, such as solar, wind, hydro and biofuels. Solar, wind, and hydro energy can be used to produce electricity, but the only alternative to liquid transportation fuel is liquid biofuel [2].

With the need to reduce carbon emissions, and the dwindling reserves of crude oil, liquid fuels derived from plant material – biofuels – are an attractive source of energy. Moreover, in comparison with other forms of renewable energy such as wind, tidal, and solar, liquid biofuels allow solar energy to be stored, and also to be used directly in existing engines and transport infrastructure. Currently, bio-ethanol from, for example, corn starch, sugar cane or sugar beet, and biodiesel from oil crops such as palm and oilseed rape, are the most widely available forms of biofuel [3].

Biodiesel is made from biomass oils, mostly from vegetable oils. Biodiesel appears to be an attractive energy resource for several reasons. For example: biodiesel appears to have several favourable environmental properties resulting in no net increased release of carbon dioxide and very low sulphur content [4, 5]. The release of sulphur content and carbon monoxide would be cut down by 30% and 10%, respectively, by using biodiesel as energy source. Using biodiesel as energy source, the gas generated during combustion could be reduced, and the decrease in carbon monoxide is owing to the relatively high oxygen content in biodiesel. Moreover, biodiesel contains no aromatic compounds and other chemical substances which are harmful to the environment. Recent investigation has indicated that the use of biodiesel can decrease 90% of air toxicity and 95% of cancers compared to common diesel source [6]. Also, biodiesel is better than diesel fuel in terms of flash point and biodegradability. On the other hand, biodiesel appears to have significant economic potential because as a non-renewable fuel that fossil fuel prices will increase inescapability further in the future [7].

Alcoholysis or transesterification of triglycerides has emerged as the most common method for biodiesel production with obtaining accepted fuel qualities. This process consists of three sequential reversible reactions: the triglyceride (TG) in the oil is converted to di-glyceride (DG), then to mono-glyceride (MG) and finally to glycerol with alkyl esters (biodiesel) formed in each step [8]. Conventional biodiesel mainly comes from soybean and vegetable oils, palm oil, sunflower oil, rapeseed oil as well as restaurant waste oil [7]. The number of carbon in the carbon chain of the diesel oil molecular is about 15, which is similar to that of the plant oil with 14–18 carbons. The structural characteristic of biodiesel determines that biodiesel is a feasible substitute for conventional energy. Nevertheless, the production cost is generally high for biodiesel. The price of

[1*] *Corresponding author: Balikesir University, Department of Mechanical Engineering, 10100, Balikesir, Turkey.* *veligokhandemir@balikesir.edu.tr*

biodiesel is approximately twofold that of the conventional diesel at present. The production cost of biodiesel consists of two main components, namely, the cost of raw materials (fats and oil) and the cost of processing. The cost of raw materials accounts for 60% to 75% of the total cost of the biodiesel fuel therefore, the major bottleneck limiting the development of the biodiesel industry is supply and price of feedstocks [9, 10].

Since vegetable oils may also be used for human consumption, it can lead to an increase in price of food-grade oils, causing the cost of biodiesel to increase and preventing its usage, even if it has advantages comparing with diesel fuel. In order to not compete with edible vegetable oils, the low-cost and profitable biodiesel should be produced from low-cost feedstocks such as non-edible oils, used frying oils, animal fats, soap-stocks, and greases. Among alternative biodiesel feedstocks; microalgae, the promising source of biodiesel, can grow in fresh water or marine environments, without using arable land and competing with food production. Some microalgae have high biomass and oil productivity [9]. Moreover, microalgae are present in all existing earth ecosystems and they can grow rapidly and live in harsh conditions due to their unicellular or simple multicellular structures [11] .

In this study, it is focused on the microalgae, the significant and promising source of biodiesel production especially for Turkey which imports nearly all of its oil supplies. The paper presents a critical review on the prospects of microalgae for biodiesel production via transesterification method.

2. BIODIESEL

2.1.Biodiesel Production

According to the International Energy Agency (IEA) report [12] and Shahid and Jamal [13], the world will need 50% more energy in 2030 than today, of which 45% will be accounted for by China and India. In the past 30 years, the transportation sector has experienced a steady growth especially due to the increasing numbers of cars around the world. It has been estimated that the global transportation energy use is expected to increase by an average of 1.8% per year from 2005 to 2035. Globally, the transportation sector is the second largest energy consuming sector after the industrial sector and accounts for 30% of the world's total delivered energy, of which 80% is road transport. It is believed that this sector is currently responsible for nearly 60% of world oil demand and will be the strongest growing energy demand sector in the future [14].

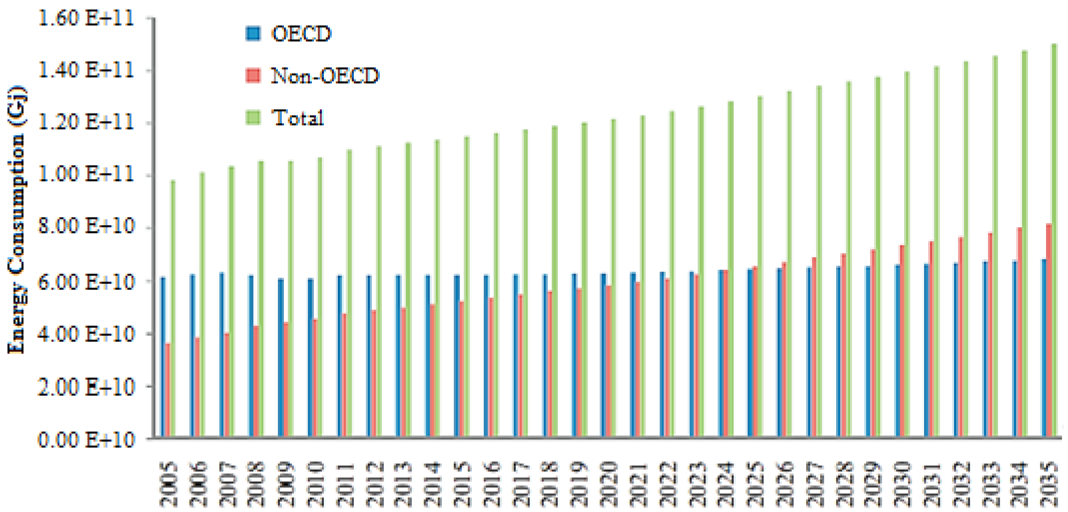

Figure 1. 1. Total world, OECD and non-OECD transportation sector energy consumption (GJ) between 2005-2035 [14]

Biodiesel can be considered as a possible substitute of conventional diesel, is biodegradable, non-toxic, renewable and has reduced emission of CO, SO_2, particulate matter, volatile organic compounds and unburned hydrocarbons as compared to conventional diesel. Biodiesel is an environmentally friendly fuel that can be used in any diesel engine without modification. The concerns of the harmful effects of fossil fuels to environment and rising energy demand of the world while fossil fuel reserves are running out, biodiesel seems to be a realistic fuel for future; it has become more attractive recently because of its environmental benefits [15].

Global biodiesel production is expected to reach 41.4 Bln L by 2025 corresponding to a 33% increase from the 2015 level. The European Union is expected to be the major producer of biodiesel. Other significant players are the United States, Brazil, Argentina and Indonesia. Policy rather than market forces will continue to influence production patterns in almost all countries [16].

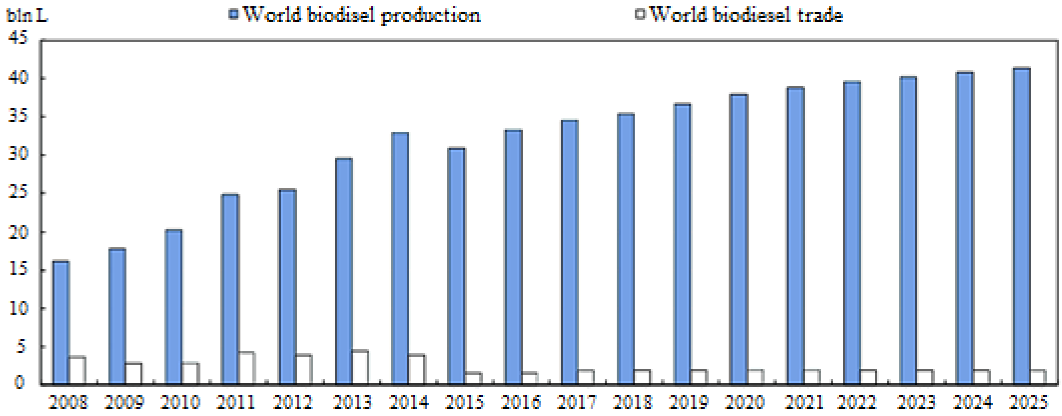

Figure 2. World biodiesel production and trade [16]

2.2.Why Microalgae?

It is projected that the growth in production and consumption of liquid biofuels will continue, but their impacts towards meeting the overall energy demands in the transport sector will remain limited due to: competition with food and fibre production for the use of arable land, regionally constrained market structures, lack of well managed agricultural practices in emerging economies, high water and fertilizer requirements, and a need for conservation of bio-diversity [17]. There are several reports on biodiesel production from edible oils; thus, its competition with food consumption has been a global concern. About 6.6 Tg (34%) of edible oil was estimated for worldwide biodiesel production from 2004 to 2007, and biodiesel is projected to account for more than a third of the expected growth in edible oil use from 2005 to 2017. Consequently, employing waste and nonedible oils in biodiesel production would eliminate the competition with food consumption; it will also allow for compliance with ecological and ethical requirements for biofuel. Algae are currently considered to be one of the most promising alternative sources of non-edible oils for biodiesel [18].

2.3.Biodiesel Production Methods

Globally, there are many efforts to develop and improve vegetable oil properties in order to approximate the properties of diesel fuels. It has been remarked that high viscosity, low volatility and polyunsaturated characters are the mostly associated problems with crude vegetable oils. These problems can be overcome by four methods; pyrolysis, dilution with hydrocarbons blending, Micro emulsion, and transesterification [14]. Transesterification is regarded as the best and most common method among other approaches due to its low cost and simplicity. Transesterification is a well-established chemical reaction in which a primary alcohol reacts with the triglycerides of fatty acids (oils) in presence of a catalyst to form glycerol and esters (biodiesel) [15].

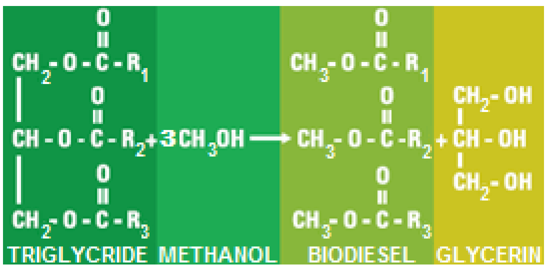

Figure 3. Transesterification reaction scheme

3. MICROALGAE

The algal organisms are photosynthetic macroalgae or microalgae growing in aquatic environments. Algae are simple organisms that are mainly aquatic and microscopic. Microalgae are unicellular photosynthetic micro-organisms, living in saline or freshwater environments that convert sunlight, water and carbon dioxide to algal biomass [19]. They are categorized into four main classes: diatoms, green algae, blue–green algae and golden algae. There are two main species of algae: filamentous and phytoplankton algae. These two species, in particular phytoplankton, increase in numbers rapidly to form algae blooms. Many species exhibit rapid growth and high productivity, and many microalgal species can be induced to accumulate substantial quantities of lipids, often greater than 60% of their dry biomass [20]. Microalgae are very efficient solar energy converters and they can produce a great variety of metabolites.

Microalgae are known as third generation feedstock used in biodiesel production. Algae cultivation has been developed for decades with the initial purpose of providing food supplements and animal feeds. During the energy crisis in 1970s, the U.S. National Renewable Energy Laboratory's (US NREL, formerly SERI) Aquatic Species Program (ASP) started to utilize algae biofuels as alternative energy sources. Although the high cost of algae biofuels during that time put a halt to the program in 1996, extensive amount of data on cultivation, harvesting, extraction, and transesterification of algae published throughout the period of ASP serves as foundations for modern studies of algae biofuels [2]. Main steps of microalgae based biodiesel production are illustrated in Figure 4.

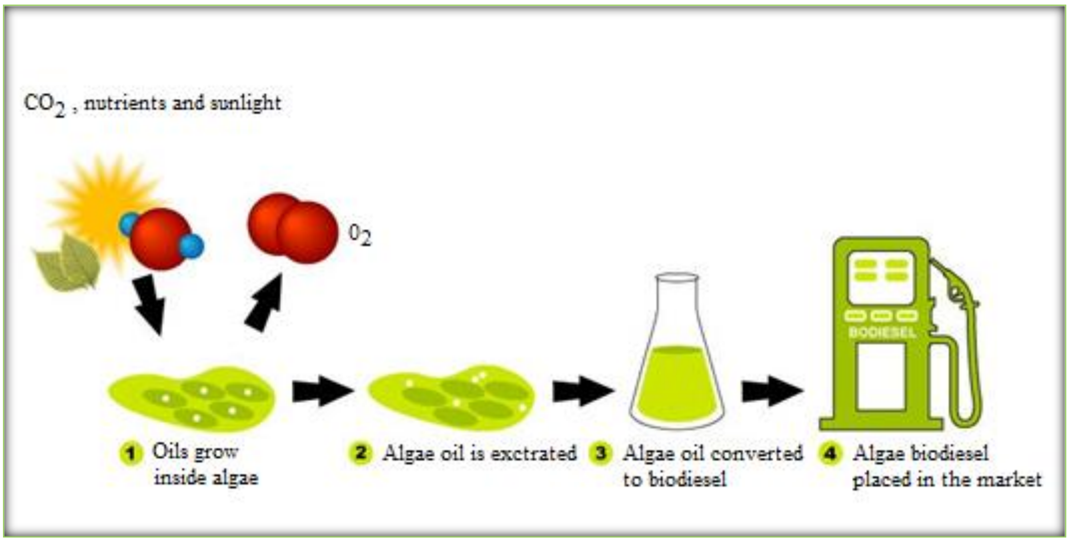

Figure 4. Main steps of microalgae based biodiesel production

Microalgae have been suggested as potential candidates for fuel production because of a number of advantages including higher photosynthetic efficiency, higher biomass production and higher growth rate compared to other energy crops. Main advantages and disadvantages of microalgae using in biodiesel production can be listed as following [7]:

Advantages:

- Fatty acid constitutions similar to common vegetable oils,
- Under certain condition it may be as high as 85% of the dry weight,
- Short-time growth cycle,
- Composition is relative single in microalgae.

Disadvantages:

- Most algal lipids have lower fuel value than diesel fuel,
- The cost of cultivation is higher compared to common crop oils currently.

In Table 1, biodiesel productivities from common seed plants and microalgae are compared. It can be seen how microalgae show a clear advantage in terms of land use because of their higher biomass productivity and oil yield. It should be also noted that although the oil contents are similar between seed plants and microalgae there are significant variations in the overall biomass productivity and resulting oil yield and biodiesel productivity with a clear advantage for microalgae [21].

Table 1. Comparition between plants and microalgae biodiesel properties [11]

Plant sources	% seed oil content (wt in biomass)	Oil yield (L oil/ha year)	Land use (m^2 year/kg biodiesel)	Biodiesel productivities (kg biodiesel/ha year)

Corn	44	172	66	152
Hemp	33	363	31	321
Soybean	18	636	18	562
Jatropha	28	741	15	656
Camelina	42	915	12	809
Canola	41	974	12	862
Sunflower	40	1070	11	946
Castor	48	1307	9	1156
Palm Oil	36	5366	2	4747
Microalgae (low oil content)	30	58700	0.2	51927
Microalgae (medium oil content)	50	97800	0.1	86515
Microalgae (high oil content)	70	136900	0.1	121104

3.1. Microalgal Biotechnology for Lipids Production

Oil levels of 20–50% are common in microalgae. The whole technical process in the production of biodiesel from microalgae has been well investigated in recent years. The entire production process ranging from the cultivation of high-lipid microalgae to the production of biodiesel from the microalgal oils has also been explored. In the laboratory conditions, the ideal oil content could reach 56–60% of total dry biomass by genetic engineering or heterotrophic culture techniques. These technological advances suggest that the industrial production of biodiesel from microalgal oils may be feasible in the near future. The main methods for lipids production using microalgae are [7]:

a) Biosynthesis of lipids/fatty acids in microalgae

- The elongation and desaturation of carbon chain of fatty acids
- The formation of acetyl coenzyme A (acetyl-coA) in cytoplasm
- The biosynthesis of triglycerides in microalgae

b) Phototrophic cultivation of microalgae for lipids production

c) Heterotrophic cultivation of microalgae for lipids production

d) Genetic engineering for lipids production

3.2. Microalgae Cultivation Technology

Industrial reactors for algal culture are at present known as open pond and photobioreactor systems. Photobioreactors are different types of tanks or closed systems in which algae are cultivated. Open pond systems are shallow ponds in which algae are cultivated. Nutrients can be provided through runoff water from nearby land areas or by channeling the water from sewage/ water treatment plants. Technical and biological limitations of these open systems have given rise to the development of enclosed photoreactors. Microalgae cultivation using sunlight energy can be carried out in open or covered ponds or closed photobioreactors, based on tubular, flat plate or other designs. A few open systems are presented for which particularly reliable results are available. Emphasis is then put on closed systems, which have been considered as capital intensive and are justified only when a fine chemical is to be produced. Microalgae production in closed photobioreactors is highly expensive. Closed systems are much more expensive than ponds. However, the closed systems require much less light and agricultural land to grow the algae. High oil species of microalgae cultured in growth optimized conditions of photobioreactors have the potential to yield 19,000–57,000 liters of microalgal oil per acre per year. The yield of oil from algae is over 200 times the yield from the best-performing plant/vegetable oils [22].

3.2.1. Open Pond Systems

Open ponds are natural waters (lakes, lagoons, ponds), artificial ponds or containers. Many different designs have been suggested for pond construction but generally four major pond design have been developed and operated at a large-scale (Figure 5) [21]:

a) Unstirred ponds (lakes and natural ponds),
b) Inclined ponds,
c) Central pivot ponds,
d) Raceway ponds.

One of the major advantages of open ponds is that they are easier to construct and operate than most closed systems. However, major limitations in open ponds include poor light utilization by the cells, evaporative losses, diffusion of CO_2 to the atmosphere, contamination and requirement of large areas of land [23].

Open pond cultivation systems are considered to be the most economical culture systems for large-scale microalgal cultivation. However, the productivity of open pond microalgae cultivation systems is strongly correlated to the location of the pond, the layout of the pond system, microalgae species and weather conditions. The calculation-based results showed that climate conditions such as temperature changes and solar irradiation play very important roles in open race-way ponds [24].

Figure 5. Different designed open pond systems [21]

3.2.2. Photobioreactors (PRB)

Algae can be harvested using a device called photobioreactors, this is also known as a PBR. The PBD is a self-contained system with a controllable environment. It allows the supply of light, nutrients, carbon dioxide, air, and temperature can be regulated. Using a PBR can prevent or at least minimise contamination (from other algae species and bugs), and allows easier cultivation of one algae strain. It also offers better control over a range of other growing conditions. In addition to this a, closed system such as the PBR reduces evaporative water losses, and has lower carbon dioxide losses which all-in-all means higher cell concentrations. In other words there are more grams of algae produced per litre of water [23].

Closed systems can be classified as horizontal tubular photobioreactors; stirred photobioreactors; airlift and bubble column photobioreactors represented in Figure 6. The main factors affecting PBR cultivation are known as temperature, pH, light, carbon uptake, oxygen generated, mixing rates, and nutrient uptake. The advantages and disadvantages of the respective PBRs are summarized in Table 2. [24].

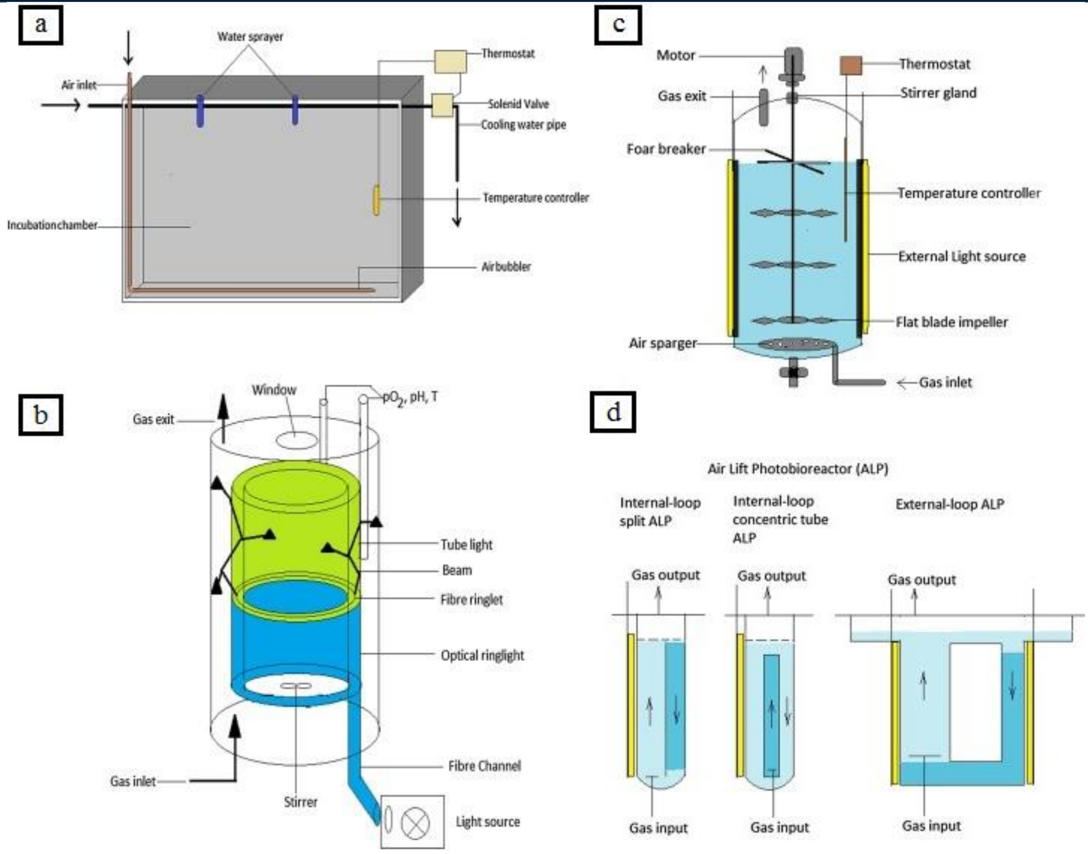

Figure 6. Diagrammatic representation of the different types of photobioreactors used for microalgal cultivation [24]

Table 2: Advantages and disadvantages of different PBRs [24]

Type of photobioreactor (PBR)	**Advantages**	**Disadvantages**
Horizontal tubular PBR	The shape is itself an advantage for their orientation towards sunlight which results in high light conversion efficiency	High concentration of dissolved O_2 causes photo bleaching and reduces photosynthesis efficiency High energy consumption
Stirred PBR	Most conventional reactor, agitation is provided with the help of impellers CO_2 enriched air bubbled through the bottom	Lack of internal light Low surface area to volume ratio and mechanical agitation limits its use
Airlift PBR	High mass transfer, good mixing achieved Good for immobilization of algae	Due to its complexity there is difficulty in scaling up
Bubble column PBR	Low capital cost, high surface area to volume ratio, lack of moving parts Satisfactory heat and mass transfer, efficient release of O_2	At gas flow rate less than ≤ 0.01 m s^{-1} circulation flow pattern do not exist because of the lack of back mixing Lack of internal light

Among the different PBRs available for microalgal biomass production, the airlift reactor seems the most suitable reactor for flue gas CO_2 sequestration. High gas transfer, uniform mixing, low hydrodynamic stress, and ease of control are the characteristic advantages of this reactor. But, none of these configurations present in the bioreactor can effectively control all the various parameters that are required for utmost microalgal growth, metabolic activity, and bio-fixation of CO_2 particularly at large scale production process [24].

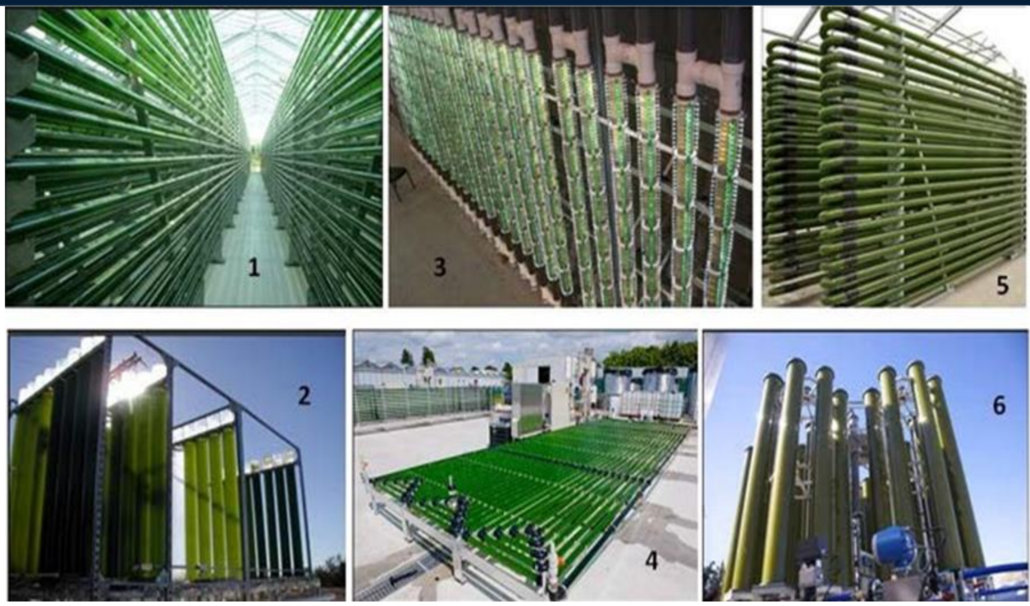

Figure 7. Different closed photobioreactors for production of microalgae in the world [25]

3.3. Microalgal Industry

The area of microalgae biotechnology is rapidly developing, attracting funding and investment worldwide. Examples shown in Table 3 indicate the range of products from large-scale microalgae cultivation and include a description of the different cultivation methods, sectors and location. Large-scale cultivation facilities for the production of nutritional supplements are predominant as these are economically feasible due to the high value end product (e.g. pigments and nutrients). Over 80% of the world's green algae producers are currently located in Taiwan, with Inner Mongolia in China and Israel being the top three producers of Dunaliella worldwide. The use of large-scale microalgae cultivation for wastewater treatment is being developed in some regions and this is discussed in more detail later. There is funding from governments in the US, EU, Brazil, China, India, Canada and other countries worldwide in both universities and commercial facilities. Many petro-based companies including Exxon, Shell, BP, Statoil, ENAP, Chevron are investing in biofuel R&D for production of methanol, ethanol, bio-butanol, biodiesel, and bio-crude as well as bio-based chemicals [26].

Table 3. Some examples of industries investing in large scale microalgae cultivation [26]

Algae Types	**Cultivation**	**Industry/Product**	**Location**	**Link**
Cyanobacteria	Closed (PBR)	Biofuel (Ethanol, biodiesel)	USA (Florida)	www.algenolbiofuels.com
Unknown	Closed (Heterotrophic)	Biofuel (Biodiesel)	Brazil	solazyme.com
Unknown	Closed (Heterotrophic)	Biofuel (Jet fuel)	USA (New Mexico)	www.sapphireenergy.com
Chlorella	Closed (PBR)	Nutraceutical (Dietary supplement)	Germany	www.algomed.de
Haematococus	Open (Raceway)	Nutraceutical (Astaxanthin)	Israel	www.algatech.com
Haematococus /Spirulina	Open (Raceway)	Nutraceutical (Dietary supplement)	USA (California)	www.earthrise.com
Haematococus	Closed (PBR)	Nutraceutical (Astaxanthin)	Sweden	www.bioreal.se
Spirulina	Open (Raceway)	Nutraceutical (Dietary supplement)	USA (California)	www.earthrise.com
Spirulina/Chlorella	Open (Centre Pivot Ponds)	Nutraceutical (Dietary supplement)	Taiwan	www.wilson-groups.com

Dunailella	Closed (PBR)	Nutraceutical (β-caretone)	Israel	nikken-miho.com
Unknown	Open (Biofilm)	Wastewater treatment	USA (Florida)	www.aquafiber.com

3.4. Algae Oil Extraction

According to ASTM standards, biodiesel procreated from microalga feedstock shows similar affection to standard biodiesel. Downstream process leads with harvesting, dewatering, extraction of algal oil and ends with transesterification of lipid constituents into biodiesel. It is arduous to explain processing due to its specificity as well as dependency on the required product. After harvesting of algal biomass, next step is drying and extraction of oil. Selection of methods for drying and extraction purpose needs to be of special concern due to some valuable products such as proteins, carbohydrates etc. containing algal species are also formed. Extraction of algal oil from biomass can be done by mechanically, chemically or combination of the two. Mechanical extraction is a conventional method which includes bead mill, press, high press homogenization, ultrasonic, autoclave and microwave assisted oil extraction. Non mechanical methods are solvent extraction, supercritical fluid extraction and osmotic shock. In case of extraction carried out chemically, it involves solvents such as hexane, ethanol, chloroform, diethyl ether etc. One of the major detriments during solvent extraction is denaturing of by-products. It also comprises risk of explosion and decontamination of the final product. Methods used for cell disruption are based on cell wall of algal species as well as required product. Mechanical methods used for biomass extraction elect to overcome the possibility of contamination that occurs in case of chemical extraction. If approximately 80%(w/w) lipid content is obtained from algal species, then the method is regarded as better and appropriate [27].

3.5. Biodiesel Production Methods Using Microalgae

Biodiesel production from algae is generally done by one of three methods. The first is a two-step protocol in which algae oil is extracted with organic solvent and then converted to biodiesel using a catalyst, such as an acid, a base, an enzyme or heterogeneous ones. The second method directly produces biodiesel from algae biomass using an acid catalyst at atmospheric pressure and ambient temperature. The third method is one-step conversion to biodiesel at high pressure and high temperature in the absence of a catalyst. Each method has innate advantages and disadvantages. Method 2 requires high concentrations of sulphuric acid since moisture in the biomass is a limiting factor for conversion efficiency. In contrast, moisture can be ignored under the subcritical or supercritical conditions of method 3; however, side reactions happen at subcritical or supercritical conditions that produce organic acids and heterocyclic nitrogen compounds from the degradation of proteins and carbohydrates. These contaminants lower the quality of biodiesel or interfere with the purification process. From an economics and energy cost point-of-view, oil extraction directly from wet algal slurry is thought to be preferable. Biodiesel is produced from algal oils by transesterification and has similar properties as petro-diesel [9].

3.6. Economic Overview of Microalgal Biodiesel Production

The cost of building a biodiesel plant depends upon factors like feedstock, location of the plant, plant capacity, plant design and equipment. When biodiesel is produced from Soya or rapeseed oil the cost of biodiesel production increases because the cost of feedstock is the largest expense [24].

Therefore, use of non-edible feedstock like jatropha oil reduces the cost incurred on feedstock to a considerable amount. The economic analysis of Jatropha biodiesel revealed the cost of production of jatropha ethyl ester to be 0.40 € per liter [28] whereas, the cost of production of biodiesel from palm oil is 0.57 € per liter [22].

Although the use of non-edible oil for biodiesel production reduces the cost of production yet, there are major drawbacks which prevent the industry to flourish. A jatropha plant takes 2–3 years to grow and produce seeds. Under such circumstances, the various advantages of microalgae over other terrestrial crops make them an interesting perspective for the future. Medipally [29] claims that when the influential factors like irradiation, mixing, media constituents are well optimized then the production cost could be reduced to 0.68 € per kg. At these price microalgae could become a promising feedstock for biofuel production.

4. BIODIESEL IN TURKEY

4.1. Requirement of Biodiesel

Turkey which is not a producer of gas and oil, supplies 96% of its gas demand and 90% of its oil demand by imports. Because the dependency on importation is so high, energy security and continuity of energy supply have vital importance for Turkey [30].

The 2020 projection related to the Blue Book published by the Ministry of Energy in 2011 is shown in Table 4. It is predicted from the table that in a decade, the energy need would increase at a rate of 157% for the industry sector; it would increase at a rate of 64.7% for the residential sector; and it would increase at a rate of 122% for the transportation sector [31].

Table 4. Energy projection of Turkey (Ttoe) [31]

Year	Industrial	Housing	Transport	Total final energy	Total primary
20	49,270	32,650	22,370	111,705	142,861
20	52,056	34,500	23,700	117,950	150,890
20	54,766	36,450	25,100	124,300	160,211
20	57,633	38,507	26,541	130,968	170,154
20	60,991	40,400	28,000	137,996	178,455
20	64,842	42,150	29,480	145,403	187,923
20	69,144	43,900	31,000	153,310	198,911
20	73,795	45,700	32,500	161,610	210,236
20	78,732	47,549	34,039	170,292	222,424
20					

According to the data from Turkish Statistics Institute (TUIK), while the number of diesel-powered vehicles in 2015 (9,576,896) is about three times higher than in 2004 (3,346,355), there is no significant increase is observed in the number of gasoline vehicles (from 5,569,192 to 5,977,352). It is expected that the requirement of diesel fuel in Turkey will be increased dramatically in future especially in transportation sector [32]. For this case, alternative fuels for transportation are essential to supply requirements.

On the other hand, when Kyoto Protocol, Turkey's “Intended Nationally Determined Contributions (INDCs)” report and the energy demand in Turkey are taken into account, utilization of biofuels instead of petroleum based fossil fuels became prominent [33].

It is clear that with the increasing energy demand and environmental concerns of Turkey, renewable biofuel biodiesel is getting more importance day by day.

4.2. Biodiesel Feedstocks in Turkey

The conventional feedstocks for biodiesel production are vegetable oils and fats, such as rapeseed, soybean, sunflower, coconut and palm oil. Among them, vegetable oils are the most common used ones as biodiesel raw materials. Depending upon environmental condition, the sources of biodiesel vary from country to country like soybean for North America, sunflower and rapeseed for Europe, palm for Southeast Asia, coconut for tropic and sub-tropic area etc. [34].

Although Turkey is an agricultural country, vegetable oil production is not sufficient compared to the consumption rates. The production and importation of crude vegetable oil are shown in Figure 8 [35]. According to the data (TUIK), importation rates of crude vegetable oil is pretty higher than production rates. In the circumstances, biodiesel production from vegetable oil is not realistic for Turkey, hence new generation biodiesel feedstocks like microalgae must be cultivated and used to supply needed biodiesel raw material without affecting food prices such as edible vegetable oils.

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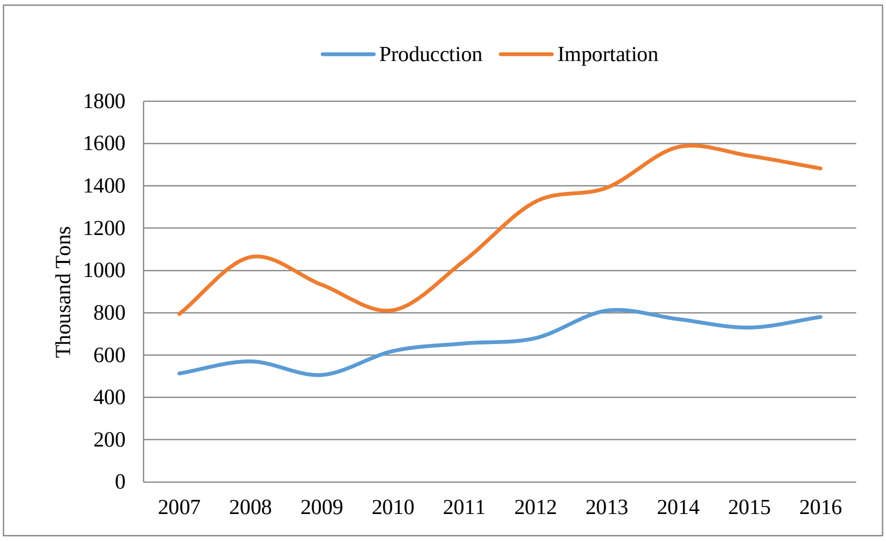

Figure 8. Crude vegetable oil production and importation of Turkey [35]

5. CONCLUSION

Because of the superior advantages over the petroleum diesel fuel, the use of biodiesel and biodiesel/diesel blends in internal combustion engines has attracted much attention in recent years. However, high costs of oleaginous materials are the major problem hindering commercial production and being widespread of biodiesel fuel. In addition, using conventional feedstocks such as vegetable oils in biodiesel production compromise production of food or another products derived from crops. In this case, microalgae are getting promising biodiesel feedstock since microalgae can be easily cultivated even in harsh conditions, including salty and sewage receiving areas without causing any negative impacts on food security, global food markets, water scarcity, and deforestation. Therefore, in the countries such as Turkey where oil crops, waste cooking oil and animal fat cannot realistically satisfy the demand of biodiesel feedstock, the investigations and government aids must be focused on large scale microalgal biomass cultivation, and development of microalgae-based technologies to minimise technical and economic constraints.

BIOGRAPHY

Veli Gokhan DEMIR graduated from mechanical engineering at Sakarya University in 2008. He has a master degree in mechanical engineering from Balikesir University and he has been a Ph.D. student since 2011. In his Ph.D. work, he has investigated about production of biofuels and their combustion efficiencies. His main research interests are in the field of energy efficiency improvement, biomass energy utilization, and combustion in engines. Currently, he is a research assistant in mechanical engineering at University of Balikesir.

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Wastewater Treatment by Floating Macrophytes (*Salvinia Natans*) Under Algerian Semi-Arid Climate

Laabassi AYACHE[1*], Harzallah DAOUD[2], Boudehane ASMA[1], Fercha AZZEDINE[3]

Abstract

Macrophyte pond has developed strongly in the field of wastewater treatment for irrigation in rural areas and small communities. Their association allows, in some cases, to increase the hydraulic capacity while maintaining the highest level of quality.
The present work is devoted to the treatment of domestic wastewater under climatic conditions of Algeria (semi-arid) through a system using two tanks planted with Salvinia natans.
The performance study and treatment efficiency of the system overall shows that the latter provides a significant removal of nitrogen pollution: total Kjeldahl nitrogen NTK (85.2%), Ammonium NH_4^+*-N (79%), Nitrite* NO_2^-*-N (40%) also, a major meaningful reduction of biochemical oxygen demand* BOD_5 *was observed at the output of the system (96.9 %). As* BOD_5*, the chemical oxygen demand (COD) removal was higher than 95 % at the exit of the two tanks. A moderately low yield of phosphate-phosphorus (*PO_4^{3}*-P) was achieved with values not exceeding 37 %. In general, the quality of treated effluent meets the Algerian standard of discharge and which allows us to select a suitable species in constructed wetland treatment systems under semi-arid climate.*

Keywords: *Nutrient removal, Salvinia natans, semi-arid climate, Wastewater treatment*

1. INTRODUCTION

In most countries of the world, there has been growing and irreversible interest of the public for the protection of the environment. In Algeria, for instance, the water pollution problem is quite serious and therefore, purification techniques including constructed wetlands (CWs) using macrophytes are currently widely used for treatment of wastewater. CWs become an interesting alternative for the treatment of wastewater, seen the great benefits that they exhibit, they are less expensive to build and operate, are constructed directly on the wastewater discharge site, require little mechanized equipment and ultimately are less sensitive to changes in pollutant loads [1].

The main functions of CWs include surface water storage, holding and recycling nutrients, providing wildlife habitats, stabilizing shorelines, controlling and buffering storm related flooding, recharging groundwater, roviding treatment for pollutants in water [2]. Furthermore, CWs can effectively remove organic matter, suspended solids, metals, and excess nutrients (such as nitrogen, phosphorus, etc.) through various processes including filtration, sedimentation, biological and microbiological adsorption, and assimilation [3].

[a] *Corresponding author: Department of Ecology and Environment, Faculty of Natural and Life Sciences, University of Batna2, Algeria.* laabassiayache@gmail.com
Department of Ecology and Environment, Faculty of Natural and Life Sciences, University of Batna2, Algeria. biologie-ecologie@hotmail.fr
[2] *Laboratory of applied microbiology. Faculty of Natural and Life Sciences, University of Sétif 1, 19000 Algeria.* harzaldaoud@yahoo.co.uk
[3] *Department of Agronomy, Faculty of Natural and Life Sciences, University of Abbas Laghrour Khenchela Algeria.* ferchazzed@yahoo.fr

Macrophyte-based wetland systems (MBWS) are reported to be effective for the treatment of primary, secondary and tertiary urban wastewater, domestic, stormwater, agricultural and industrial wastewater [4, 2, 5], however, the challenge is to maximize efficiency the lowest possible cost [6]. The choice of plants is an important issue in the filters planted with macrophytes because they have to survive the potential toxic effects of sewage and their variability. The use of local plants with economic and environmental interests in the sewage systemmakes them more exciting.

Aquatic plants, emergent or free floating, acquire more and more importance in the world especially in countries with hot climates where the photosynthetic efficiency is important. The produced biomass is valued using biomethanation or by incorporation in animal nutrition [7]. Floating or emergent aquatic plants, such as water hyacinth (*Eichhornia crassipes* (Mart) Solms), water lettuce (*Pistia stratiotes L*.), *Salvinia natans* (L.), cattail (*Typha latifolia L*.), bulrush (*Scirpus validu .L*.), are able to treat wastewater with high purification yields [8, 9, 10].

2. MATERIALS AND METHODS

2.1. Experimental device and methods

The experiment was carried out under semi-arid conditions at the town of Merouana (35°37'43''N, 05°54'42'E) located 500 km East of Algiers (Fig. 1), which has a semi-arid to arid Mediterranean climate with an average rainfall of about 240mm per year and an average temperature of about 5 to 38°C. The experimental device used for the present study depicted in Figure 2. Thre biofiltration unit, comprised two tanks of 75 liters capacity (50 cm(L) x 50 cm(W) x 60 cm(H)). The tanks are filled to 5 cm in depth and 30 cm with respectively gravel (5-10mm) and soil with silty clay-sandy texture (31% clay, 20% silt and 49% sand). The tanks were planted with *S. natans* (36.5 g per tank).

The systems supplied by raw domestic wastewater (25 liters/day) acquired from Merouana municipal sewage treatment works, and Table 1 summarizes its physicochemical characteristics. Tanks inclined at 10° to the surface such that water can be directly downstream, and fitted with a drain at the bottom for percolating water collection (effluent). Wastewater passes from a tank to another through a 4-cm (outside diameter) perforated PVC pipe. The experiment lasted eight months from April to November 2015.

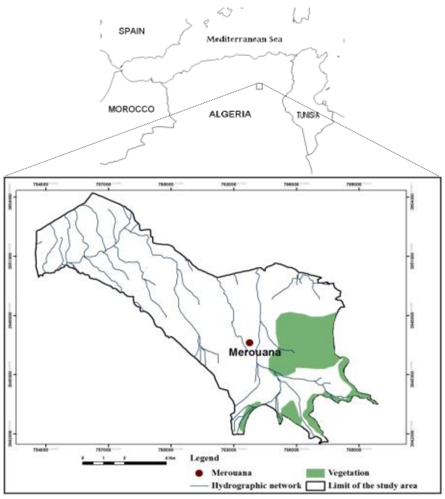

Figure 1. Location map of analyzed area.

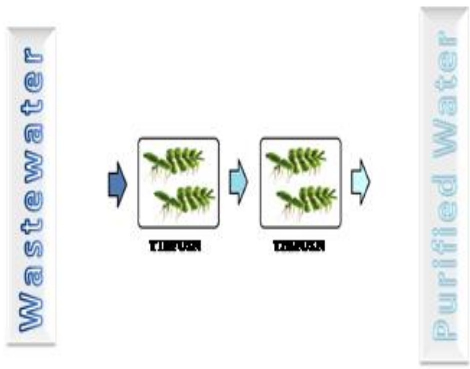

Figure 2. Macrophyte-biofiltration system used for wastewater treatment. T1 BFUSN, T2 BFUSN(Tanks 1 and 2 of second biofiltration unit planted with Salvinia natans).

.2.2. Wastewater quality monitoring and statistical analyses

The CWs placed in operation in April 2015. Their removal efficiency and treatment performance evaluated in eight sampling campaigns, which took place in the eight-month period from April to November 2014.

Wastewater samples (influent and effluent) were collected and stored in glass bottles, transported to the laboratory and analyzed immediately for biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total Kjeldahl nitrogen

(TKN), nitrate-nitrogen (NO_3-N), nitrite-nitrogen (NO_2-N), ammonium-nitrogen (NH_4-N) and phosphate–phosphorus (PO_4-P) according to French standard methods [11]. In addition, measurement of temperature (T) and pH had done using a portable instrument (ProfiLine pH 3110, WTW). We used at least five repetitions of each sample to achieve sufficient accuracy.

Treatment efficiency of chemical parameters was calculated as the percentage of removal for N and P as follows:

Removal efficiency (%) = $\left(\frac{Ci\text{-}Ce}{Ci}\right)$ *x 100*, where Ci and Ce are the influent and effluent concentrations in mg/L.

Data analyzed using one-way ANOVA and least significant difference tests (LSD at alpha = 0.05) to find differences among means of the different physicochemical parameters of wastewater before and after treatment. Statistical analyses carried out using STATGRAPHICS Centurion XV (Manugistics, Rockville, MD, USA)

3. RESULTS AND DISCUSSION

Constructed wetlands (CWs) using macrophytes are currently widely used for treatment of wastewater. In order to investigate whether the CWs using emergent macrophyes (EM) and floating macrophytes (FM) were effective for the treatment of domestic wastewater, we carried out the present study the aquatic plant species, namely *S. natans* an FM

Overall, our results indicate that the biofiltration system (FM) is highly effective in the treatment of domestic wastewater (Tables 1, 2 and Fig. 3a-i).

3.1. Mean physicochemical parameter variation

Table 1 summarizes results of the measured physicochemical proprieties of wastewater before and after biofiltration treatment. Figure 3, however, displays the seasonal variation of all these parameters throughout the eight-month period of experience. In contrast to the mean values of the wastewater temperature, which showed only slight spatial variations along the biofiltration unit and generally ranged from 18.2 to 24.6ºC depending on the season (Fig. 3a), all the studied parameters were showed a significant variation after wastewater biofiltration (Table 1).

As revealed by Figure 3b, the mean pH value of input water used in this study was 7.2 and ranged from 7 to 7.5. However, at the outlet of biofiltration units, the pH values were ranging from 7.1 to 8.3. This decrease in pH values was statistically significant ($P<0.01$).

In contrast to the slight decrease observed in the mean values of wastewater temperature at the outlet the biofiltration unit, can be explained by the fact that water surface was fully hedged by *S.natans* (Fig. 3a and Table 1), the mean values of pH were significantly increased (Table 1). Similar results observed in previous studies [12- 13]. Both decrease in temperature and increase in pH can be explained by the algal growth observed at the surface of each tank since foliar cover may preserves the tank surface against summer drying and offer shade to bacteria and the fact that algae can absorb CO_2 faster than it can be replaced by bacterial respiration [12].

3.2. Pollutant removal efficiency

Table 2 presents the variation of mean removal efficiency along the various biofiltration unit for all the pollutants. Overall, we calculate the removal for each constituent based on its concentrations at the inlet and outlet of the biofiltration unit. As displayed by Table 2, with the exception of nitrate (NO_3-N), the biofiltration system exhibited high percentages of removal efficiency of nitrogen from wastewater namely in term of NH_4-N, and TKN.

Regarding nitrogen pollution, our results indicate high average removal efficiencies of the biofiltration system, particularly for ammonium (NH_4-N) and TKN. Consistent with this, in aquatic ecosystems, the decrease in NH_4-N content was usually explained by the transformation of NH_4-N into NO_3-N (the so-called nitrification), which is favored by aerobic conditions, plus a subsequent denitrification [14]. Another possible way is volatilization as NH_3, which is inducible by the increase of pH [15]. Under natural growth conditions, NH_4-N is probably the main N source preferred for most aquatic macrophytes as revealed by results of numerous studies [16-17].

Table 1. Physicochemical parameter and pollutant concentration statistics

		INLET	OUTLET BFUSN	F	LSD5%
pH	Mean	7.18 (c)	7.41 (bc)	5.50**	0.29
	SD	0.17	0.23		
	Min	7.0	7.1		
	Max	7.5	7.75		
T °C	Mean	21.13 (a)	19.94 (ab)	1.63 n.s	n.s
	SD	2.25	2.10		
	Min	18.2	17.3		
	Max	24.6	23.3		
NH_4-N	Mean	64.36 (a)	13.38 (bc)	264.3***	5.51
	SD	8.46	2.29		
	Min	51.84	10.42		
	Max	76.18	16.46		
NO_3-N	Mean	2.43 (b)	3.61 (b)	25.77***	10.11
	SD	0.93	2.32		
	Min	1.4	1.0		
	Max	3.9	6.9		
NO_2-N	Mean	0.128 (a)	0.083 (ab)	3.73*	0.056
	SD	0.05	0.06		
	Min	0.08	0.02		
	Max	0.20	0.22		
TKN	Mean	102.4 (a)	15.84 (b)	97.43***	86.52
	SD	22.81	11.01		
	Min	69.6	6.40		
	Max	131.3	40.1		
PO_4-P	Mean	10.95 (a)	6.86 (b)	10.66***	3.85
	SD	1.47	1.90		
	Min	8.9	5.1		
	Max	13.2	11.1		
BOD_5	Mean	311.3 (a)	8.31 (b)	43.7***	302.07
	SD	129.7	3.65		
	Min	112.4	4.2		
	Max	466.1	15.5		
COD	Mean	981.7 (a)	40.56 (b)	209.08***	935.64
	SD	171.4	4.47		
	Min	683.5	33.2		
	Max	1230.1	47.1		

Table 2. Removal efficiency (%) of different nutriments for the three units

		BFUSN	F	LSD5%
NH_4-N	Mean	79.0 (a)	18.18***	3.45
NO_3-N	Mean	17.1 (a)	n.s	n.s
NO_2-N	Mean	40.0 (a)	n.s	n.s
TKN	Mean	85.2 (a)	4.32*	7.75
PO_4-N	Mean	36.9 (a)	n.s	n.s
BOD_5	Mean	96.9 (a)	n.s	n.s
COD	Mean	95.7 (a)	5.04*	1.25

*, **, *** indicate significant differences at $P<0.05$, 0.01 and 0.001 respectively. n.s, not significant. Different small letters mean significant differences ($P < 0.05$) among treatments.

The lower removal of NO_3-N in the outlet water compared to wastewater, on some individual occasions, bear witness to the great nitrifying activity. In agreement, aquatic macrophytes have well-developed internal air spaces (aerenchyma) throughout the plant tissues that ensures the transfer of oxygen to the roots and rhizomes [18]. The oxygen that diffuses through the roots stimulates growth of nitrifying bacteria in the rhizosphere [19]. In general, the positive removal efficiencies of BFUSN can probably due to macrophytes uptake [20] and/or the process of denitrification [21].

Nitrite concentrations of the inflow and the outflow are of secondary importance for the evaluation of the overall annual nitrogen removal of the wetland [22]. In general, the low outflow concentrations (< 1mg/L) been brought about by nitrification of NH_4-N to NO_3-N and NO_2-N at aerobic plant roots, with subsequent rapid denitrification to the atmosphere in the anaerobic parts of the substrate or is immobilized by plant uptake, adsorption, and precipitation [23].

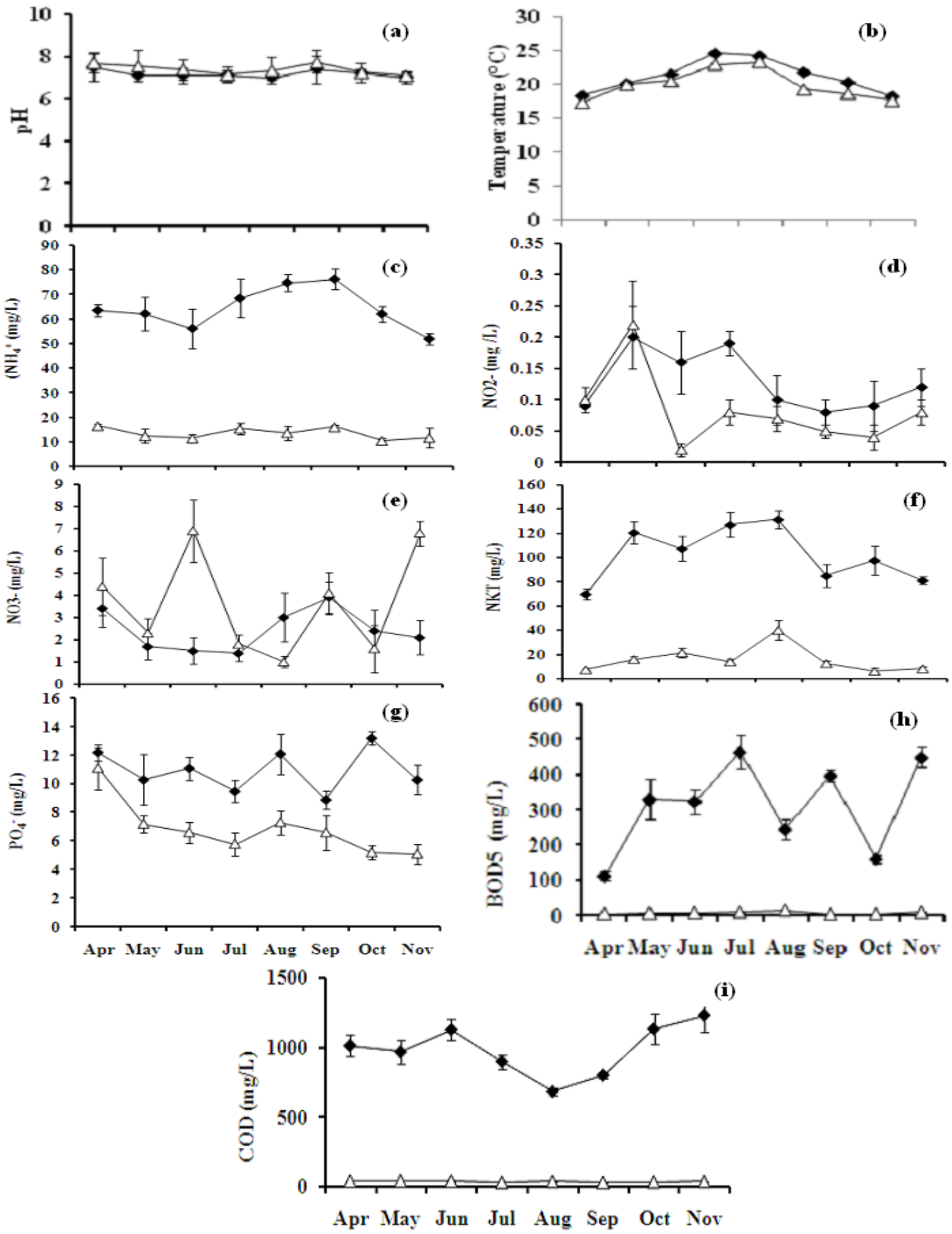

Figure 3. Time-course of change in Temperature (a), pH (b), NH_4-N (c), NO_2-N (d), NO_3-N (e), TKN (f), PO_4-P (g), BOD_5 (h), COD (i) throughout the period of study (Mean ± SD).

The high levels of TKN removal efficiencies in all the treatments are probably due to macrophytes that play a major role in eliminating TKN through nitrification, metabolism, and storage processes [24, 25, 26]. TKN removal efficiency increases with increase in pH [27-28].

In addition, it appears from the same figure that the concentration of the main forms of nitrogen (NH_4-N, NO_3-N and TKN) and PO_4-P as well as BOD_5 and COD in wastewater showed highly significant decreases ($P<0.001$) after biofiltration (Table 1 and Fig. 3).

Table 2 also showed the variation in removal of orthophosphate from the wastewater in the various experimental devices. Overall, there is no significant difference in the removal efficiency of PO_4-P among the biofiltration unit. The efficiencies of removal in BFUSN increase by 09-60.6% with an overall average of 36.9%. It is worth noting that even though PO_4-P concentrations increased in the outlet waters on some individual occasions.

The moderately high level of phosphorus monitored as orthophosphate (PO_4-P) could be due to direct use of PO_4-P by plants [29] or attributed to adsorption on the soil particles and precipitation reactions [30]. However, it also added that release of orthophosphate and clogging of the system could explain this low average reduction.

The average concentrations and overall efficiency elimination of BOD_5 in the influent and effluent throughout the study period displayed in Figure 3h and Table 2 respectively. The removal of BOD_5 found higher (96.9 %).

Otherwise, the higher reduction of BOD_5 can be attributed to several mechanisms (physical and biological processes) including sedimentation and filtration associated with settleable solids or filterable material, in addition to oxidation mainly by aerobic bacteria (protozoa, rotifers, etc.) attached to plant roots [31].

The load of domestic wastewater chemical oxygen demand (COD) fluctuates greatly between 683.5 mg/L and 1230.1 mg/L with a mean value of 981.7 mg/L. Thus, at the outlet of the three units follows fluctuations in domestic wastewater with significant picks (Fig. 3i). Overall, compared to domestic wastewater, the treated wastewater quality is significantly better. The removal rates of COD (95.7 %).

Like BOD_5, COD reduction is almost entirely due to physical processes such as filtration and adsorption rather than biological processes associated with the microbial community or with the plants [32]. These findings are in agreement with some studies reported in the literature, which found better COD removal whether using floating macrophytes [33-28].

4. CONCLUSION

This work provides an opportunity to highlight the potential of floating plants (*S. natans*) to treat the domestic wastewater under semi-arid conditions. Overall, our result indicates that the bioinfiltration unit provide a significant removal of the organic (BOD_5, COD) and inorganic (TKN, NH_4-N and PO_4-P) pollutants from domestic wastewater. The effluent quality was lower than the Algerian standards related to effluent quality for agricultural reuse purposes, therefore, it is possible to reuse the treated wastewater for restricted irrigation and can be environmentally friendly. The good results given by *S. natans* (rare plant) involve its use in wastewater treatment in order to preserve this kind of plants. Finally, the use of this kind of biofiltration system for the treatment of other types of water pollution (e.g. microorganisms and heavy-metal pollution) is required.

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Estimating Willingness to Pay for Improved Domestic Water Services in Terengganu, Malaysia: A Comparison between Contingent Valuation and Choice Modelling Approaches

***Mahirah KAMALUDIN*[1]*, Kuna SANDRAN*[2]*, Nor SHUHADA*[2]**

Abstract

Many environmental resources are characterized as public goods, such as water quality, biodiversity, and a stable climate. It is reasonable to question whether environmental resources are public goods in a fully pure sense. With low water quality, for example, those enjoying it may cause some degree of rivalry, when good water quality is not accessible to everyone. Unsustainable and excessive water consumption harms the environment by changing the water table and depleting ground water supplies. The objective of this study is to assess the willingness to pay of consumers in Terengganu for improvements in domestic water services. Excessive water consumption, frequent interruptions, urbanization, climate change, rapid social and economic growths are putting higher demands for quality of services and the water provider is unable to cope with the growing number of populations. Water price was last reviewed about 20 years ago and demonstrated among the lowest in Malaysia. This study has employed Contingent Valuation (CVM) and Choice Modelling (CM) methods to investigate water demand among the consumers, focusing on improvement in water services. This study found that consumers are ready and willing to pay for new proposed water prices as long as they are guaranteed with high standards in services. They are willing to pay about RM0.58 applied on the first 30m3 which is 11.53 percent higher than the current water price. Moreover, the findings have several implications for the water companies, by reducing the frequency of water interruption becomes the main concern of the consumers for a positive change in their water services. The estimated water prices can be suggested for implementation in the water industry which will support numerous upgrading projects for sustainable water supply for future generation. A sustainable water service is also helping the environmental, economic, and social sustainability of the communities with these utilities served.

Keywords: Economic Valuation; Contingent Valuation Method, Choice Modeling, willingness to pay, water service.

1. INTRODUCTION

Water is fundamental to life; however access to safe and clean drinking water is scarce nowadays. Water consumption has been growing at more than twice the rate of population increase. Moreover, many of the water systems that keep the ecosystems flourishing and feed the human population have become stressed. There is sufficient water on this planet for all but water is distributed unevenly and too much of it is wasted, polluted, and inefficiently used. In many parts of the world, the water resource is also unsustainably managed. At the global level, water providers and related authorities are facing pressure in water management. Population increases, changes in urbanization, and climate

[1] *Corresponding author: School of Social and Economic Development, Universiti Malaysia Terengganu, Terengganu, Malaysia. mahirah.k@umt.edu.my*

[2]*School of Social and Economic Development, Universiti Malaysia Terengganu, Terengganu, Malaysia.*

change force the providers to re-evaluate their policies and guidelines in water management. Basically good water management is tied to poverty reduction and improvement in health. Cheaper water prices may have burdened heavily on the producer's side, as it is too costly to upgrade their services. Cheap water price makes consumers take water for granted. Consumers believe that they can afford to pay the lower water price, thus they do not take any positive actions to conserve water. Lack of financial sources limits numerous projects while ignoring the consumer demand may create frustration at both sides; consumers and the producer. Previously, the events have demonstrated costly experiences because of frequent interruptions in services. Increasing water demand makes water supply insufficient to cater the whole population. Thus, new development and improvement in water services should be implemented without any delay in order to meet the increasing water demand.

The study investigates domestic water services in the state of Terengganu, Malaysia, using willingness to pay (WTP) approach. A survey was conducted to seek the value that people will place on water and their willingness to pay higher water rates for improved domestic water services. This study uses Contingent Valuation Method (CVM) and Choice Modelling (CM) methods to determine consumers' WTP and based on the WTP value obtained, the aggregate monetary benefits of improving water services for the consumers of Terengganu is estimated. The CM is able to determine marginal values and implicit prices for each attribute, which is related to the water services. This study includes a hypothetical change in the water services in the state from its current condition to improved conditions until the consumers believe it is at the acceptable level for their daily use.

1.1 Background of the Study

Sole water provider is Syarikat Air Terengganu Sdn. Bhd (SATU) operates in every district in the state. Their company's missions are to supply sufficient high quality of clean water and to improve the quality of services in order to fulfill consumer satisfaction. Their corporate visions are to support sustainable development, to concern and protect the environment, and to educate society about the importance of water conservation. Presently, water tariffs seem too cheap and the water provider is not able to generate enough revenue to cover the full cost of capital investment, operation and maintenance. In 2015, the state ranked second lowest in terms of domestic water prices in Malaysia about MYR0.52/USD0.13 applies for first 30m^3. Low water prices will limit implementation of infrastructure projects to upgrade facilities and it implies a low value of water, though the sources are valuable and insufficient. There are many difficulties in pricing the water as water demonstrates as public good supply and this valuable resource does not have well defined market. Though, it is still very costly and involves high investment when it comes to supply the services to consumers. In 2012, the state was supplying water roughly 96% of the state's population. There are two main sources of water supply in Terengganu which are from river extraction and dams. About 440 million litres per day is direct extraction from river and 187 million litres per day is from storage dams in 2012 (Malaysian Water Association, 2013). SATU serves about 85.2% for domestic users and 14.8% for non-domestic users. Based on statistics from Malaysian Water Association (2013), it shows that about 99.1% in urban areas and 92.9% in rural areas get connected to water supply.

2. PREVIOUS STUDIES ON APPLICATION OF CHOICE MODELLING AND CONTINGENT VALUATION METHOD

CVM captures the estimation of WTP by asking people directly what they are willing to pay for goods or services in the future (Wedgwood and Sansom, 2003). Meanwhile, the strength of CM is that it can measure the trade-off based on the attributes that respondents are willing to make in order to decide the best preference in the selection of those attributes. The CM is able to assess the benefits transfer when environmental goods have measurable attributes, which can be estimated (Hanley et. al, 1998). The CVM and CM have been used to estimate economic values for all types of ecosystem and environmental services. These methods are broadly used in many environmental studies in order to value the quality of environmental sources.

A study conducted by Hanley et al., (1998) shows that there are many advantages of the CM method over the CVM method in estimation of economic values for conservation and claimed that the CM method is more suitable in the estimation of marginal values of the wildlife and landscape characteristics. Adamovicz et al., (1998) carried out a study to measure passive use values in an enhancement program and found that the CM method performs well compared to CVM method, and if error variance is put into consideration, the preferences over income between the two methods are insignificantly different. Jin et al., (2006) maintains that CM method has its advantages over the CVM method in the valuation of waste management programs and concluded that the CM method is better in understanding different management attributes which help to choose the solid waste management options in efficient ways. However, the CVM offers limited number of scenarios and usually involves only one or two scenarios (MacDonald et al., 2005). The CM approach concerns respondent preferences about the attributes of the scenario rather than the specific scenario (Adamowicz et al., 1998). The CVM is low in cost to implement and produces a single policy option, while the CM has the advantage since its produces a value function which can be used to estimate values with multiple policy options. The CM is preferred more than CVM because it is important to value individual attributes. The CM provides a wider range of scenarios and organizes the experiment as a trade-off process between the attributes. Thus, it shows that CM is more cost-affective (Bennett and Blamey, 2001).

3. RESEARCH METHODOLOGY

In this study, survey was conducted on 1200 of household by using structured questionnaires designed to gather information for the CVM and CM approaches to determine willingness to pay for improved water services in Terengganu. A pre-test survey was conducted with 25 respondents in order to get realistic bid amount and to ascertain how significant the questions are. The pre-test was conducted for two times since in the first time of pre-test, the problem of yea-saying bias was occurred for CVM questions and there were not a consistent combination in attributes and their levels for CM questions. In final survey, respondents received a set of questionnaire with situations that ask how much they are willing to pay for improvements in the domestic water services. The amount that the respondents would be willing to pay depends on how strong they feel about the improvement in that program. The sampling consisted of domestic users of water supply in the state; who have registered active accounts with water provider. Besides, most of the respondents were the head of households since they are accountable for monthly water bill and we would like to know their contribution and WTP regarding to the services.

3.1 Contingent Valuation Method (CVM)

The CVM was proposed by Ciriacy Wantrup in 1947 and he believed that prevention of soil erosion will generate some extra market benefits. The one possible way to estimate these benefits is to elicit the individual's willingness to pay for these benefits through a survey method (Hanemann, 1994). In the CVM, only a price or bid is offered to respondents. The respondents are asked whether or not they would pay or accept a specific single amount for a program in question. The WTP question was,*"Would you be willing to pay* MYR *X for an improvement in water services so that your households can enjoy high standard of services in the future?"*. When a respondent is asked to pay a specific amount of money or price bid due to an improvement in domestic water services in the state, there will be a probability to obtain "yes" or "no" answers. Thus, the model can be formulated following Hanemann *et al.* (1991) as follows;

$$\text{Prob}\{\text{No}\} \Leftrightarrow \text{Prob}\{WTP_{max} < BID\} \Leftrightarrow G(BID;\theta) \quad (1)$$

$$\text{Prob}\{\text{Yes}\} \Leftrightarrow \text{Prob}\{WTP_{max} > BID\} \Leftrightarrow 1 - G(BID;\theta) \quad (2)$$

where, *BID* is the proposed price bid, WTP_{max} is the maximum willingness to pay (WTP) and $G(BID, \theta)$ is the cumulative distribution function (CDF) of WTP. This study uses CDF model to regress against the independent variables since the response variable is dichotomous, by taking 0 - 1 values (Gujarati, 2003). If the proposed price bid (*BID*) amount is more than the consumer's maximum willingness to pay, then they are not willing to pay for that amount. Conversely, if the bid is below their maximum willingness to pay amount, the probability of answering to that amount is "yes", showing that they will maximize utility and are willing to pay for that specific amount. The probability of the consumer willing to pay RM *X* is specified as follows according to Bishop and Heberlain's pioneering study, $G(BID;\theta)$ is the log-logistic cumulative density function:

$$\Pr_i^Y = [1 + e^{-(\alpha + \beta BID)i}]^{-1} \equiv 1 - G(BID;\theta) \quad (3)$$

Then, by employing Hanemann's suggestions, the log-likelihood function for the CVM that has two parts for "yes" and "no" answers; which is given as follows:

$$\begin{aligned} \ln L^{CVM} &= \sum_{i=1}^{N}\{c_i^y \ln \Pr_i^Y + c_i^n \ln \Pr_i^N\} \\ &= \sum_{i=1}^{N}\{c_i^y \ln[1 - G(BID;\theta)] + c_i^n \ln G(BID;\theta)\} \quad (4) \end{aligned}$$

where c_i^y takes a value of 1 if the *i*th consumer is willing to pay, answering "yes" to the initial bid and 0 otherwise, whereas c_i^n is 1 if the *i*th consumer states "no" and 0 if not. *N* is considered as consumers who participated in this study. The estimation of mean WTP can be derived based on Cameron (1988) as stated in the following equation:

$$WTP = \frac{b_0 + \sum_{i-2}^{n} b_i X}{-b_1} \quad (5)$$

where β_0 is the estimated constant, β_1 is the coefficient for the price bid, and β_i is a vector of coefficients for the socio-economic characteristics of the respondents.

3.2 Choice Modelling (CM)

CM is another stated preference technique that is frequently employed in estimation of values for environmental trade-offs (Bennet and Blamey, 2001). This method is based on the idea that a good can be depicted by its attributes and the levels that it takes. Respondents will be given a set of choices based on the attributes of the subject. Respondents are presented with different descriptions of the subject, differentiated in their attributes and their levels, and they are asked to rank, then rate or choose their most preferred option. The method has advantages since it offers a richer data set, benefit transfer potential, context flexibility, strategic bias reduction and framing effect control (Do and Bennet, 2007). The results can be used to determine the amount of money that people are willing to pay to move on from *status quo* to improved situations which are defined by different combinations of attribute levels (Bennet and Blamey, 2001). The CM portrays a series of water service combinations and consists of water prices presented to respondents in order to observe their most preferred choices which they derive the greatest utility.

This study portrays the probability of consumer *c* choosing alternative *i* in the choice set. The random utility model is linked with the probability of consumer utility in choosing the best option in the choice set. The random utility model depends on characteristics of the alternatives, characteristics of the consumer who picks the choices, and the variables which are the combination of the alternatives. The model specifically demonstrates that the utility which a consumer *c* correlates with alternative *i* is stated as:

$$U_i^c = V_i^c + \varepsilon_i^c \tag{6}$$

The probability of consumer *c* in choosing alternative *i* can be indicated in parametric function as follows:

$$Prob_i^c = f(x_i^c, x_j^c\,; i \neq j, \beta) \tag{7}$$

Where,

$Prob_i^c$ = Probability of consumer *c* in choosing alternative *i*

x_i^c = Parameter of observable characteristics of alternative *i* for consumer *c*

x_j^c = Parameter of observable characteristics of alternative *j* for consumer *c*.

McFadden (1974) as cited by Hanley *et al.* (1998) states that the analysis of CL model assumes that the random error terms are independently and identically distributed (IID) based on Gumbel distribution and follows extreme value Type 1. The probability of consumer *c* chooses the alternative *i* over alternative *j* with the presence of the random term can be written as follows:

$$\begin{aligned} Prob_i^c &= Prob\{(U_i^c > U_j^c)\} && ;\ i \neq j \\ &= Prob\{(V_i^c + \varepsilon_i^c) > (V_j^c + \varepsilon_j^c)\} && ;\ i \neq j \\ &= Prob\{(V_i^c - V_j^c) > (\varepsilon_i^c - \varepsilon_j^c)\} && ;\ i \neq j \end{aligned} \tag{8}$$

It can be seen that the probability of the sum of random utility terms of alternative *i* is greater than the other random utility term of alternative *j*. This study assumes that the V_i^c shows a linear parameter and generalized specification of utility function can be shown as follows:

$$V_i^c = \beta_1 x_i^c + \beta_2 x_{1i}^c + \beta_3 x_{2i}^c + \dots + \beta_s x_{si}^c \tag{9}$$

where β is vector of parameters to be estimated and *x* indicates a vector of all independent variables in the model.

$$Prob_i^c = \frac{\exp(\beta' V_i^c)}{\sum_j^J \exp(\beta' V_j^c)} \tag{10}$$

where, $Prob_i^c$ demonstrates the probability of consumer *c* choosing alternative *i* and x_i^c and x_j^c are vectors expressing the attribute *i* and *j*. Based on Equation 9, the β coefficients indicate the taste of parameters which are attributes that directly affect utility. It can be used to estimate the marginal rate of substitution (MRS) or at which consumers are willing to trade-off between the attributes. The substitution rate can be estimated by dividing the β coefficient with another β coefficient (monetary attribute) and multiply it by -1 and the equation is as follows:

$$\rho_k^c = \frac{\beta_{attribute}}{\beta_{price}} \times -1 = -\frac{\beta_{attribute}}{\beta_{price}} \tag{11}$$

This study examines how much that households in Terengganu would be willing to pay for three key results of improvements in the services in order to measure the value that households place on water services. First, increasing water quality; second, reducing water supply disruptions; third, increasing water pressure. Better water quality, water supply and water pressure are not things that are bought and sold in the markets. Thus, specific non-market valuation techniques were used to estimate their value. The orthogonal design allowed generating 15 water service options.

Respondents were given with a number of choice card sets which described the three proposed improvements in water service policies. This study exhibits a range of impacts that these programs might have on the water quality, water disruptions and water pressure as in Table 1. The choice cards also listed the amount of money that the policy options would cost a household. Willingness to pay (WTP) can be indirectly estimated from the choices by including water price as one of the attributes in the study. The aim of this method is to increase the level of the attribute, for instance, water quality at QUAL1 (*status quo*) to improve level, QUAL2 or QUAL3.

Table 1. Water Service Attributes and their Levels

Attributes	**Levels**	**Descriptions**
Water Quality (QUAL)		Connection of water supply at homes with high quality, safe for direct human consumption, colourless, tasteless, odourless and comply with standard of drinking water quality.
QUAL1	Satisfactory	
QUAL2	Good	
QUAL3	Very Good	
Water Disruption (DIST)		Reducing the frequency of water supply disruptions at homes.
DIST1	Always	
DIST2	Sometimes	
DIST3	Never	
Water Pressure (PRES)		Condition of water pressure when the water gushes out from the tap water.
PRES1	Low	
PRES2	Moderate	
PRES3	High	
Water Price (PRICE)		Water price describes household monthly water bills charged by water provider; Syarikat Air Sdn. Bhd.
PRICE1	Current Price	
PRICE2	Low (Increases 28% from current price)	
PRICE3	Moderate (Increases 56% from current price)	
PRICE4	High (Increases 90%from current price)	

Table 2. Attributes and Expectation Sign

Attribute	Descriptions	Expectation Sign
Water quality	Connection of water supply at homes with high quality, safe for direct human consumption, colorless, tasteless, odorless and comply with standard of drinking water quality	Positive
Water disruption	Reducing the frequency of water supply disruptions at homes.	Positive
Water pressure	Condition of water pressure when the water gushes out from the tap water.	Positive
Water price	Water price refers to household monthly water bills charged by water provider; Syarikat Air Sdn. Bhd., presented as amount increase over the current bill.	Negative

4. RESULTS AND DISCUSSIONS

4.1 Socio Demographic Characteristics of the Respondents

Table 3 presents the results of the respondent demographic profiles. The majority of respondents were head of households with female (50.1%) and male (49.9%). The percentage for both genders was about the same. Majority of the respondent (34.5%) were between 41 and 50 years old where the mean for the age groups is 42 years old. The present study found that the participants mostly had university/college education (55%) as their highest education level, followed by secondary school (31%), primary school (12%) and no formal education (2%). The results are reported that average household monthly income was MYR4182.50. Household size ranged from 1 to 5 members, with a mean of 6 for the whole sample. A majority about 424 of respondents (35.3% from the sample) was government servants, respondents who are working at private sectors (20.1%), managing business (12.5%) and others (32.1%). Most of the respondents are about 94% had a job between 1 to 3 members in their family.

Table 3. Descriptive Statistics for respondents, n=1200

Demographic characteristics	Frequency	Percentage (%)	Mean	Std. deviation
Gender				
Male	599	49.9		
Female	601	50.1		
Age group (Years)				
20 – 30	207	17.4		
31 – 40	336	28		
41 – 50	413	34.5	42.13	11.42
51 – 60	185	15.4		
61 – 70	42	3.7		

> 70	17	1.6		
Education level				
University/college	662	55		
Secondary school	367	31		
Primary school	141	12		
No formal education	30	2		
Household income				
Less than RM2000	312	26		
RM2001 - RM4000	446	37		
RM4001 - RM6000	263	22	RM4182.50	RM4242.80
RM6001 - RM8000	102	9		
RM8001 - RM10,000	58	5		
More than RM10,000	19	2		
Size of household				
1 - 5	701	58.4		
6 - 10	471	39.3	6.444	3.069
> 10	28	2.4		
Head of household's occupation				
Government sector	424	35.3		
Private sector	241	20.1		
Businessman	150	12.5		
Others	385	32.1		

4.2 Determinants of Households' Willingness to pay for Water Services

4.2.2 Estimation of Contingent Valuation Method (CVM)

In CVM, this study offers 5 group different prices to different respondents. The prices are RM0.52, RM0.54, RM0.56, RM0.58 and RM0.60 in order to demonstrate diversifications in the price bids. About 97 of respondents are willing to pay RM0.60 which is the highest proposed price bid in this study. The probability of respondents state "Yes" is high when then proposed price bid is low as shown at proposed price bid RM0.52; about 149 of respondents accept the offer. According to Tietenberg (2000) the demand theory states the higher the prices of goods, the lower the quantity demanded of the goods.

Table 4. Logit Model (n=1200)

	Coefficient	t-value	Coefficient	t-value
	Preliminary Regression		**Final Regression**	
Constant	9.906	1.412***	9.650	1.380***
Price Bid	-17.282	2.285***	-17.192	2.278***
Income	0.000175	0.000034***	0.000179	0.000033***
Education	-0.188	0.076***	-0.185	0.067***
Job	0.040	0.064		
Home	-0.081	0.058		
Race	-0.497	0.228***	-0.485	0.226***
Household size	-0.045	0.027**	-0.043	0.027*
Age	0.011	0.006**	0.011	0.006**
Announcement	-0.406	0.144***	-0.346	0.131***
Experience	-0.086	0.130		
Report	0.111	0.139		
Consumer’s awareness	0.534	0.137***	0.511	0.134***
-2 Log likelihood	1474.490		1478.085	
Cox & Snell R Square	0.136		0.133	
Nagelkerke R Square	0.182		0.178	

Note: Significant level at 15% (*), 10% (**) and 5% (***).

The logit model presents that the log of the odds ratio is a linear function of independent variables. For this method, the data was analysed by using “Statistical Package for Social Science” (SPSS) Version 21 software. Table 4 demonstrates preliminary and final regression models to determine consumers’ WTP in the study. According to these models, preliminary regression model includes all variables in first round and final regression is chosen statistically significant variables towards the dependent variable. In order to develop the best-estimated model, this study rejected the insignificant variables in preliminary regression such as job, home, experience and report water disruptions to water company. Price bid portrays a negative relationship towards consumers’ WTP and significant at 5% level as $p < 0.05$ (Table 4). This shows as suggested water price increases, the probability of respondents stating “Yes” decreases. Based on Mezgebo *et al.,* (2013) the price bid (BID) has negative sign relates to economic theory; when the price rises, the willingness to pay for goods and services decreases. This study found that the respondents were concerned regarding to the amount that they were asked to pay for improving the services. Household income exhibits a positive sign with 5% significant level that shows as household income increases, consumer’s WTP increases. As household income increases the probability of respondents to say “Yes” will increase too. This is because more people can afford and willing to pay for higher water bills for upgrading water services as they have ability to increase utility. The result also in line with previous studies by Carson *et al.,* (1994), Alias and Shazali (2005) and Mamat *et al.,* (2013) which also indicates a show a positive sign on income towards the WTP.

Besides, the level of education presents negative sign with WTP and significant at 5% level where the higher the level of education achievement, the lesser of consumers' willingness to pay for new increments in water price. This is because most of the households have low income and they are willing to pay but not as the suggested stated amount for improvements of water services in Terengganu. However, few studies prove this relationship is not important and does not give practical effect on willingness to pay (Ibrahim, 2012; Wang and Mullahy, 2006). Moreover, household size presents a negative relationship with WTP and significant at 0.15% level. The realation shows the more household members; then the lesser their willingness to pay for water bills as most of households from rural areas with low household income in this study. Previous studies by Mahirah and Khalid (2013) demonstrate that household size has a negative impact to WTP in which the households would reduce the WTP as their members become bigger. Age of respondents portray negative effect on WTP at 0.05 level of significant. This is because of elder people demanded more water than younger people. Normally most of elder people are more responsive to quality of the services at home. They are more involving in household chores and taking care of families' health. Besides, the result of announcement by water company regarding to the water supply disruptions bring negative impact towards households' WTP. Respondents should get a notice regarding to any disruptions of service in their area. This survey shows that most of the respondents are not been noticed about interruptions of services. Variable of "Awareness" exhibit a positive effect towards WTP and significant at 5% level. The variable explains that the respondents are alert that high expenses are needed to reduce Non Revenue Water (NRW) in water services. It can be seen that the respondents are aware that the expenses for to lessen the level of NRW are costly to be implemented. A study by Mezgebo *et al.*, (2013) states that a positive sign between households' awareness and WTP which have greater awareness about the availability of irrigation water and environment complications. Moreover, the calculated mean value based on Equation 12 is RM0.5772 applied on the first 30m^3. The current water price is RM0.50m^3 and it increases about 7.7%. Though the calculated mean water price is still below than national average price which is RM0.65 applied on the first 30m^3.

4.2.2 Estimation of Choice Modelling (CM)

Estimation for CM was employed by using econometric software which is NLogit Version 5. A Conditional Logit model was applied in order to interpret the data collected through the CM. The dependent variable for this model was the choice of a water alternative whereas the independent variables were presented by the attributes of water services.

Table 5. Estimated Coefficients for Households' Willingness to Pay in Terengganu, Malaysia

Variables	**Coefficient**	**t-value**
Water Quality (QUAL)		
Good (QUAL2)	3.7682	7.190***
Very Good (QUAL3)	3.8076	7.573***
Water Disruption (DIST)		
Sometimes (DIST2)	4.0899	9.251***
Never (DIST3)	0.3394	3.984***
Water Pressure (PRES)		
Moderate (PRES2)	0.2881	2.100**
High (PRES3)	-2.9269	-11.384***
Water Price (PRICE)	-3.1706	-4.658***
Marginal Values of the Attributes: (β's coefficients/-β's price)		
Good (QUAL2)	1.18	12.636***
Very Good (QUAL3)	1.20	9.827***

Sometimes (DIST2)	1.29	9.133***
Never (DIST3)	0.11	6.556***
Moderate (PRES2)	0.09	1.932*
High (PRES3)	-0.92	-7.263***

Note: Significance level; (***)1% level, (**) 5% level, (*)10% level.

Based on Table 5, the overall coefficients and signs are as expected and present positive signs except for *High* (PRES3) in water pressure attribute. All coefficients for attribute levels are significant at the 1% level except for a *Moderate* (PRES2) water pressure which significant at 5% level. The result indicates that at highest level of the attribute (PRES3), it portrays a negative relationship towards dependent variable. Preferences of water quality attribute levels showed a similar pattern. The conditions of water quality such as colourless, tasteless and odourless are most favoured by respondents during the interview session. In terms of water disruptions, preferences in *Sometimes* and *Never* indicate that respondents prefer in lessening the frequency of water supply interruptions. For water pressure, both *Moderate* and *High* water pressure has an effects on willingness to pay for water services but in different signs. It shows that respondents more preferred *Moderate* water pressure compared to *High* water pressure. Probably due to *'High'* water pressure can cause water leakage in plumbing and piping system; besides, the respondents do not expect the water services can improve to the highest level as the current situation of water pressure is too worsening. Table 5 presents an estimation of the WTP for every option for improving domestic water services. Hence, Marginal willingness to pay was used in order to estimate marginal values of the attributes for a change from current to alternative situation. It can be estimated as in Equation (11).

The result of marginal willingness to pay at level 'good to very good' for water quality attribute is at RM1.20. An improvement of services in terms of water disruptions from level of 'sometimes to never' is at RM0.11. These values illustrate how much respondents are willing to pay for any improvement in water services for each level. Meanwhile, the differences in marginal values in water pressure at level 'low to moderate' is at RM0.09 and level 'moderate to high' is at negative values RM0.92. 'Water pressure' attribute exhibits relatively low values compared to other attributes and it has a level incurred negative value. Surprisingly, most households concern about water disruptions at their homes as the attribute generates the highest willingness to pay which is RM1.29 compared than other attributes. The marginal rates of substitution of water disruption attribute in Level 2 (Sometimes) is highest which is presenting consumers are willing to pay for water disruption improvements. Though, the main problem in the service is water pressure as the demand is very high in the state has 12 water plants which is need to cater for 1.15 million of population in Terengganu. Similarly, Mahirah *et al.,* (2006) found that respondents choose to improve water interruptions to reduce the frequency of disruptions in Kelantan from moderate level to high level (less water service disruptions) as it generates the highest marginal values based on the CM model.

4. CONCLUSION

The finding demonstrates that the CM has a greater capacity to describe selected choices by consumers. The evidence from this study finds that the CVM method is described by just one variable which is the bid price and socioeconomic parameters. Conversely, the CM method is explained according to many attributes or chracteristics. Hence, it is able to measure the welfare benefits of any number of different programs by varying the attribute levels for further consideration in the policy review. In CVM method we obtained only the value of the estimated WTP which is RM0.57 applied on the first 30 m^3. However, in CM method we can get numerous individual marginal values based on their attribute levels which are selected by respondents. Comparing those methods will produce different results and with different aspects too. This study presents that the aspect of level of water service disruption is most concerned by the respondents since it produce the highest marginal willingness to pay among others attributes. Water provider in the state should be taken into account the efficient and equitable allocation of water to urban and rural consumers. The survey was conducted in the state shows that households are not happy with the current level of water services, particularly in terms of water pressure. Better water pricing is needed in order to implement various programs in the services. Water prices should reflect the cost of water production in order to promote market efficiency. Although the government fails to protect the consumers and sometimes it harms others, controlling the prices can avoid the pressure of price increases. If the water price is increased, it can lessen the financial burden of water companies by providing needed funds for further improvement in infrastructure, upgrade services and financial development. Revising prices can help the water companies to reduce cost somewhat but they still have to operate until the optimum production is achieved. For the time being, consumers feel that the water is too cheap and this leads to water wastage and excessive water consumption. By increasing the prices the public will be aware to conserve water and avoid water wastage. Besides, the public must be educated based on the needs, benefits, problems and responsibilities surrounding water conservation. Without changes in water consumption in the next several years, the most precious natural resource diminishes and the world becomes less inviting and self-sustaining.

BIOGRAPHY

Mahirah is a senior lecturer at Economics Department and an associate fellowship of Institute of Oceanography and Environment (INOS), University Malaysia Terengganu, Malaysia. Her expertise is in economic valuation and environmental economics.

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Evaluation of air quality in the city of Istanbul during the years 2013 and 2015

Ayse Emel ONAL[1*], Osman Faruk BAYRAMLAR[1], Elif EZIRMIK[1], Bugra Taygun GULLE[1], Fatma CANATAR[1] , Dilan CALIK[1], Dilber DERYOL NACAR[1], Leyla Evin AYDIN[1], Ahmet BARAN[1], Zeynep KIRDI HARBAWI[1]

Abstract

Air pollution has been the most important health issue in recent years. In this study, the aim was to evaluate the results of regular measurements of air pollutants PM10 and SO_2 concentrations in the city of Istanbul by taking the years 2013 and 2015 as a sample. The data were obtained through the website http://www.havaizleme.gov.tr, which was published by the Administration of Marmara Clean Air Center of Ministry of Environment and Urbanization in Turkey. For the years 2013 and 2015, the mean SO_2 concentration was 8.35±6.04 and 10.60±7.16 µg/m³. The mean PM10 concentration was 73.06±30.63 µg/m³ for 2013 and 51.57±18.84 µg/m³ for 2015. The acceptable upper limit values by WHO (World Health Organization) for daily mean SO_2 and PM10 concentrations respectively are 20 µg/m³ and 50 µg/m³. In Istanbul, SO_2 concentrations were above the upper limit values recommended by WHO but, PM10 concentrations during 2013 and 2015 were over the recommended limit values by WHO. As the particulate matter pollution is high concentrations during these two years, it has shown that air pollution emerges as a problem awaiting solutions in Istanbul, where is industrially intense, highly populated and also with high traffic density.

Keywords: *Istanbul, Air Pollution, PM10, SO_2*

1. INTRODUCTION

Air is one of the most indispensable and essential substance for human life. A human-being can survive only for up to 4 minutes without breathing air. Clean air consists of 78% nitrogen (N_2), 20% oxygen (O_2), 0.9% argon (Ar), 0.04% carbon dioxide (CO_2) and very small amounts of neon (Ne), methane (CH_4), helium (He), hydrogen (H_2), krypton (Kr). About 0.25% of the atmospheric mass is water vapor. Today, pollutants originating mainly from heating, industry and traffic disrupt air quality and so cause air pollution.

Air pollution has been the most important health issue in recent years. EPA (Environmental Protection Agency) determined 6 criteria air pollutants for outdoor air. These pollutants are particulate matter of 10 microns in diameter (PM10), carbon monoxide (CO), lead (Pb), sulfur dioxide (SO_2), nitrogen dioxide (NO_2) and ozone (O_3) (1). Nowadays, it is well-known fact that these pollutants increase the incidence of asthma and chronic obstructive pulmonary disease (2-4).

[1*] Corresponding Author: Prof. Ayse Emel Onal, M.D., Istanbul University, Istanbul Medical Faculty, Department of Public Health, Istanbul, Turkey, onale@istanbul.edu.tr

In addition, myocardial infarction, angina pectoris, hypertension among cardiovascular diseases, also cerebrovascular diseases and associated paralyses have increased due to air pollution (5, 6). Air pollution leads to damages in the nervous system and so causes headache and anxiety; moreover, air pollution is held responsible for the increase in some neurological diseases such as Alzheimer’s and Parkinson’s diseases. Air pollution has unfavorable effects on fertility and child’s health, too. It gives rise to low birth weight and premature birth (7). Besides, air pollution has been held responsible for the etiology of some cancers like breast and prostate cancer, which have been increasingly incident over the recent years (8).

Air pollution affects the environment, human health and thus life negatively. Climate change, depletion of the ozone layer and acid rains stems from air pollution. For this reason, air pollution must be monitored with Air Quality Index (AQI). This index, which was identified by Environmental Protection Agency (EPA), has been adapted and used as "National Air Quality Index" for Turkey. Air quality index is calculated for five main pollutants. These pollutants are particulate matter of 10 microns in diameter (PM10), carbon monoxide (CO), sulfur dioxide (SO_2), nitrogen dioxide (NO_2) and ozone (O_3). The Air Quality Index is calculated by using these five parameters and this index is expressed in colors: We refer the values between 0-50 green as "good"; between 51-100 yellow as "moderate"; between 101-150 orange as "sensitive"; between 151-200 red as "unhealthy". The values between 201-300 are referred as "bad" (purple), whereas the ones between 301-500 are considered "dangerous" (brown) (9). These pollutants are measured daily at monitoring stations and their concentrations are published at the website of Turkish Ministry of Environment and Urbanization (10). But, to make comments on results and so to benefit from them in the field of health require knowing this basic information.

In Turkey, the Ministry of Environment and Urbanization have measured all the criteria air pollutants except lead (Pb) daily in each city and in each district up to today since 2005. In Istanbul, there are 31 Air Quality Monitoring Stations at 39 districts; at some districts, more than one monitoring stations exist. Yet, there are losses at some parameters for several districts. The parameters, which are obtained most regularly, are PM10 and SO_2. In this study, our aim was to evaluate the measurement results of PM10 and SO_2 concentrations, which are regularly measured pollutants in the city of Istanbul, by sampling from the years 2013 and 2015.

2.MATERIALS AND METHODS

Between the years 2013 and 2015, the air quality was audited by the Administration of Marmara Clean Air Center (MTHM). The data of Istanbul were obtained through the website http://www.havaizleme.gov.tr, which was published by the Administration of Marmara Clean Air Center. The acceptable upper limits by WHO (World Health Organization) for daily average, for SO_2 and PM10 respectively are 20 µg/m3 and 50 µg/m3 (11). For evaluation, the months of January, April, June and September in 2013 and 2015 were chosen since these are the months that the data were either complete or included the highest numbers of days with measurement.

Among the data of these months, the measurement results of PM10 and SO_2 were entered into SPSS 21.0 software package and then evaluated as mean, standard deviation. The monthly mean values with each other for the same year and with the other year's equivalent monthly mean values were compared statistically. The suitability of variables for the normal distribution was examined by Kolmogorov-Smirnov Test. For the variables, which are distributed normally, Independent Samples t Test was used. For the statistical comparison of the means of more than two groups, One-Way ANOVA Test was used.

3.RESULTS AND DISCUSSION

For the years 2013 and 2015, the mean SO_2 concentration was 8,35±6,04 µg/m3 and 10,60±7,16 µg/m3. The mean PM10 concentration was 73,06±30,63 µg/m3 for 2013 and 51,57±18,84 µg/m3 for 2015. The mean concentration of PM10 was above the recommended limit values determined by WHO for both years.

For the city of Istanbul, the measurement results of mean SO_2 and PM10 concentrations in January 2013 and January 2015 was shown in Table 1, whereas the ones in April for the same years in Table 2, the ones in June for the same years in Table 3 and the ones in September for the same years in Table 4 can be seen.

Table 1- The measurement results of SO_2 and PM10 concentrations among air quality criteria pollutants in Istanbul in January 2013 and January 2015 (µg/m^3).

	n	Minimum	Maximum	Mean	Std. Deviation
SO_2 (2013)	31	2.0	28.0	7.32	5.71
PM10 (2013)	31	5.0	138.0	61.90	35.70
SO_2 (2015)	31	6.0	51.0	16.94	9.84
PM10 (2015)	29	25.0	104.0	53.38	23.95

Table 2- The measurement results of SO_2 and PM10 concentrations among air quality criteria pollutants in Istanbul in April 2013 and April 2015 ($\mu g/m^3$).

	n	Minimum	Maximum	Mean	Std. Deviation
SO_2 (2013)	30	8.0	27.0	15.10	5.02
PM10 (2013)	30	29.0	189.0	86.63	37.41
SO_2 (2015)	30	3.0	15.0	7.43	2.76
PM10 (2015)	28	18.0	67.0	38.86	15.93

Table 3- The measurement results of SO_2 and PM10 concentrations among air quality criteria pollutants in Istanbul in June 2013 and June 2015 ($\mu g/m^3$).

	n	Minimum	Maximum	Mean	Std. Deviation
SO_2 (2013)	30	1.0	16.0	7.70	4.00
PM10 (2013)	27	40.0	139.0	73.26	24.19
SO_2 (2015)	30	5.0	23.0	12.17	3.71
PM10 (2015)	30	33.0	76.0	55.70	12.45

Table 4- The measurement results of SO_2 and PM10 concentrations among air quality criteria pollutants in Istanbul in September 2013 and September 2015 ($\mu g/m^3$).

	n	Minimum	Maximum	Mean	Std. Deviation
SO_2 (2013)	30	2.0	6.0	3.30	0.84
PM10 (2013)	30	50.0	105.0	70.83	14.67
SO_2 (2015)	27	2.0	9.0	5.11	1.34
PM10 (2015)	27	26.0	91.0	58.22	15.68

Except the mean PM10 concentration during April 2015, all of its concentrations were above the upper limit values recommended by WHO; whereas the mean SO2 concentrations were under the upper limit values recommended by WHO throughout all of these months within these two years. Among the chosen months, SO_2 concentration was detected as the highest in 2013 during April and in 2015 during January; on the other hand, PM10 concentration was detected as the highest in 2013 during April and the highest in 2015 during September.

Table 5- The comparison of mean concentration of SO_2 measurements for the year 2013 during January, April, June and September by One Way ANOVA Test.

SO_2	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2177.4	3	725.78	38.703	.000
Within Groups	2194.1	117	18.75		
Total	4371.4	120			

Table 5 shows the statistical comparison of mean concentration of SO_2 measurements during the four months observed for the year 2013 by One -Way ANOVA Test. Among the four months' means, there is a statistical significance at high level. The comparison of mean concentration of PM10 measurements for the year 2013 during January, April, June and September by using One-Way ANOVA Test can be seen in Table 6. It was detected that the measurements of mean PM10 concentrations showed a statistical significance between different months.

Table 6- The comparison of mean concentration of PM10 measurements for the year 2013 during January, April, June and September by One Way ANOVA Test.

PM10	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	9535.6	3	3178.52	3.614	.015
Within Groups	100253.0	114	879.41		
Total	109788.6	117			

The statistical comparison of mean concentration of SO_2 measurements for the year 2015 during January, April, June and September by using One Way ANOVA Test can be seen in Table 7; there is a statistical significance at high level among the means. The statistical comparison of mean concentration of PM10 measurements for the year 2015 during January, April, June and September by using One Way ANOVA Test was shown in Table 8; there exists a statistical significance at high level among the means.

Table 7- The comparison of mean concentration of SO_2 measurements for the year 2015 during January, April, June and September by One Way ANOVA Test.

SO_2	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	2432.2	3	810.74	25.889	.000
Within Groups	3570.1	114	31.32		
Total	6002.3	117			

Table 8- The comparison of mean concentration of PM10 measurements for the year 2015 during January, April, June and September by One Way ANOVA Test.

PM 10	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	6326.7	3	2108.91	6.863	.000
Within Groups	33801.2	110	307.28		
Total	40127.9	113			

Taking the results in January and September as one group called "cold seasons" and the results in April and June as another group called "hot seasons", for SO_2 concentration, a statistical significance at high level was detected in 2013 between both seasons (t:-6.361; p:0.000); on the contrary, the same statistical difference wasn't detected for the year 2015 (t:1.239; p:0.218). For PM10 concentration, these values were calculated as (t:-2.539; p:0.012) for the year 2013 and (t:2.353; p:0.020) for the year 2015. There was a statistical significance between summer and winter seasons in terms of air pollution. In winter, the level of air pollution was more severe than summer. PM10 seemed to play an important role in air pollution. When PM10 and SO_2 results were compared according to the districts, Uskudar was ranked first among the districts with the highest mean PM10 concentration measured 89.57±64.48 µg/m3. The district of Uskudar was followed by Aksaray (62.80±28.66 µg/m3), Maslak (59.89±37.93 µg/m3) and Alibeykoy (54.68 ±28.36 µg/m3). As seen among SO_2 measurements, it was detected that mean SO2 measurements were even above the WHO recommended limit values in Uskudar (55.91±28.19 µg/m3) and in Sultanbeyli (42.87±29.60 µg/m3); on the other hand, the mean SO_2 measurements were under the limit values in other districts.

According to European Environment Agency (EEA)'s data, 97.2% of the urban population in Turkey has been exposed to PM10 at unhealthy levels (12). Air pollution within cities is also known to have negative effects on health (13). Among different Turkish cities, there are limited number of studies indicating the status of air pollution. The annual mean PM10 concentrations recommended are 58 µg/m3 in Turkey, 40 µg/m3 in European Union (EU) and 20 µg/m3 by WHO. According to WHO's data, the annual mean PM10 concentrations between the years 2008-2015 are 85 µg/m3 for the world, 235 µg/m3 for Eastern Mediterranean countries with high income, 158 µg/m3 for Eastern Mediterranean countries with low income, 123 µg/m3 for Southeastern Asia, 119 µg/m3 for Africa and 104 µg/m3 for Western Pacific Mediterranean countries with low-middle income. This value for European countries with low-middle income is 55 µg/m3, thus the city of Istanbul is shown as "moderately polluted" on WHO's maps in terms of air quality (Air Quality Index – Yellow: Between 51-100). Eastern Mediterranean and Southeastern Anatolian cities of Turkey are demonstrated as "sensitive" (Air Quality Index – Orange: Between 101-150) (14). In this study, the levels of PM10 concentrations were found to be above the recommended limit values by WHO in Istanbul during the years 2013 and 2015. No research made in Istanbul about this subject was found during literature survey. In a doctoral thesis research conducted in Kirklareli, air pollution and meteorological parameters were detected to increase the number of hospital admissions due to cardiovascular and respiratory diseases (15). In a study conducted in Duzce, the annual mean PM10 concentration was found to be 106.42±102 µg/m3, whereas the annual mean SO2 concentration was found to be 6.15±5.39 µg/m3 (16). Air pollution occurs due to local, regional and global problems. Therefore, it is possible to take measures with multidimensional studies. Industrial activities, increased level of traffic, destruction of forests, combustion of biomass and continuous energy production trigger climate change and as a result of this situation, natural disasters like sea level rise, floods, hurricanes, drought may emerge. In each country, a national air quality monitoring network should be established as it is in Turkey. So as to reduce air pollution, as society, we should use public transport, use energy-efficient appliances and energy-saving light bulbs, use clean energy such as wind, geothermal and solar energy and also organize public education on these issues.

4 CONCLUSIONS

In conclusion, the lower levels of air pollution during the summer months give rise to thought that the level of heating-based pollutants decrease and the traffic reduces relatively in the city of Istanbul during the summer months. As the particulate matter pollution is within high concentrations during these two years and throughout all the seasons, it has shown that air pollution emerges as a problem awaiting solutions in Istanbul, where is industrially intense, highly populated and also with high traffic density.

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Kinetics of Granulated Waste Tyre Pyrolysis via Thermogravimetry and Model-free Methods

Peter T. CHEROP[1*], Sammy L. KIAMBI[1] , Paul MUSONGE[1]

Abstract

There has been an increase in global consumption of waste tyres over the years. However only a portion of the total amount of waste tyres can be recycled or reused for other applications. Land-filling has been considered an alternative to address the problem of continued waste tyres accumulation, but huge space is needed for this and the reusable resources are wasted. This therefore has led to environmental and economic problem of disposal of the large mass of waste tyres. Waste tyre pyrolysis, which is the thermal decomposition in absence of oxygen, can be used to recover both energy and material. Thermogravimetric analysis (TGA) is the technique commonly used to evaluate the weight loss kinetics associated with the vaporisation of materials during pyrolysis. The purpose of this study was to establish the kinetics of thermal degradation of waste tyres by TGA and to compare the activation energies (E) obtained using two model-free methods. The experiments were carried out in a nitrogen environment and a temperature range of 20°C to 600°C at three heating rates. Results show that the pyrolysis process of the tyre crumb occurs in three stages as the various components of the tyre undergo decomposition. A mean activation energy of approximately 232 kJmol^{-1} was obtained using the two models.

Keywords: *Waste tyre, Activation energy, Thermal degradation, Model-free.*

1.INTRODUCTION

The amount of waste tyres dumped all over the world is roughly 1.5 billion [1], but only 15-20 % is reused whereas the remaining percentage is simply dumped into the earth [2]. The valorisation of waste plastics and tyres plays a big role in the reduction in fossil fuel consumption and helps to address the issue of climate change [3]. Due to the high calorific value of waste tyres (33-35 MJkg-1), recovery of energy is considered an alternative to recycle them [4]. Pyrolysis, which is the process of thermal degradation in absence of oxygen, can be potentially involved to recover energy from waste tyres. During pyrolysis, the organic volatile matter in the tyres is transformed into low-molecular weight products, whereas the inorganic constituents, are retained as solid residue [5].

Tyres are made up of more than 100 different substances such as rubber, steel, silica gel, carbon black etc. During tyre production, the rubbers commonly used are natural rubber (NR), butadiene rubber (BR),) and styrene-butadiene rubber (SBR).The degradation of these components occurs at different temperature ranges. The thermal degradation behaviour of waste tyres depends on the type of rubber as well as its contents [6, 7].

The study of kinetics of waste tyre pyrolysis has recently been an area of interest since understanding of kinetics of this process is important in the design and optimisation of industrial scale waste tyre recycling units. Model-free and model-fitting methods are commonly used to determine the kinetic parameters during solids decomposition [8-10].

The following expression is commonly used for thermal degradation of solids:

$$\frac{d\alpha}{dt} = k(T).f(\alpha) \qquad (1)$$

where α is the degree of conversion, $k(T)$ the reaction rate constant, and $\frac{d\alpha}{dt}$ the conversion rate over time. The conversion degree, α is determined as:

[1*]*Corresponding author: Durban University of Technology, Department of Chemical Engineering, P.O Box 1334, Durban 4000, South Africa.: tumwet2@gmail.com*

$$\alpha = \frac{w_0 - w_t}{w_0 - w_f} \qquad (2)$$

where w_0 is the initial weight of the sample, w_t the weight of the sample at a given temperature, and w_f the final mass of the sample.k(T) is expressed according to Arrhenius law as :

$$k(T) = A.\exp^{-\frac{E}{RT}} \qquad (3)$$

where E is the activation energy, R the gas constant, and A the pre-exponential factor.Combining equations (1) and (3) yields:

$$\frac{d\alpha}{dt} = A\,.\,e^{-\frac{E_a}{RT}}.\,f(\alpha) \qquad (4)$$

Equation (5) is the underlying equation used in determination of kinetic parameters in non-isothermal degradation of solid materials.

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}.\int_{T_0}^{T}.\,e^{-\frac{E}{RT}}\,dT \qquad (5)$$

where $g(\alpha)$ is the conversion integral function.

The Friedman (FR) method [11] is one of the iso-conversional methods used to calculate the activation energy. The expression for FR equation is:

$$\ln\left(\frac{d\alpha}{dt}\right) = \mathrm{Ln}\left[\beta\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = \mathrm{Ln}(A_\alpha) + \mathrm{Ln}[\,f(\alpha)]\text{-}\frac{E_\alpha}{RT_{\alpha,i}} \qquad (6)$$

where E_α and A_α represent the activation energy and pre-exponential factor at a specific conversion degree respectively. The slope in the plot of $\mathrm{Ln}\left[\beta\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right]$ against $\frac{1}{T_{,i}}$ yields the activation energy. The Kissinger-Akahira-Sunose (KAS) method [12, 13] is expressed as folows:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AE_a}{R\,g(\alpha)}\right)\text{-}\frac{E_a}{RT} \qquad (7)$$

where the plot of $\ln\left(\frac{\beta}{T^2}\right)$ versus $\frac{1}{T}$ gives a straight line. The slope from this plot is then used to determine the E

The aim of this study was to establish the non-isothermal kinetics of pyrolysis of waste tyres by applying two model-free methods to the TG/DTG data in order to determine the activation energies. The models used were KAS and FR.

2. MATERIALS AND METHODS

Tyre crumb from Mathe group, South Africa was used during this study. The elemental analysis of the tyre crumb was done using vario EL cube elemental analyser, while the thermogravimetric analysis was carried out in a Differential Scanning Calorimeter – Thermo Gravimetric Analyser SDT Q600. The tyre crumb samples were heated from 20°C to 600°C at three different heating rates in nitrogen (100 $mLmin^{-1}$) environment to prevent oxidation of the samples. Three heating rates of 2°C, 5°C, and 10°C min^{-1} were used to establish the behaviour of thermal degradation of the tyre crumb, while the TA Instruments software was used to extract the data that aided to plot the TG and DTG curves.

3. RESULTS AND DISCUSSION

3.1. Elemental Analysis

The elemental analysis results showed that the carbon content in the tyre crumb was 83.54 wt. % while the hydrogen content was 7.55 wt.%.The contents of nitrogen and sulphur were 0.35 wt.% and 1.84 wt.% respectively whereas the oxygen content (calculated by difference) was 6.73 wt.%.

3.2. Thermal Degradation of the Tyre Crumb

The TG/DTG thermograms of the tyre crumb thermal degradation for the heating rates of 2, 5 °C , and 10 °C min^{-1} are shown in Figures 1,2, and 3 respectively.

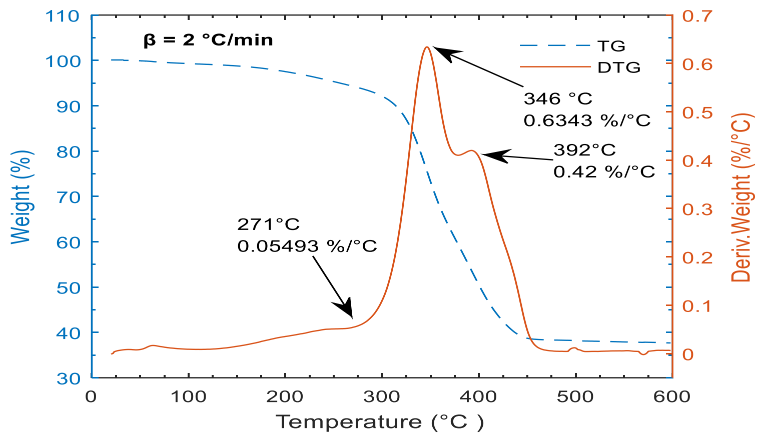

Figure 8.TG/DTG thermogram at 2 °C/min

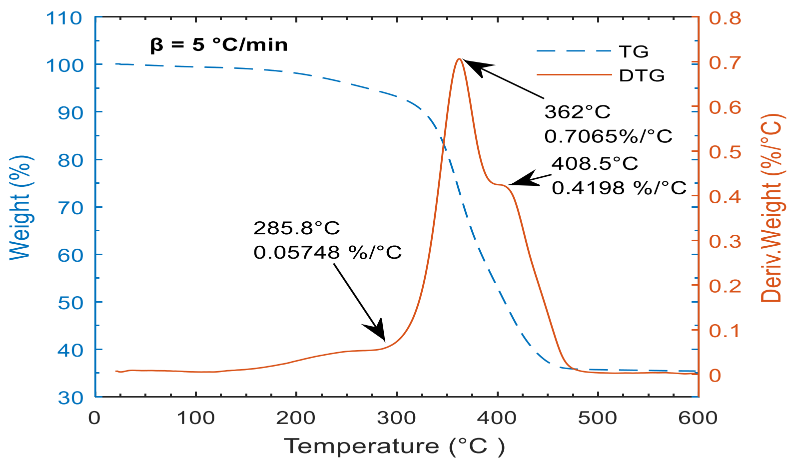

Figure 9. TG/DTG thermogram at 5 °C/min

The thermal decomposition started at about 270 °C and 285 °C and was complete at about 460 °C and 480 °C for the heating rates of 2 and 5 °C min^{-1} respectively. At the heating rate of 10 °C min^{-1}, the decomposition started at about 290 °C and was complete at about 495 °C. There was no further weight loss above the temperature of 500 °C for the three heating rates. Three stages of decomposition are notable from the peaks seen in the DTG curves i.e. removal of lubricants and oil in the waste tyre with a mean temperature peak value of about T_m = 285 °C, breakdown of NR with T_m = 367 °C and breakdown of BR and SBR with T_m = 411.0 °C. The TG/DTG thermograms indicate that the temperature peaks increase as the heating rates increase during the three-stage thermal degradation process.

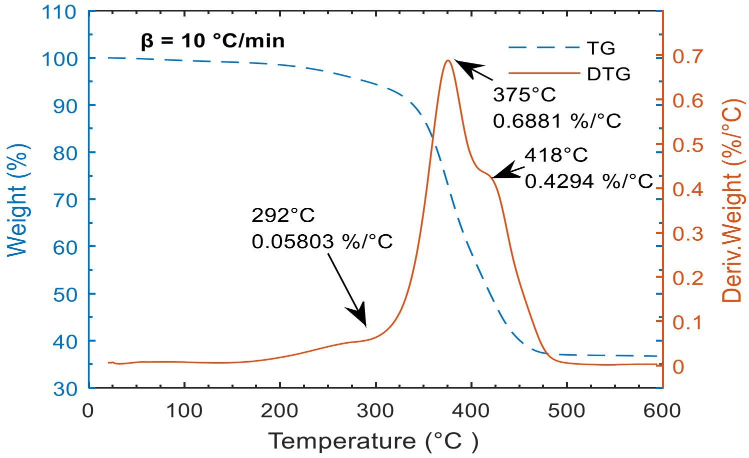

Figure 10. TG/DTG thermogram at 10 °C/min

3.3 Non-isothermal Kinetics of Tyre Degradation

The KAS and FR models were used to determine the activation energies. The two models aided to establish the relationship between the conversion degree and the activation energies. Using KAS model, the plot of $\ln\left(\frac{\beta}{T^2}\right)$ against $\frac{1}{T}$ gave a slope of $-\frac{E}{R}$, from which the activation energy was determined while the plot of $\ln\left(\frac{d\alpha}{dt}\right)$ versus $\frac{1}{T}$ was used to determine the activation energies by the FR model. The kinetic plots of tyre crumb thermal degradation using the two models are shown in Figures 4 and 5.

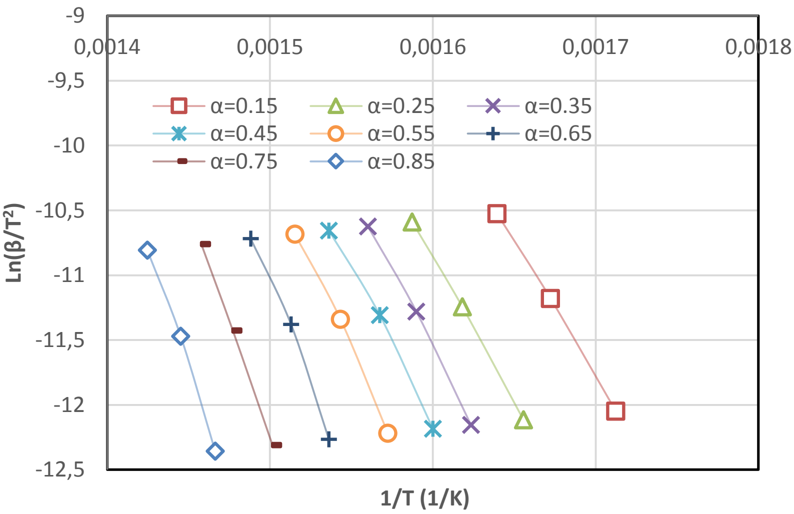

Figure 11. KAS plot at various conversion degrees

The degrees of conversion considered using the KAS and FR models ranged between 0.15 - 0.85. Figure 6 shows the variation of activation energy with conversion degree for the two models. The relationship between the activation energies obtained from KAS and FR models at same conversion degrees is shown in Figure 7.In both models, the activation energy increases with conversion degree up to α = 0.45 where the activation energy drops (Figure 6).The trend of increasing activation energy with conversion degree then continues without any further fluctuation. The mean activation energies obtained using KAS and FR models were 231.76 $kJmol^{-1}$ and 231.92 $kJmol^{-1}$ respectively. This clearly shows that the values obtained from the two models are similar and it indicates that the models used can accurately predict the non-isothermal thermal degradation of the tyre crumb. The similarity in E values from KAS and

FR models is further justified by the linear relationship (Figure 7) between the E values from the two methods. The regression coefficient values obtained from the plots using the two models were high. The lowest R^2 values using the KAS and FR methods were 0.9895 and 0.9903 respectively while the highest values were 0.9998 and 0.9999.This indicates the thermogravimetric data fit well into the models used.

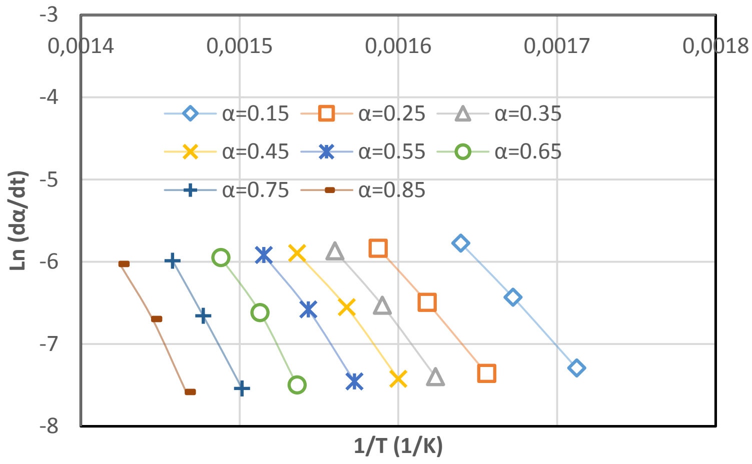

Figure 12. FR plot at various conversion degrees

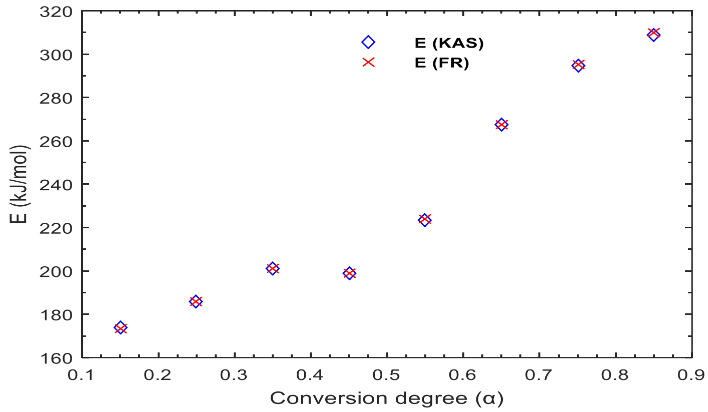

Figure 13. Activation energy versus conversion degree

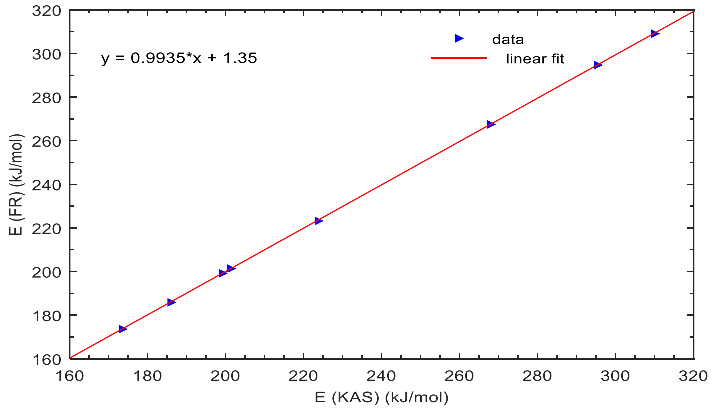

Figure 14. E_{FR} versus E_{KAS}

4. CONCLUSION

This study aimed to establish the thermal degradation process of the tyre crumb by applying two model-free methods to the thermogravimetric analysis data. The thermogravimetric analysis was carried out at heating rates of 2°C, 5°C, and 10°C min^{-1} in presence of nitrogen. Results show that the pyrolysis process of the tyre crumb takes place in three stages as the various components of the tyre undergo decomposition. The activation energy generally increases with increasing conversion degree in the early stages of thermal degradation. There is, however, a slight drop in activation energy at $\alpha = 0.45$, after which the trend of increasing activation energy with conversion degree continues. A mean activation energy of approximately 232 $kJmol^{-1}$ was obtained using the KAS and FR models, an indication that the values from the two models are similar. The data obtained from this kinetic study could play a big role in the optimisation of the design of industrial scale waste tyre pyrolysis units.

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Green Chemistry Analysis of Baker's Yeast Process Wastewater Treatment with Microalgae

Dicle CELIK[1], Togayhan KUTLUK [1], Kadriye OKTOR[2]*

Abstract

Baker's yeast production constitutes an important portion of production industry in Turkey. In many parts of the yeast production process, high quality water is used and discharged as effluent. According to water pollution control regulations, the wastewater of yeast production in food industry is characterized with respect to the given limits of chemical oxygen demand (COD), suspended solids (SS), oil, grease, pH, and color. Inert COD caused by molasses is hard to refine; therefore, advanced treatment technologies are used to achieve the regulation limits. In this study, wastewater obtained from production facilities was centrifuged under 4000 rpm for 20 minutes to get rid of SS. After SS was removed, the wastewater was diluted to different concentrations. 6 ml microalgae cultures incubated in erlenmeyer flasks. Here, organic substances of effluent had become nutritional source for microalgae. After 40 days of incubation, the grown microalgae were centrifuged under 5000 rpm for 5 minutes to get separated from the media. The COD of baker's yeast process wastewater treated with microalgae had been found to be quite lower than regulation limits. The efficiency of COD refinement had been almost 94%. This promising biological treatment had been assessed with respect to 12 principles of green chemistry to evaluate its greenness. This method satisfies 8 principles: waste prevention by no sludge formation, atom economy, safer solvents and auxiliaries, energy efficiency, renewable feedstock, reducing derivatives, bio-catalysis, and design for degradation. Since there exist no chemical synthesis, the remaining 4 green chemistry terms are not applicable.

Keywords: *Baker's Yeast Wastewater, Green Chemistry, Microalgae*

1. INTRODUCTION

Baker's yeast wastewater is one of the most studied topics in wastewater treatment field because of its pollutant properties. The characteristics of baker's yeast effluent are high chemical and biochemical oxygen demand (COD and BOD), acidity (pH range 4-5), recognizable odor, and dark brown color [1]. The raw material used for baker's yeast is molasses. The dark brown color of molasses is due to its melanoidin content; moreover, the wastewater has brown color and high COD because of this untreated melanoidin in the effluent [2]. For the treatment of baker's yeast wastewater, various methods and studies are being conducted, such as adsorption [3], [4], coagulation/flocculation [5], chemical oxidation [6], [7], electrocoagulation [1], [8], [9], electrochemical processes [10], membrane processes [11] – [14], ozonizing [15] – [17], advanced oxidation processes [18], ultrasound [2], [19], and so on. However, the oxygen demands of the effluent is a major problem to deal with. For example, combined biological treatment of anaerobic digestion and aerobic systems are effective for decreasing BOD beyond to limits; yet, they fail on COD resulting in inhibition of recycling used water [1].

Microalgae treatment is a recent method on wastewater treatment. These systems can be useful for treating city sewages, agricultural wastes, and industrial wastes [20] because microalgae remove coliform bacteria, reduce COD and BOD, remove nitrogen and phosphorus, and eliminate heavy metals [21]. Moreover, microalgae treatment can be a green alternative to conventional methods. Greenness of a method is becoming a selection criterion as it means being environment friendlier.

[1] *Kocaeli University, Department of Chemical Engineering, 41380, Izmit/Kocaeli, Turkey.*

[2]**Corresponding author: Kocaeli University, Department of Environmental Engineering, 41380, Izmit/Kocaeli, Turkey. oktor@kocaeli.edu.tr*

In this study of microalgae treatment, it is aimed to research the probability of decreasing COD lower than legislative limits; which are 1200 mg/L for 2 hours composite sample and 1000 mg/L for 24 hours composite sample for yeast industry [22]. Another aim of the study is to see if microalgae use is environment friendly, or not. Assessment of this novel method with respect to 12 principles of green chemistry is a practical tool for this purpose. According to literature, the greener the method is, the more principle provided out of the 12 principles [23]. Therefore, this biotechnological process has been assessed regarding each principle of green chemistry.

2. MATERIALS AND METHODS

2.1.Experimental Setup

Microalgae culture of *Chlorella variabilis* was used in this study. A baker's yeast manufacturing facility's process effluent was collected prior to any industrial treatment for being used as a growth medium. Before incubation, wastewater was centrifuged at 4000 rpm for 20 min to remove the solid impurities, and then it was diluted with tap water to following ratios: 0%, 10%, 20%, 30%, and 40%. In Kocaeli University wastewater laboratory, COD content of the wastewater was identified by using DR2800 Hach Lange LCK 314 standard cell kit. The cell concentration and growths were determined by using Jenway 6800 UV Vis. spectrophotometer at 680 nm.

After the pretreatment for removal of suspended solids (SS), microalgae were cultured in 250 mL open flasks for 40 days at 27 °C in a 200-rpm shaking incubator INNOVA 40. The experimental setup can be seen in figure 1. The necessary illumination for microalgae was provided by a 7W 2700K LED lamp.

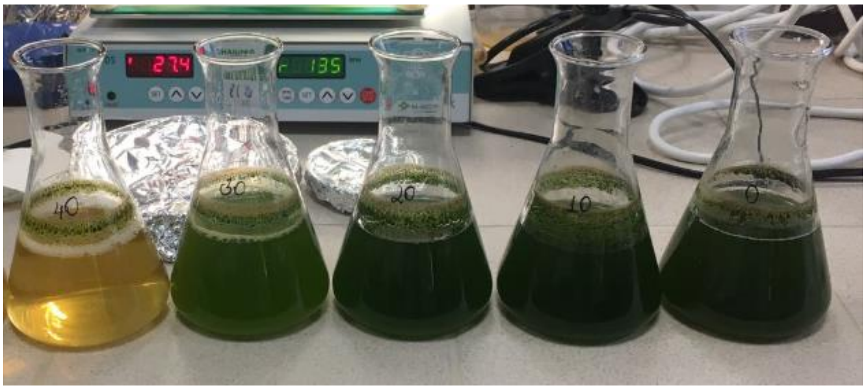

Figure 1. The experimental setup of microalgae treatment to baker's yeast manufacturing process wastewater.

The growth rates of *Chlorella variabilis* cultures were determined by using equation 1:

$$\mu = \frac{\ln(x_2 - x_1)}{t_2 - t_1} \quad (1)$$

where *x* is the cell concentration (*g/L*), *t* is the time (*h*). Maximum growth rate (μ_{max}) is the growth rate obtained during the logarithmic phase of the growth plots.

2.2. Green chemistry analysis

Green chemistry is a recent environmentalist concept, which is increasingly gaining importance nowadays. Paul T. Anastas and John C. Warner proposed to use the term "*Green Chemistry*" first in 1991 and they developed the 12-principle in 1998 [24]. The concept of green chemistry and its 12 principles are useful guides for investigating and determining if a given method is environmentalist (green) or not. The use of the tool is analyzing the method for each one of the principle stated in Table 1 to see how many of them are ensured.

Table 5. Green chemistry's 12 principles and their brief explanations. [23]

Principle	Explanation
1. Prevention	Preventing waste is better than cleaning.
2. Atom economy	To maximize the incorporation of all reagents used into the final product
3. Less hazardous chemical synthesis	Less toxic means lower hazard at workplace and to environment.
4. Designing safer chemicals	At design stage, the chemical toxicity should be minimized.
5. Safer solvents and auxiliaries	Solvents must be replaced with less toxic alternatives.
6. Energy efficiency	Synthetic methods having equilibrium conditions at or close to T_{room} and P_{atm}.
7. Using renewable feedstocks	Renewable feedstocks should be used rather than depleting sources.
8. Reducing derivatives	Unnecessary derivatization should be minimized or avoided if possible, since they require additional reagents and generate waste.
9. Catalysis	Efficiency and yield of synthesis must be increased.
10. Designing for degradation	At the end of the useful life, items should be easily degraded.
11. Real-time analysis	In-process monitoring prior to hazardous substance formation.
12. Inherently safer chemistry	Raw materials and chemicals should be inherently safe.

3. RESULTS AND DISCUSSIONS

3.1. Experimental results and discussion

The COD content of the effluent at the outlet of the process stream was 2500 mg/L and this sample was diluted up to 40% to be incubated for 40 days at 27 °C. At the end of the incubation period, each flask content was then analyzed in terms of COD content with DR2800 Hach Lange LCK 314 standard cell kit. The experimental results and analysis shown in table 2 states that COD content was lowered drastically below the given legal limits for COD. Removal of COD up to 94% from the effluent has been a successful result in terms of wastewater treatment. Moreover, as can be seen in table 2, this result is obtained for any concentration. It can be concluded that pre-dilution is not a necessary step for microalgae treatment method.

Table 2. COD analysis results of the samples with various dilutions.

Dilution	COD (mg/L)
0%	172
10%	150
20%	173
30%	140
40%	142

When cell concentrations and growth rates are calculated, it is observed that the maxima are reached when there was no dilution. The maxima are $x_{max} = 1.24\ g/L$ for cell concentration and $\mu_{max} = 0.0038\ h^{-1}$ for cell growth rate. These results confirm that pre-treatment dilution is not effective for this type of system.

3.2. Green chemistry analysis results and discussion

The green chemistry analysis of this specified wastewater treatment with microalgae is performed step by step for each principle and overall findings are tabulated in table 3.

Prevention: Any advanced industrial wastewater treatment yields in formation of sludge. However, this method has no sludge formation; thence, waste prevention is achieved.

Atom Economy: All the inlet stream is used as feed of the microalgae without any side product formation. So, it can be said that all atoms are incorporated by growth of microalgae.

Less hazardous chemical synthesis: Since there exist no chemical synthesis, this principle is not applicable.

Designing safer chemicals: The wastewater treatment has no chemical design. This element is also not applicable.

Safer solvents and auxiliaries: When compared with conventional industrial treatment technologies, microalgae treatment replaces severe chemicals. Henceforth, this principle is successfully placed.

Energy efficiency: The microalgae are living things and this avails to process the wastewater treatment under mild conditions, at ambient temperature and pressure, which means the lower use of energy.

Using renewable feedstocks: Microalga itself is a renewable feedstock as it can be cultured.

Reducing derivatives: The product of microalgae treatment method is grown microalgae only. This means that there is no formation of any other compounds. This principle is fulfilled in parallel with atom economy.

Catalysis: The system uses enzymes of microalgae as its bio-catalysts.

Designing for degradation: Microalgae is a biodegradable end product of the treatment. It can be disposed, degraded or used furtherly in some other processes.

Real-time analysis: This principle is applicable for industrial applications and continuous processes. It is not applied for laboratory trials.

Inherently safer chemistry: Although the microalgae method is safer than conventional methods, it is not because of inherent safety. Replacing severe chemicals is related to 4th principle, so this last principle is not applicable since the method is not offering a new chemical.

Table 3. Results of green chemistry analysis of baker's yeast wastewater treatment with microalgae.

Principle	**Analysis***
1. Prevention	+
2. Atom economy	+
3. Less hazardous chemical synthesis	N/A
4. Designing safer chemicals	N/A
5. Safer solvents and auxiliaries	+
6. Energy efficiency	+
7. Using renewable feedstocks	+
8. Reducing derivatives	+
9. Catalysis	+
10. Designing for degradation	+
11. Real-time analysis	N/A
12. Inherently safer chemistry	N/A

** "+" stands for meeting the principle, "-" stands for not meeting the principle, and "N/A" stands for not applicable principle.*

4. CONCLUSIONS

Baker's yeast effluent is hardly treatable wastewater with definitive dark brown color and specific odor caused by melanoidins of molasses. Manufacturers of baker's yeast are dealing with eliminating this color and unpleasant odor for environmental reasons and public health. Current applications of this process' wastewater is combined advanced treatment technologies which includes using severe chemicals, sludge formation and microbiological treatments. Moreover, the facilities should deal with remaining sludge of wastewater treatment. In this study, it is aimed to employ a novel approach to water treatment technologies while making treatment process environment friendlier. In order to achieve this target, microalgae are cultivated to process effluent obtained from an industrial yeast manufacturer. The compounds in the effluent had become feeds of microalgae. Henceforth, the growth of microalgae had been observed as it is the biological process of water treatment in the system. Additionally, COD amount in the wastewater was measured, because it was also aimed to specifically decrease COD content below legislative limits. The result of the microalgae treatment has been promising as COD content is lowered successfully beyond limits. Meanwhile, it can be concluded from the experiment that dilution of the wastewater prior to cultivation is not necessary. Lastly, the aim to make the water treatment greener has successfully achieved. The green chemistry analysis shows that overall treatment process is environment friendly. However, it should be denoted that scale up studies should include economic feasibility searches.

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Preparation of Ionic Liquid Mediated Sol-gel Silica for the Removal of Cr(VI) Ions from Aqueous Solutions

Nilay GIZLI[1]*, Merve ARABACI[2]

Abstract

In this study ionic liquid mediated sol-gel silica adsorbents are prepared and used for the removal of Cr (VI) ions from aqueous solutions. For this purpose silica based adsorbents containing ionic liquids (ILs) are synthesized by sol-gel method. Thus the high extracting ability of ILs are combined with the surface properties of silica substances. Commercial (Aliquat 336® and EMIMTf2N) and synthesized ([A336][NO3]) ionic liquids are incorporated directly by sol-gel operation. Silica based adsorbents are being initiated with silica precursor (TEOS), water, alcohol and ionic liquid hydrolysis in the presence of an acid catalysts then completed with a condensation reaction. Physicochemical and morphological characterization of prepared adsorbents have been investigated by FTIR, SEM and BET analysis. The sorption behaviors of adsorbents have been investigated by using a series of batch sorption studies. Sorption percentages of the adsorbents were enhanced by containing ILs up to 99% with the adsorption capacity of 31.74 mg/g. It can be concluded that sorption of Cr(VI) ions from aqueous solution by sol-gel silica based adsorbents containing Aliquat 336 takes place favorably and these type of adsorbents are promising agents in the adsorption processes.

Keywords: *Adsorption, Cr(VI) Removal, Ionic Liquid, Sol-gel, ,*

1. INTRODUCTION

Chromium has a wide range of industrial application areas such as; metal plating, leather tanning, pigment and coating industries [1]. Chromium in aqueous solutions exists in a range of oxidation state from -2 to +6. Cr(VI) exhibits toxic effects for living organisms, therefore the allowable limit is kept at low concentrations. World Health Organization (WHO) has set this limit as 0.05 mg/L for the drinking waters [2]. For that reason it is very important to develop a process for selective removal of Cr(VI) ions from aqueous solutions.

Removal and extraction of dissolved heavy metal ions from aqueous media are generally accomplished by several methods including chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation, flocculation, flotation, and electrochemical methods [3-5]. Among all these methods, adsorption is considered as the effective technique for the removal of heavy metals from aqueous solution because of advantages like the low cost, availability, profitability, ease of operation and efficiency [6, 7].

In general, the efficiency of the adsorption depends on many factors, including the surface area, pore size and distribution of it, as well as the surface chemistry of the adsorbents. The sorbents with a high specific surface area as a result of the porous character are generally needed for high adsorption efficiency [8].

Ionic liquids (ILs) are organic salts which have liquid form at room temperature. Because of this, they are recognized as Room Temperature Ionic Liquids (RTILs). The large number of possible ILs structures and their unique properties such as high thermal stability, non-flammability, negligible vapor pressure make them feasible to consider them as an opportunity to contribute to greenness in the various field in which they can be applied [9]. In addition, ILs have adjustable hydrophobicity, polarity and selectivity compared with organic solvents when used for extraction [8, 10]. ILs can be used as metal extraction reagent for separation of metal ions. There are many advantages of ILs in separation processes such as high separation efficiency and high selectivity. However, some drawbacks of ILs are found in some liquid-liquid separation processes, such as large amount used, high viscosity leading unfavorably to dissolve and

[1*] *Corresponding author: Ege University, Department of Chemical Engineering, 35100, Bornova/Izmir, Turkey. nilay.gizli@ege.edu.tr*

[2] *Ege University, Department of Chemical Engineering, 35100, Bornova/Izmir, Turkey. mmervearabaci@gmail.com*

diffuse, difficulties of separation and recovery, and the low interface area [11]. To overcome these shortcomings, ILs can be incorporated onto highly porous solid supports in many different ways, such as simple impregnation, grafting, polymerization sol–gel method and encapsulation [12]. Among these, sol-gel method has an incredible attention because of the advantages such as; (i) easy and inexpensive; (ii) functional groups are readily anchored on the substrate; and (iii) it can be used for the deposition of substrates that have complex surfaces or large surface areas [13].

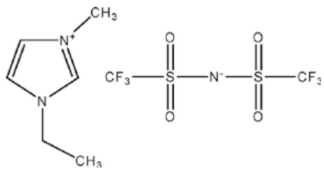
In this study, Ionic Liquid (IL) Mediated Sol-gel Silica adsorbents were prepared and used for the removal of Cr(VI) ions from aqueous solution. Three different types of ILs such as Aliquat 336, EMIMTf2N and [A336][NO3] were incorporated onto silica adsorbents by following the one-step sol-gel process. Physicochemical and morphological characterization of prepared adsorbents has been investigated by Fourier Transform Infrared Spectroscopy (FTIR) Scanning Electron Microscopy (SEM), Brunauer Emmett Teller (BET) analysis. In addition, thermal behavior of prepared adsorbents was also characterized by Thermogravimetric Analysis (TGA). The sorption behaviors of adsorbents were investigated by a series of batch sorption experiments. Effect of the type of ILs on the adsorption performance was investigated as well as sorption percentages.

2. MATERIALS AND METHODS

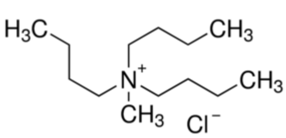
2.1. Materials

In this study, tricaprylylmethylammonium chloride (trade name Aliquat 336, (C8H17)3CH3NCl), 1-Ethyl3methylimidazolium bis(trifluoromethylsulfony) imide[EMIMTf2N] and tricapryl methyl ammonium nitrate [A336][NO3] were used as ionic liquids. [A336][Cl] and EMIMTf2N were obtained from Sigma Aldrich, [A336][NO3] was synthesized by anion metathesis reaction. Tetraethyl ortosilicate with the formula of Si(OC2H5)4 (TEOS) was used as a precursor for obtaining SiO_2 matrix. Required concentration of chromium solution was prepared by using potassium dichromate salt, $K_2Cr_2O_7$. Also, 0.1M of HCl and 0.1 M of NaOH solutions were used to adjust the pH of the solution.

Chemical structures of commercial ionic liquids are shown in Figure 1.



(a)



(b)

Figure 15. Chemical structures of commercial ionic liquids a) EMIMTf$_2$N b) Aliquat 336

2.2. Synthesis of the Task Specific Ionic Liquid

A336 [NO3] (task specific IL) was synthesized by anion metathesis reaction of Aliquat 336 with KNO_3 solution. Reaction can be given as follows;

$$A336[Cl] + KNO_3 \longrightarrow A336[NO_3] + KCl$$

Ionic liquid (A336[Cl]) and 2 M of KNO_3 solutions were contacted for 1 hour by vigorous stirring. The phases were then separated by using a separating funnel followed by washing with distilled water. These steps were repeated for 4 times. Completion of the reaction was controlled by checking the Cl^- ion content of the ionic liquid by using $AgNO_3$ indicator.

2.3. Adsorbent Preparation

Sol-gel process was used for the preparation of sorbents based on nanoporous silica oxide matrices in whose interconnected network, ionic liquid got trapped. In this manner, 5 mL of TEOS as a silica precursor and 2.5 mL of EtOH were mixed in an ultrasonic media. And various amount of IL (0-14%) were added into TEOS-EtOH solution. and mixed at 40°C during 30 min. Then, 2.5 ml of aqueous HCl solution (37 wt %) was added as dropwise and the solution was mixed during futher 2 hours. Then, the solution was poured into the petri dishes and left to dry at ambient conditions. Finally obtained products was ground into powders for the subsequent characterization and adsorption studies

Prepared sorbents are abbreviated according to type of IL, as given in Table 1.

Table 6. Abbreviation of prepared silica adsorbent*s*

ID	Ionic Liquid
SG-A	Aliquat 336
SG-TS	[A336] [NO_3]
SG-IL	[EMIMTf_2N]

2.4. Characterization

The structural formation of the prepared adsorbents was investigated by using a Fourier Transform Infrared spectrometer (FTIR-Pelkin Elmer Spectra 100) in the wave number range of 650-4000 cm-1 to identify the functional groups. The surface morphology of adsorbents was investigated by using Scanning Electron Microscope (SEM) and qualitative element composition was analyzed using Energy Dispersive X-ray (EDX) operated in QUANTA 400 F Field Emission Spectrometer. The microscope was operated at an accelerating voltage of 20.00 kV. The particles were coated with a gold layer in order to make them conductive. Surface area and pore volume of silica adsorbents was analyzed by Brunauer–Emmett–Teller (BET) in Micromeritics Gemini V model. Thermal Gravimetric Analysis (TGA) was carried out using Perkin Elmer Diamond TG/DT model to investigate the thermal behavior of the silica particles.

2.5. Batch Sorption Studies

The adsorption of Cr (VI) ions from aqueous solutions onto the silica based adsorbents was investigated by a series of batch sorption tests to obtain the adsorption performances of adsorbents as removal percentage.
For batch adsorption studies, solution varying concentration (50-700 mgL^{-1}) of Cr(VI) were equilibrated with 50 mg of adsorbents by shaking at 150 rpm using a NUVE model ST 30 water-bath shaker. After equilibration, the adsorbents were removed and the supernatants were analyzed for Cr(VI) concentration by using Atomic Absorption spectrophotometer (Varian 10 +) (AAS).

The percentage of Cr(VI) removal, R(%) was calculated by using the following expression:

$$R(\%) = \frac{(C_0\text{-}C_e)}{C_0} * 100$$

where C_0 and $C_e$are the initial and equilibrium concentrations (mgL^{-1}), respectively.

The adsorption capacity of the prepared adsorbents was evaluated using the following equation:

$$q_e = \frac{(C_0\text{-}C_e)*V}{m}$$

where q_e is the adsorption capacity (mg/g), C_0 and $C_e$are the initial and equilibrium concentrations (mgL^{-1}), respectively. V is the volume of Cr(VI) solution and m is the mass of dry adsorbent

3. RESULTS

3.1.Characterization

3.1.1 FTIR analysis-Physicochemical Characterization

FTIR spectrums of the prepared adsorbents are shown in Figure 2.
In the FTIR spectra of untreated silica materials (Figure 2 a), has a peak at 3258.80 cm^{-1} wavelength which can be attributed as an indication of unreacted –OH structure. At this wavelength, –OH peaks are decreased or disappeared with the increasing in the amount of ionic liquid in the sol-gel process.
The FTIR spectrum of [A336][Cl] (Figure 1.c), the peaks around the position of 2923 cm^{-1} can be attributed to the characteristic absorption of -CH3 of alkyl chain and at the position of 1466 and 1378 cm^{-1} are based on the structure of quaternary ammonium moiety of the ionic liquid. The peak located at 1465 cm-1 (Figure 2 b) is pronounced functionalization of silica particles with [A336][Cl] type ionic liquid.
Peaks appeared at 3159 and 1574 cm^{-1}wavelengths (Figure 2 e) can be attributed as the C=N bonds of the imidazolium ring. Also, the bands around 1067 and 795 cm^{-1} indicate the asymmetric and symmetric stretching of Si—O—Si vibration, respectively. These data are the important indications for the ionic liquid presence in SG-IL structure.

The peaks around the position of 2924 cm^{-1} can be attributed to the characteristic absorption of -CH3 of alkyl chain and the bands between 1467 and 1328 cm^{-1} are based on the structure of quaternary ammonium moiety of the ionic liquid. The peak located at 1326 cm^{-1} (Figure 2 f) is pronounced functionalization of silica particles with [A336][NO3] type ionic liquid.

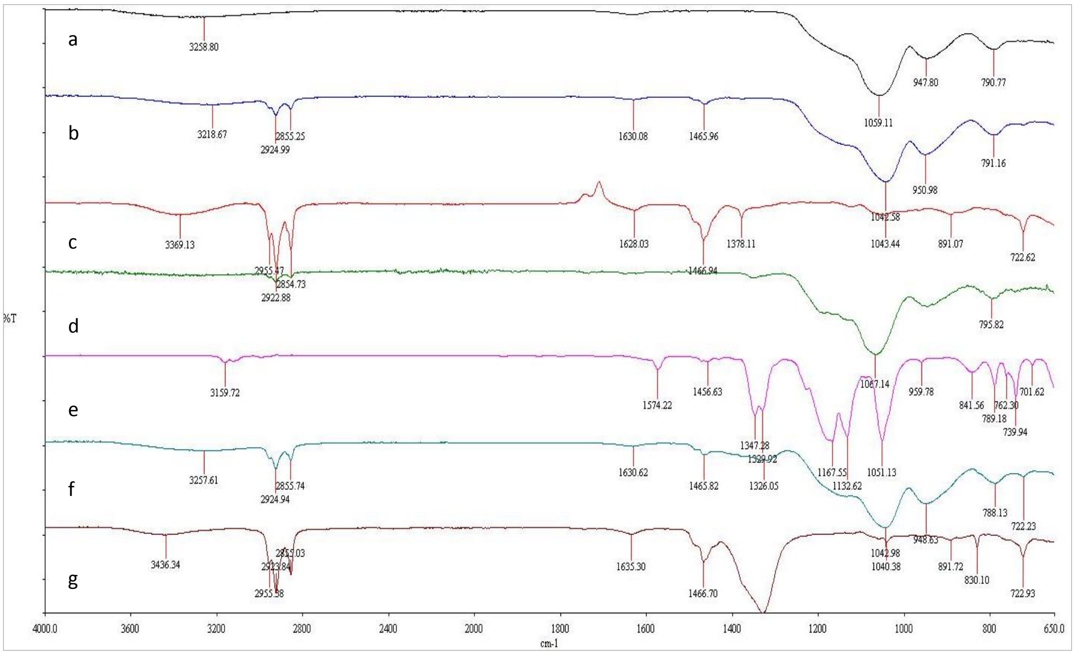


Figure 2. FTIR spectra of ionic liquid functionalized silica based adsorbents ***a)*** *before functionalization (SG-0)* ***b)*** *adsorbent (SG-A) functionalized with [A336][Cl]* ***c)*** *ionic liquid [A336][Cl] (Aliquat 336)* ***d)*** *adsorbent (SG-IL) functionalized with EMIMTf$_2$N* ***e)*** *ionic liquid EMIMTf$_2$N* ***f)*** *functionalized with [A336][NO$_3$] adsorbent (SG-TS)* ***e)*** *ionic liquid [A336][NO$_3$]*

3.1.2 BET Analysis-Surface Properties

BET surface area [m^2g^{-1}] and pore width [A°] values of silica based and ionic liquid functionalized silica adsorbents are shown in Table 2.

Table 2 BET analysis data of prepared adsorbents

Adsorbents	**Surface Area [m^2/g]**				**Pore Volume [cm^3/g]**	**Pore Size [A°]**
	BET	**Langmuir**	**t-Plot Micropore**	**t-Plot External**		
SG	577.0834	744.6663	148.7083	428.3751	0.307997	21.3485
SG-IL	299.7985	402.8222	-	372.4833	0.230098	30.7003
SG-TS	593.26	755.6763	-	-	0.3365	20.6932
SG-A	602.35	762.3354	-	-	0.32426	20.3324

As shown in Table 2. Silica based adsorbents functionalized with various type of ILs were characterized to be mesoporous with average pore diameter of 2 nm and BET surface area in the range of 300 -600 m^2g^{-1}. Pore volumes of SG-TS and SG-A are higher than SG (untreated) type adsorbents while average pore diameters of adsorbents containing TS and A type ionic liquids are lower than SG leading to higher surface area. On the other hand Surface Area of SG adsorbents decreases with modification with IL type ionic liquids. This may be attributed that the surface area is occupied by the long alkyl chain of EMIMTf$_2$N type ionic liquid.

3.1.3 SEM Analysis -Morphological Characterization

The morphological characteristics of SG-A, SG-TS and SG-IL were evaluated respectively, using a scanning electron microscope (SEM) as shown in Figure 3.

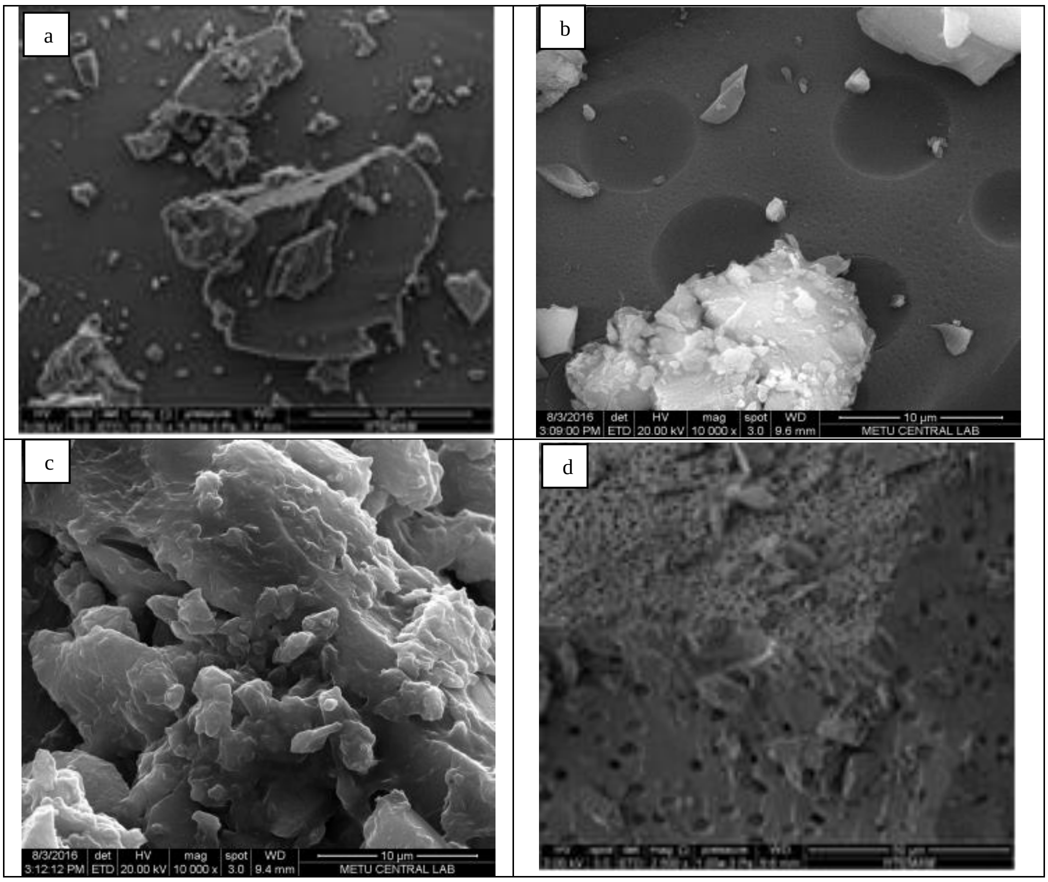


Figure3. SEM images of prepared adsorbents with the magnification rate of 10000 a) SG b) SG-A c) SG-TS d) SG-IL

In the SEM images of silica materials having none IL content, it is observed that, the surface area of SG has nonporous and nonhomogeneous structures. Unreacted alcohol and other residues are evident on the surface. Pore structure formation is observed by presence of the ionic liquid especially Aliquat 336, [A336][Cl], (SG-A) and imidazolium based IL, EMIMTf$_2$N, (SG-IL). From the SEM images it can be concluded that ionic liquids acted as porogens in the preparation of silica adsorbents.

3.1.4 TGA-Thermal Behavior Analysis

Thermal stability of the silica based adsorbents containing various amount of ILs ara shown in the Figure 4.

In TGA results (Figure 4),it is clearly observed that silica adsorbents without IL content (SG) is started to decompose at low temperatures around 50 °C. The adsorbents containing imidazolium based ionic liquid with the weigh percentages of 20 and 40 %, have a weight loss at the higher temperatures because of high thermal stability of IL. It can be concluded that IL increases the thermal stability of silica materials.

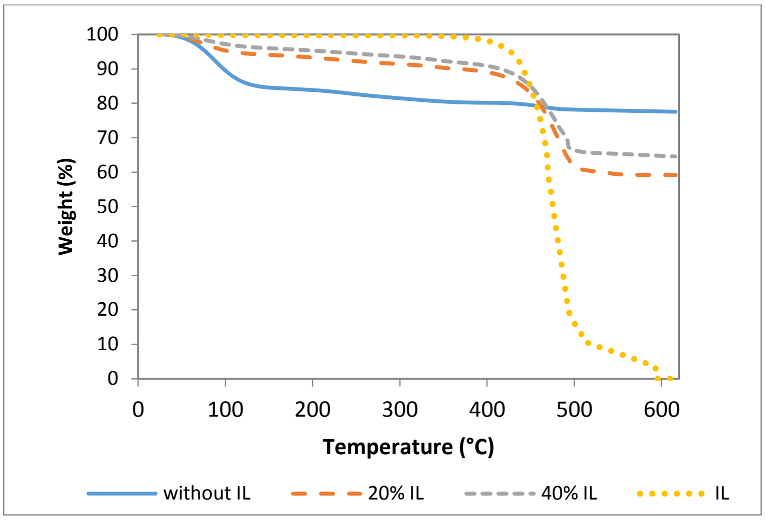


Figure 4. TGA results of SG-IL adsorbents

3.2.Effect of IL type on the sorption of Cr(VI) ions

Sorption performances of silica based adsorbents containing various amount and type of ionic liquid were evaluated as removal percentage of Cr(VI) ions from aqueous solution. Effect of ionic liquid amount were also examined by using two different ratio of ILs on the mass basis such as 0.5 and 0.7 g-IL/g-silica precursor. Results are shown in Figure 5.

It can be confirmed from Figure 5 that SG-TS and SG-A type adsorbents showed a better removal performance for Cr(VI) in comparison to untreated silica adsorbent (SG). Although the results of SG-A and SG-TS exhibited quiet similar results, SG- A can be chosen as adsorbent for the further studies. Because of the fact that SG-TS needs additional step for synthesis of ionic liquid comparing with the preparation of SG-A .

Sorption percentages of the adsorbents have been enhanced by containing Aliquat 336 type ionic liquids (SG-A) up to 99%.

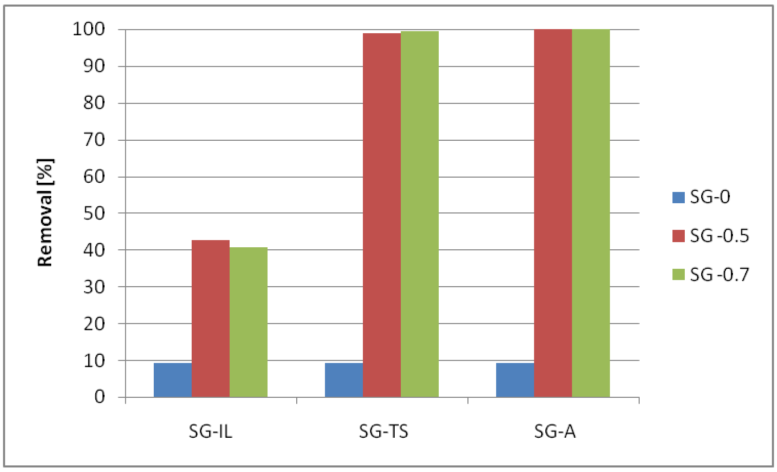


Figure 5. Removal efficiency of silica based synthesized by using various type of ionic liquids for the sorption of Cr(VI) ions.

Adsorption capacity of SG-A type adsorbents was calculated as 31.74 mg.g-1 and it is also observed that increase in IL content has no pronounced effect on the sorption performances.

4. CONCLUSIONS

In this study ionic liquid mediated sol-gel silica adsorbents are prepared for the removal of Cr (VI) ions from aqueous solutions. Physicochemical and morphological characterization of prepared adsorbents concluded that ionic liquids acted as porogens and increased the thermal stability of the silica based adsorbents.

Based upon the experimental results, Cr(VI) sorption percentages achieved with silica adsorbents containing ionic liquid were higher than that of untreated adsorbents due to synergistic effect of electrostatic interaction with IL and Cr(VI) ions. Sorption percentages of the adsorbents were enhanced by containing ILs up to 99% with the adsorption capacity of 31.74 mg/g. It can be concluded that sorption of Cr(VI) ions from aqueous solution by sol-gel silica based adsorbents containing Aliquat 336 takes place favorably and these type of adsorbents are promising agents in the adsorption

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A modelling methodology for assessing use of datacenter waste heat in greenhouses

Marcus SANDBERG[1], Mikael RISBERG[2], Anna-Lena LJUNG[3], Damiano VARAGNOLO[3], Shaojun XIONG[44] , Michael NILSSON[5]*

Abstract

In Sweden, the number of datacenters establishments are steadily increasing thanks to green, stable and affordable electricity, free air cooling, advantageous energy taxes and well-developed Internet fiber infrastructures. Even though datacenters use a lot of energy, the waste heat that they create is seldom reused. A possible cause is that this waste heat is often low grade and airborne: it is therefore hard to directly inject it into a district heating system without upgrades, which require additional energy and equipment that generate extra costs. One option for reusing this heat without needs for upgrades is to employ it for heating up greenhouses. But assessing the feasibility of this approach by building physical prototypes can be costly, therefore using computer models to simulate real world conditions is an opportunity. However, there is a lack of computer modelling methodologies that can assess the possibility of using waste heat from datacenters in greenhouses in cold climates.

The objective of this paper is therefore to propose such a methodology and discuss its benefits and drawbacks in comparison with other research studies. This methodology combines computational fluid dynamics, process modelling and control engineering principles into a computer model that constitutes a decision support system to study different waste heat and greenhouse or mushroom house scenarios.

The paper validates the strategy through a case study in northern Sweden, where we assess the amount of produced waste heat by collecting temperature, relative humidity, and fan speed data for the air discharged from the datacenter.

The resulting methodology, composed by conducting measurements and computer models, calculations can then be used for other datacenter operators or greenhouse developers to judge whether it is possible or not to build greenhouses using datacenter waste heat.

Keywords: *Computational Fluid Dynamics, Cooling, Datacenter, Measurements, Simulations, Waste Heat Recovery*

1. INTRODUCTION

In the digital age of today, also known as digitalization, with cloud-based solutions and wide use of social media, the number of datacenters is increasing to handle the new demands on information storage. Datacenter servers consume a lot of energy and generate a lot of heat so these servers need efficient cooling solutions to not overheat. This has attracted datacenter operators to northern Europe since the opportunities for free air cooling by using the outside air are favorable. Other aspect like stable green electricity, robust digital infrastructure and reasonable energy taxes are also reasons. There are examples of research aiming to make datacenters more energy efficient such as the FIT4green project, [1], where the energy need for the automation technology was focused and the GAMES project, [2], where developing smart datacenters to decrease energy need was is focus. There are studies on how to absorb the heat during

[1*] *Corresponding author: Luleå University of Technology, Department of Civil, Environmental and Natural Resources Engineering, SE-97187, Luleå, Sweden,* marcus.sandberg@ltu.se

[2] *Luleå University of Technology, Department of Engineering Sciences and Mathematics, SE-97187, Luleå, Sweden,* mikael.risberg@ltu.se, anna-lena.ljung@ltu.se

[3] *Swedish University of Agricultural Sciences, Department of Forest Biomaterials and Technology, SE-90183, Umeå, Sweden,* shaojun.xiong@slu.se

[4] *Luleå University of Technology, Department of Computer Science, Electrical and Space Engineering, SE-97187, Luleå, Sweden,* damiano.varagnolo@ltu.se, michael,nilsson@ltu.se

the cooling of the servers, e.g. [3], but to the authors knowledge, studies on how to use or reuse the heat from the datacenter ventilation systems are lacking.

Although newly built datacenters use technology that allow for using server heat for heating up the building there are still waste heat being let out to the free air. There is a challenge to use this waste heat that is usually low grade, up to 30-40℃ although there are examples of such technology [4]. Ward et al [5] presented an approach that decentralizes the datacenters into nodes and where the waste heat from each node is used for heating adjacent buildings or facilities. We see a need of tools that help evaluating the opportunities for using datacenter waste heat in greenhouses. Therefore, we started a project in collaboration with many stakeholders within the energy, datacenter and food growing area, which is presented in this paper.

2. THEORETICAL FRAMEWORK

2.1. Process modelling

To model the heat transfer solution between the datacenter and greenhouse the process simulation software such as aspen plus, [6], can be used. Aspen plus uses basic engineering relationships and mass and heat balance to determine the outputs for the system. By varying some specific design parameters of the heat transfer solutions, correlations can be obtained that can be used for greenhouse dimensioning.

2.2. Computational fluid dynamics

With computational fluid dynamics (CFD) it is possible to numerically retrieve information about airflow and temperature inside a greenhouse [7]. The detailed knowledge provides the possibility to evaluate designs prior to construction but it is at the same time crucial that the models are set up with quality and trust in focus. The heat transfer situation of a greenhouse is complex with the joint effects of sun radiation, heat radiation, ventilation, external convection and conduction, heat transfer through the ground, condensation at the walls, leakage of air etc. The conditions inside the greenhouse are furthermore subjected to transient variations with regards to external conditions such as time of day, time of year and current weather situation. In this context, CFD can be a valuable tool in the assessment of external heat sources, e.g., the waste heat from a datacenter.

2.3. Control engineering related modelling

Solving a control problem (in terms of deciding how to steer actuators like ventilation, heating and cooling units based on current measurements from the plant) may benefit from the knowledge of mathematical models of the plant itself. If available (and with the caveats written below), models may indeed be used to forecast what will be the outcome of taking a specific control action. This means that (at least theoretically) models may enable choosing the current action as that one that leads to the “best” forecasted performance (with the metric “best” to be opportunely defined).

This paradigm is known as the predictive-control paradigm [8]. Implementing it, nonetheless, requires sufficiently lightweight mathematical models: since the control-decision problem should be taken “now”, the system needs to compute forecasts of the future outcomes sufficiently fast. This means that CFD tools - typically computationally intensive - are in general not suitable for implementing predictive control schemes.

Obtaining control-oriented models can then performed in different ways: one is to derive simplified descriptions (typically in terms of ordinary differential equations) using first-principles and physical knowledge of the plant. Another one is to employ data-driven approaches, where past measurements from the plant are used to compute statistical estimates of the inputs-outputs map (an operation that is often referred to as the "identification" of the system). Notice that often these two paradigms are blended into so-called "grey-box" modelling strategies where the structure of the model is fixed using first-principles, and then the parameters of this model is then populated using measurements from the plant and opportune statistical estimation algorithms).

Using a data-driven approach typically leads to more accurate models than using just first-principles and physical knowledge. In the case described in this paper, nonetheless, the plant needs still to be built, so actual measurements are not available. Our approach to perform control-oriented modelling of our data center - greenhouse system is then to follow a hybrid approach: if a CFD model is available, then the CFD simulator can be used as a virtual plant to obtain virtual measurements. This eventually allows using classical system identification strategies to obtain a control-oriented model; this control-oriented model then is used to design a plant control algorithm, and finally this controller can be embedded into the original CFD model so to perform a virtual feedback loop.

3. METHOD

3.1. Case

The municipality of Boden in northern Sweden wanted to study the possibility to use waste heat from datacenters to heat up greenhouses. They need a new greenhouse for growing park flowers and plants but they also see a need in creating educational possibilities and activities for immigrants as well as providing space for commercial actors to

grow food or other crops. Hydro66 is a datacenter operator in Boden that was interested in participating in the study, see Figure 1.

Figure 1. The Hydro66 datacenter in Boden.

3.2. Measurements

Figure 2. Sensors for measuring temperature and humidity was mounted outside the outlet fans (left part) and on the inside of the outer wall (right part) to measure the incoming air.

Seven sensors, two measuring both temperature and relative humidity and five measuring temperature, were mounted at the Hydro66 datacenter in Boden. One of them was mounted on the inside of the outer wall, which is a wall with lot of small holes where outside air easily can come through, to measure temperature and humidity, see right hand side of Figure 2. The six other sensors were mounted as shown in the left-hand side of Figure 2. The temperature was logged from July 2016 until April 2017.

3.3. Model development

To determine the mass flow of hot air from the datacenter a process simulation model was created that is presented in Figure 3. The model consists of the air flow into the datacenter, the computer load that is represented as a heater in the middle and the airflow out from the datacenter. Also, some of the air is recirculated and mixed to create more stable condition inside. The inputs to the model is the outdoor temperature and heat load from the servers and output is the airflow out from the datacenter. In the model, the temperature out was controlled to 35°C. A correlation was then created from the results and used in the greenhouse dimensioning.

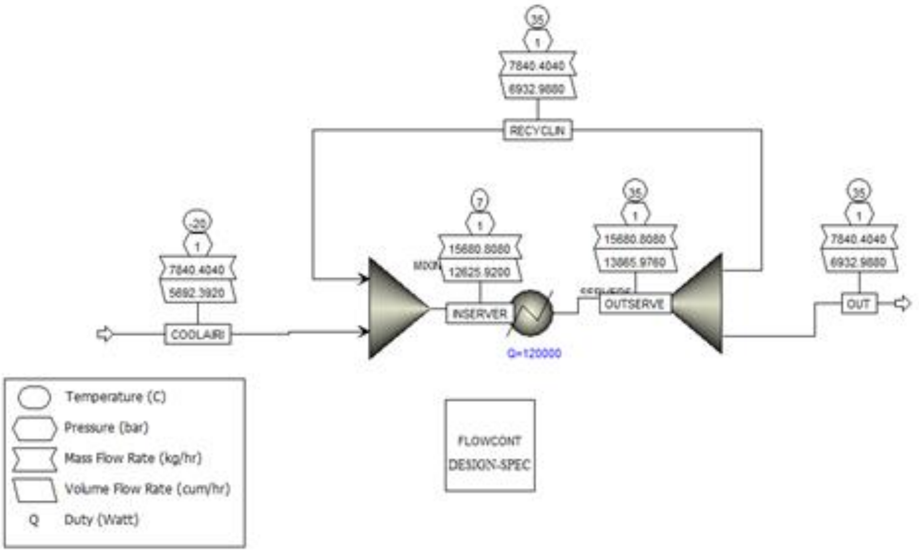

Figure 3: Process model of the datacenter used to determine mass flow of air at a specified temperature for different outdoor temperatures.

The heat transfer model presented in Figure 4 is consisting of the airflow from the datacenter that are heat exchanged with water. The heated water is then transported in a pipe to the greenhouse where used as heat. After the greenhouse, the water is then recirculated in pipe back to the heat exchanger where it is reheated. The inputs to the model is airflow from the datacenter, distance between datacenter and greenhouse and the outdoor temperature, the output is the available heat at the greenhouse. The results from the model was then converted to a correlation that are used for the greenhouse dimensioning.

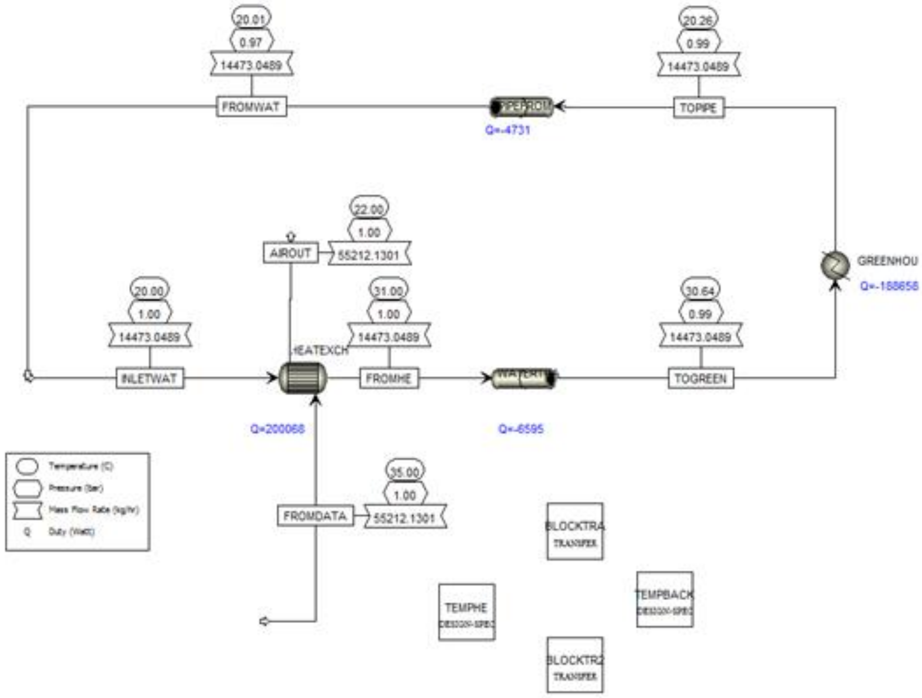

Figure 4: Process model of the heat transfer solution.

For the greenhouse dimensioning an excel spreadsheet was developed that considers the outdoor temperature based on data from the Swedish Meteorological and Hydrological Institute (SMHI), datacenter size, greenhouse building envelope and distance between datacenter and greenhouse. In this excel spreadsheet the correlation from the process model was implemented.

4. RESULTS

4.1. General framework

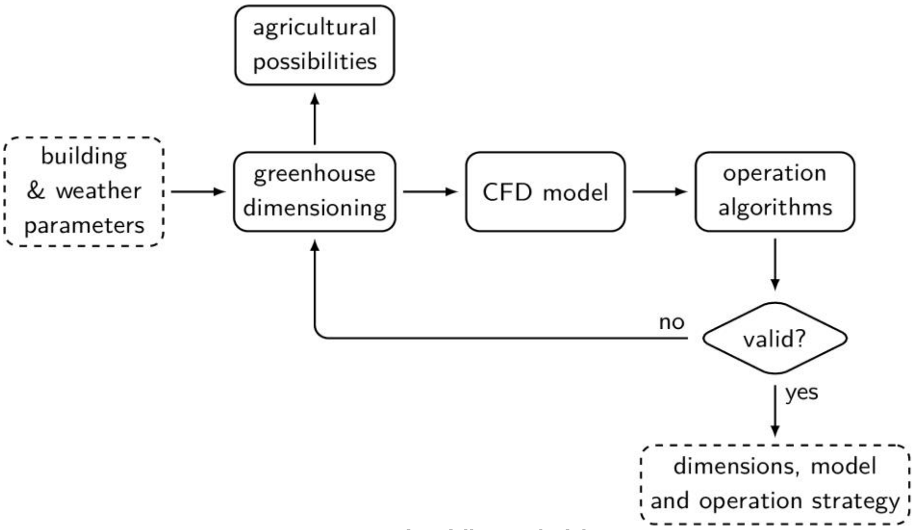

Figure 5. Proposed modelling methodology.

The methodology proposed in this paper, graphically summarized in the chart in Figure 5, is the following: starting from the requirements of having preliminary information on: the structural parameters on the datacenter (such as expected maximal power usage); the properties of the greenhouse (such as u-values of the walls); the requirements of the minimal and maximal temperature within the greenhouse; statistics on the weather conditions for the location (thus not only, e.g., daily average temperatures, but also traces of actual past evolutions so to be able to assess the extent of variations from nominal average values); and a CFD model of the datacenter.

The first step is then to perform an initial greenhouse dimensioning, considering the average weather conditions and using the first principles modeling and computations described in Section 3.3. Following this dimensioning, the designer should then: i) generate a CFD model of the greenhouse, ii) obtain the control-oriented one by performing system identification on the systems using the CFD models as virtual plants as explained in Section 2.3; iii) implement predictive control systems on top of the so-identified model; iv) eventually embed these controllers into the CFD models above. In this way, the designer obtains a complete CFD simulator of the system in closed-loop (i.e., something that simulates how the system should behave not only when the weather conditions are the nominal, but also when these change).

With this closed-loop simulator the designer can then understand if the data center - greenhouse system designed up to now can sustain the typical variations in the weather conditions. The designer can indeed understand through simulations if this system can reject weather disturbances by opportunely acting on the indoor-conditioning subsystem, and guarantee that the temperature of the greenhouse above the required one for all the colder-than-average situations collected in the traces mentioned in the first step of the methodology. The proposed methodology then works as follows: if the overall system can reject the weather disturbances as intended above, then it is meaningful to try to consider what would happen with a bigger greenhouse (i.e., change the design of the greenhouse and then re-perform the steps above). If instead the disturbances are not rejected, then it is necessary to consider a smaller greenhouse. Our proposal is then to iterate the steps above up to the moment that one finds a "big-just-enough" greenhouse.

4.2. Example

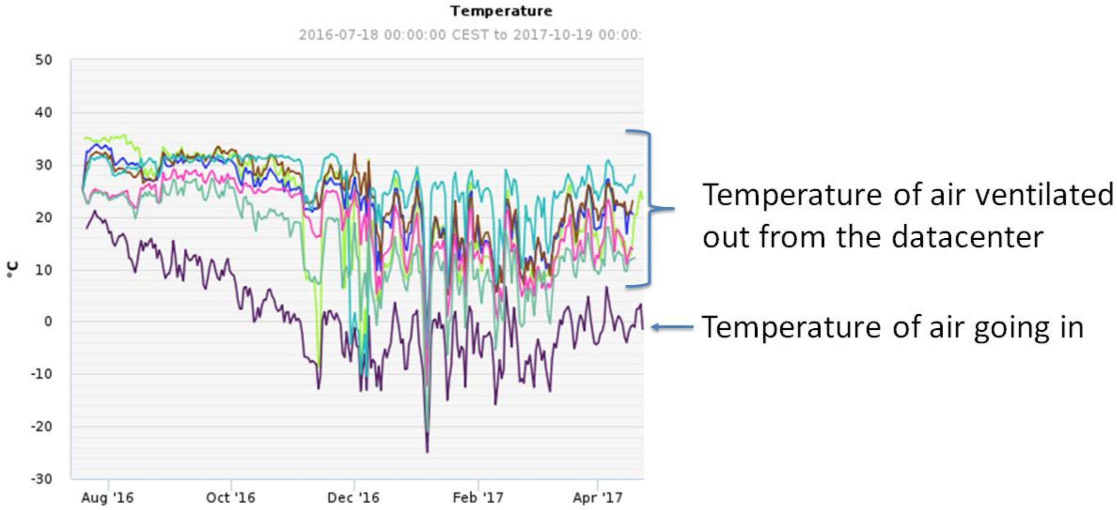

Figure 6. Measured temperature of the air ventilated out and air going into the Hydro66 datacenter.

In Figure 6 the measured temperature is presented. The temperature of the air going out is from below zero up to 35℃. When the outgoing air is below zero the ventilation fans are shut off.

In the following example, the datacenter located in Boden, not far from the Arctic circle, has a load of 1 MW and the greenhouse has a width of 12.5 m and a height of 4 m with double pane glass for the green house. In Figure 7 the results for the length of the greenhouse dependent of outdoor temperature (left) and the date (right) is presented. For a low temperature under -10 ℃ the data center can support a greenhouse that is 50 m long and when the temperature goes the down to -30 ℃ it can only support a length of 17 m. Over the year, during the winter, only a small greenhouse can be heated from the datacenter but during the summer a large greenhouse of length 300-400 m could be heated.

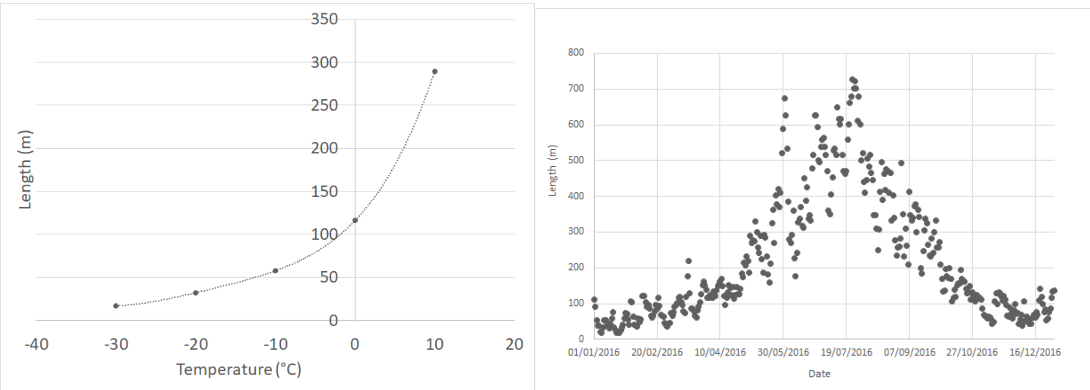

Figure 7: Example of results from the greenhouse dimensioning for a datacenter of 1 MW located in Boden, Left: Length dependent of outdoor temperature, Right: Length dependent on date.

In Figure 8 the airflow inside a suggested greenhouse is evaluated. Here it is possible to evaluate fan solutions and other ventilation related parameters.

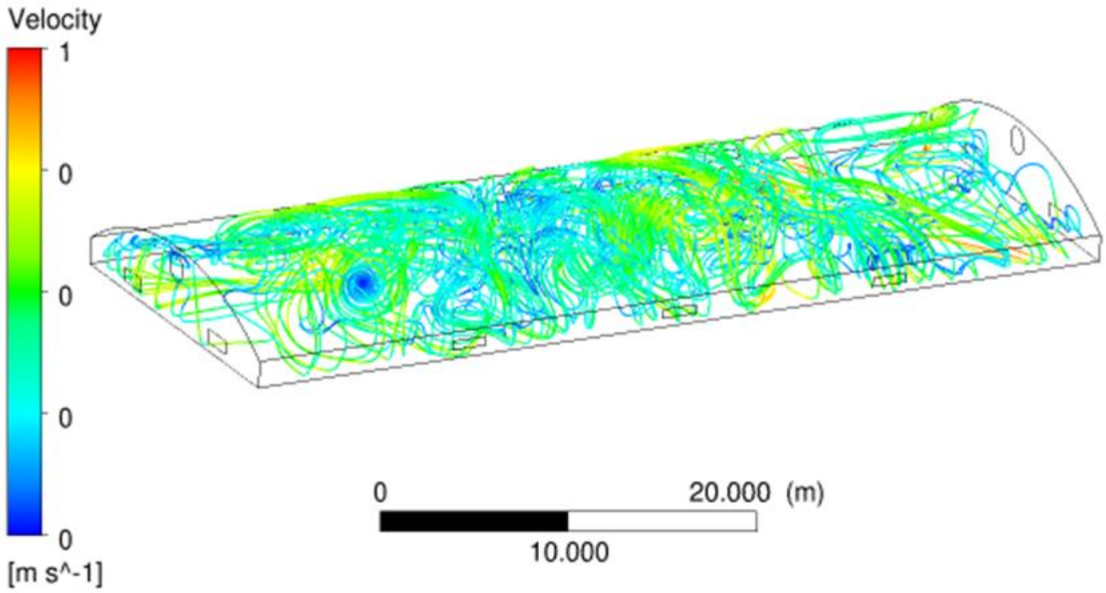

Figure 8. Computational fluid dynamics model of a suggested greenhouse.

5. DISCUSSION

During the winter only a small greenhouse can be heated from the datacenter. Therefore, if the greenhouse should be used during the coldest part of the year additional heating will be needed which for example could be district heating, pellets burner or biogas. Another option is only to use the heat to extend the growing season and not use it during the coldest months. The process modeling part have some uncertainties that needs to be addressed before the heat transfer solutions is implemented in a real system. The first one is the heat exchanger sizing after the data center. Since it's several air outlets from the datacenter one options is to have a heat exchanger connected to each outlets but this will probably end up in a very costly solution while the other options is the gather the airflows together which will be a practical problem for an existing datacenter since it is not designed according to that. The other uncertainties it how much heat that can be used in the greenhouse since currently greenhouses are not designed to use low temperature heating system and therefore more work are needed in this area.

The waste heat from the datacenter can be considered for cultivations of variable crops including vegetables, ornamental plants, berries, spices and edible mushrooms, however exact design for dedicated species is beyond this current study. The fact that the heat exiting from the datacenter is below the 35°C suggests that the target crops shall be reasonably among those species having low heat requirement for the growth. For example, the optimal air temperature during the cultivation is about 15 - 20 °C for spices (such as parsley, grass onion, basil, lemon balm etc.) and ornamental plants (such as pence, primula, geranium, etc.), and 10 - 18°C for shiitake and oyster mushrooms [9]. The exact design shall also incorporate with other inhouse climate variables such as lighting, CO^2 and relative air humidity. It is worth addressing that many edible mushrooms are growing on forest or crop residues and have a low demand of lighting (500 - 2000 lux, depending on strains and growth stages) as well as less requirements for fertilizers and pesticides. Cultivation of edible mushrooms has drawn more global attentions in recent years, because edible mushrooms are protein rich [10] and contain components good for human health [11]. Edible mushrooms have also been suggested as one of potentially alternative to substitute meat since meat production and associated transportation have caused considerable greenhouse gas emissions [12].

It is understood that a use of the waste heat from datacenters, i.e. a type of secondary energy source, for greenhouse cultivation shall contribute to a low CO^2 footprint, in general or in respect of the users. However, any implementation regarding to such a move have to consider an innovative and system solution for an optimized energy balance and cost efficiency. It could be explorable in future work, for example, an integrated cultivation of ornamental plants/vegetables that demands for light and CO^2 input, and edible mushrooms that prefer to darkness and emit CO^2. The development of a digital system enabling control and monitoring of the entire heat flow and mechanical devices from datacenter to crop growth chamber will be important and make a smart industrial integration possible.

6. CONCLUSIONS

A modelling approach using process modelling, computational fluid dynamics and control-oriented models to assess the use of waste heat from datacenter in greenhouses, have been presented. Using the models, we have shown that it is possible to run greenhouses on waste heat in the north of Sweden but you may need additional heat sources. The modelling approach could benefit from validation on real greenhouses and energy transfer solutions.

ACKNOWLEDGMENT

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Levels and Ecological Risk of Organochlorine Pesticides and PCBs in Surface Sediments and Fish along the Eastern Aegean Coast

Filiz KUCUKSEZGIN[1], Shareef K.I. MUZYED[2], L. Tolga GONUL[1], Idil PAZI[1]

Abstract

Organochlorines were measured in fish and sediment collected from Izmir and Candarli Bays. Surface sediments with three replicates were collected and all samples were extracted in microwave extraction system. The results showed that in all samples, p,p'-DDE was the predominant DDT congener. ΣCyclodiens were generally predominant contaminants. Aroclors were found in noticeably higher levels than OCPs in sediments and fish. The highest level of organochlorines was found in sediments of Nemrut which can be attributed to industrial activities. The maximum levels of ΣOCPs were found in fish collected from Gulbahce, while Aroclors were measured in Aliaga. According to selected ratios indicated no recent influxes of DDT in the sampling areas.

Keywords: *Organochlorine compounds; fish; sediment; ecological risk; Izmir Bay; Candarli Bay*

1. INTRODUCTION

Organochlorines (OCs) are generally hydrophobic substances, with low water solubility, frequently at the µg or ng per liter level. These organic compounds are highly concentrated by living organisms and concentrations can biomagnify along the food chain. Therefore, an investigation of the distribution of some OCs such as organochlorinated pesticides (OCPs) and polychlorinated biphenyls (PCBs) in fish and sediment samples can provide valuable data about contamination in a marine environment. Although their production, usage and disposal have been regulated or prohibited in most of the developed countries, OCPs are still used at present in many developing countries [1]. The production and usage of OCPs and PCBs were completely banned in Turkey in the 1990s and in 1995, respectively [2]. Although the consumption of OCs was banned in Turkey, the usage of these OCs continued illegally until the 2000s.

A number of studies have been carried out on the concentrations of metals in sediments and biota [3] in Izmir Bay, however few studies were performed on organochlorines in sediment [4], [5] and no data are available from the published literatures on the organochlorine levels in fish from the sampling areas. The aims of this study were to assess the distribution patterns of OCs in sediment and fish samples from Izmir and Candarli Bays, to evaluate the potential sources of DDTs using related indices, to find possible sources as well as potential biological risk of DDTs, PCBs in the study areas.

[1]*Corresponding author: Dokuz Eylul University, Institute of Marine Sciences and Technology, 35340, Inciralti/Izmir, Turkey, filiz.ksezgin@deu.edu.tr*

[2]*Palestine University, Pharmacy Faculty, Gaza, Palestine, xlas4@hotmail.com*

[1]*Institute of Marine Sciences and Technology, tolga.gonul@deu.edu.tr, idil.erden@deu.edu.tr*

2. MATERIAL AND METHODS

2.1. Study Area

Fish and sediment samples were collected from Izmir and Candarli Bays located in the Eastern Aegean coast (Figure 1). Izmir Bay is one of the great natural bays of the Mediterranean. Izmir is an important industrial and commercial centre and cultural focal point. The Gediz River, which flows into the Outer Bay, is the second biggest river along the Eastern Aegean and densely populated and includes extensive agricultural lands and numerous industrial areas [3].

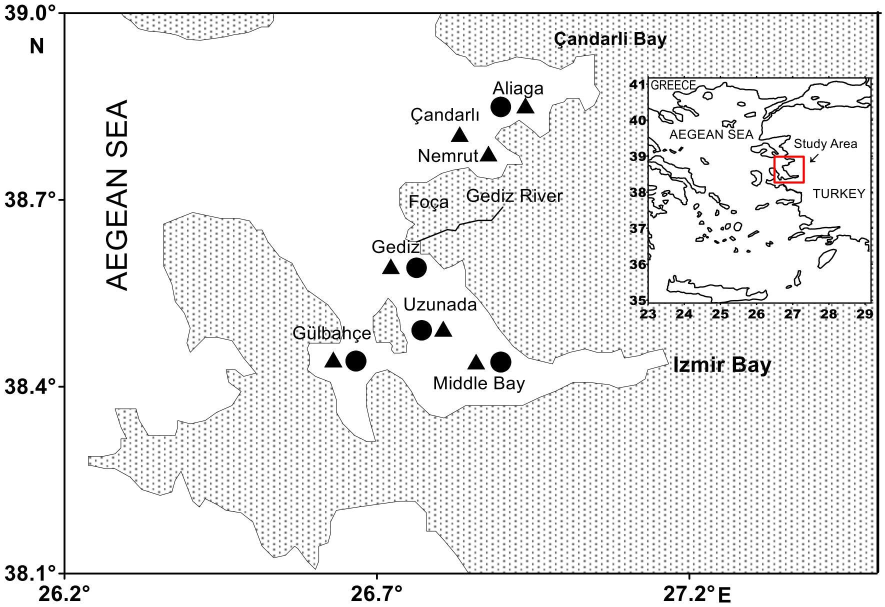

Figure 1. Biota (●) and sediment (▲) sampling sites in Izmir and Candarli Bays

Candarli Bay is a semi-enclosed bay in the Eastern Aegean. Great industry settlements located in the coastal area of Candarli, have been discharging their wastes into Bakircay River or Candarli Bay after limited treatment. Aliaga town located in the southern part of Candarli Bay, has been subjected to extensive industrial developments and is a ship dismantling area [6].

2.2. Sample Collection

Surface sediments with three replicates were collected from the seven sampling sites (Gediz, Uzunada, Gulbahce, Middle Bay, Candarli, Aliaga, Nemrut) in 2014 using a box corer sampler, wrapped in aluminum foil and stored at -20ºC for subsequent analysis in order to avoid degradation. The samples were freeze-dried, hand-sieved through 250 µm for grain size correction and homogenized, then kept until chemical analysis.

Fish *(Mullus barbatus)* were collected by trawling from five sites in Izmir (Gediz, Uzunada, Gulbahce, Middle Bay) and Candarli Bays during cruises of R.V. *K.Piri Reis* in 2014. Immediately, 25-30 organisms were dissected on the research vessel from each sites and preserved at -20º. Muscle tissues were pooled and freeze-dried and then homogenized.

2.3 Analytical Procedure

10 g of each sediment sample were extracted in microwave extraction system by adding a mixture of hexane/dichloromethane and internal standards. After pre-concentration for the extracts sulfur was removed using activated elemental copper. For fractionation, sediment samples were transferred into florosil column [7]. Quantitative analysis was performed with Agilent5975C GC/MS (DB-5MS column: 30m×0.25mm×0.25µm). To analyze OCs, GC/MS was programmed initially 70°C (2min held), then increase to 150°C with a velocity of 25°C min^{-1} then increase to 200°C with a velocity of 3°C min^{-1} and up to 280°C with a velocity of 8°C min^{-1} held for 10 min.

Three subsamples of each sample (approximately 5 gr of dried fish) were extracted with a microwave digestion system using mixture of 30ml hexane/acetone. For recovery of the method, internal standards (PCB29, PCB198, endosulfan Id4, ε-HCH) were added. The extract was then concentrated to about 10 ml and then the extract was dried with sodium sulfate and concentrated with nitrogen down to 1 ml. To avoid the lipid interfere during GC analysis sulfuric acid was used for saponification. Florisil column was used for fractionation of OCs for 3 groups using different solvents [7].

The quality of the analytical data is assured using the reference materials of IAEA-451 and IAEA-417 for the biota and sediment samples (from IAEA, Monaco), respectively.

3. RESULTS AND DISCUSSION

3.1. Organochlorine Levels in Sediment

The concentration of OCPs, cyclodienes, DDTs, Aroclors and the selected ratios of chlorinated pesticides in sediments from Izmir and Candarli Bays were presented in Table 1.

Table 1. Total concentration of OCPs, cyclodienes, DDTs, Aroclors and the selected ratios of chlorinated pesticides in sediments from Izmir and Candarli Bays (as dry weight:dry wt)

Compounds/Locations	Gediz	Uzunada	Gulbahce	Middle Bay	Aliaga	Nemrut	Candarli
ΣOCPs (ng g^{-1})	1.48	3.62	1.71	1.88	6.52	29.6	3.51
ΣDDTs (ng g^{-1})	0.29	0.88	0.16	0.46	0.96	19.2	0.58
ΣCyclodienes[1] (ng g^{-1})	1.16	2.69	1.51	1.24	4.96	8.93	2.71
ΣAroclors[2] (ng g^{-1})	8.61	11.9	14.7	12.4	97.0	562	16.8
DDD/DDE	0.27	0.31	0.17	0.29	0.45	0.196	1.89
(DDE+DDD)/ΣDDT	0.96	0.97	0.90	0.96	0.98	0.97	0.95
DDT/DDE	0.050	0.045	0.13	0.059	0.032	0.033	0.15
%DDT/ΣDDTs	3.78	3.30	9.68	4.35	2.19	2.66	4.84

[2]ΣAroclors: Aroclor1254+Aroclor1260, [1]Σcyclodienes: heptachlor + aldrin + dieldrin + endrin

Concentrations of OCPs (sum of DDTs, HCB, lindane, heptachlor, aldrin, dieldrin, endrin) in surface sediments ranged from 1.48-29.6 ngg^{-1} with an average value of 6.91 ngg^{-1}. The highest value was found at Nemrut site in Candarli Bay, while the lowest value of OCPs occurred at the Gediz site located in the outer part of Izmir Bay. The mean concentrations of OCPs were as following: 2.54 for *p,p'*-DDE, 1.88 for dieldrin, 0.58 for *p,p'*-DDD, 0.62 for endrin, 0.55 for heptachlor, 0.32 for HCB, 0.26 for aldrin, 0.091 *p,p'*-DDT and 0.063 ngg^{-1} (dry wt) for lindane. ∑Cyclodiens were the predominant contaminants in all sediment samples with the exception of Nemrut site and ΣDDTs was higher than ∑Cyclodiens in this area (Table1).

Aroclors in sediments showed in noticeably higher concentrations than OCPs at both of Candarli and Izmir Bays. Aroclors are used as industrial chemicals and their probable source is industrial waste. Aroclor 1254 levels in sediments ranged from 3.35 at Gediz site to 215 at Nemrut site and Aroclor 1260 concentrations from 1.4 at Middle Bay to 347 ngg^{-1} at Nemrut site.

p,p`*-DDT is degraded to *p,p`-DDE under aerobic and to *p,p`*-DDD under anaerobic conditions. Thus, higher or lower ratios of (*p,p`*-DDE+*p,p`*-DDD)/ΣDDTs (sum of *p,p'*-DDT and its metabolites) indicated past or recent usage of technical DDT, respectively and the *p,p'*-DDD/*p,p`*-DDE ratios of these two metabolites provide the basic biodegradable condition of the intended environmental compartments [8].

According to results appeared in Table 1, ratios of (DDE+DDD)/ΣDDT were in the range of 0.90-0.98 with entire values being >0.5. This infers that the degraded metabolites formed a significant proportion of total DDT compounds. The relatively slow degradation rate of DDT in the environment indicates early DDT influxes and by implication, non-existing DDT use throughout the region. Moreover, whole values of DDD/DDE ratio in Izmir Bay ranged between 0.17-0.31 and were lower than unity, indicating that the sediments was dominated by *p,p'*-DDE, the product of aerobic degradation of *p,p'*-DDT. This result showed that the sediments collected from Izmir Bay were mainly under oxic conditions (Table 1).

Table 2. Assessments of potential biological risks of selected OCPs in the surface sediments of Izmir and Candarli Bays using two sediment quality guidelines (SQG)

Chemical	Range (ngg^{-1})	ER-L[1]	Above ER-L (%)[5]	ER-M[2]	Above ER-M (%)[5]	TEL[3]	Above TEL (%)[5]	PEL[4]	Above PEL (%)[5]
p,p'-DDT	0.011-0.51	1.0	0	7	0	1.19	0	4.77	0
p,p'-DDE	0.12-15.6	2.2	14	27	0	2.07	14	374	0
p,p'-DDD	0.02-3.05	2.0	14	20	0	1.22	14	7.81	0
DDTs	0.16-19.2	1.58	14	46.1	0	3.89	14	51.7	0
Dieldrin	0.07-5.92	NA	-	NA	-	0.71	57	4.3	14
γ-HCH	0.01-0.17	NA	-	NA	-	0.32	0	0.99	0
Heptachlor	0.22-0.89	0.5	43	6	0	2.26	0	4.79	0
PCBs[6]	8.57-562	22.7	29	180	14	21.5	29	189	14

[1] Effect range-low value,[2] Effect range-median value,[3] Threshold effect level,[4] Probable effect level,[5] Percentage of samples above the corresponding levels, [6] Sum of Aroclor1254 and Aroclor1260. NA: Not available

As shown in Table 2, two widely used sediment quality guidelines, i.e. the effects range-low value (ERL) and effects range-median value (ERM) guidelines [9], [10], as well as the threshold effects level (TEL) and probable effects level (PEL) guidelines [11] were applied to evaluate the possible ecotoxicological risks of OCs in the study area. For *pp'*-DDE and *pp'*-DDD were higher than ERL values at one site (Nemrut site). Meanwhile, these compounds also exceeded the TEL value at the same site, but were significantly lower than the PEL and ERM values. The level of heptachlor was over the ERL value at 3 sites located in Nemrut, Gulbahce and Middle Bay, whereas it was still below the ERM, TEL and PEL values. This suggested that the levels of *p,p'*-DDE, *p,p'*-DDD and heptachlor at most sites other than Nemrut, Gulbahce, Middle Bay sites were lower than the values that may cause adverse biological risk. For DDTs, although it was not above the ERM and PEL values, 14% of total sites (Nemrut) in the study area were higher than ERL and TEL values appearing that the exposure of DDTs may cause ecological risk on the neighboring benthic organisms.

Total PCBs concentrations of the samples exceeded the ERL (ERL, 22.7 ngg^{-1} dry wt) value at Aliaga (97.1 ngg^{-1}) and Nemrut regions (562 ngg^{-1}) which suggests that PCBs can exert toxic biological effects on aquatic organisms. On the other hand, these concentrations exceeded the ERM (ERM, 180 ngg^{-1} dry wt), PEL (PEL, 189 ngg^{-1} dry wt) values just only in Nemrut site. That means, based on Canadian quality guidelines, PCB concentrations at this region can cause adverse effects on aquatic biota.

3.2. Organochlorine Levels in Fish

Tables 3 shows the concentrations of organochlorines (ng g^{-1} dry wt) and selected ratios in fish samples collected from five sites in Izmir and Candarli Bays. The maximum concentration of ΣOCPs (29.5 ngg^{-1}) was found in samples collected from Gulbahce site while the minimum concentration of ΣOCPs (5.31 ngg^{-1}) was observed in samples collected from Middle Bay of Izmir. In all samples *p,p'*-DDE was the predominant DDT congener. Highest ΣDDTs levels occurred at Gulbahce region with 7.74 ngg^{-1}, while the lowest concentration was observed at Aliaga region with value of 0.93 ngg^{-1} (Table 3).

∑Cyclodiens were the predominant contaminants in all fish samples, representing 53-89% of total OCPs. The concentrations of Σcyclodienes in the fish samples ranged between 3.84–20.7 ngg^{-1}. The mean cocentration of cyclodienes in the five sampling sites in this study was 12.6 ngg^{-1}. The highest levels of γHCH and HCB were found in Uzunada site.

Aroclor1254 concentrations ranged from 15.9 at Middle Bay to 44 ngg^{-1} at Aliaga site. Aroclor1260 concentration ranged between 14.5 at Gediz and 95.4 ngg^{-1} at Aliaga. The mean concentrations of Aroclor1254 and Aroclor1260 were 30.4 and 34.9 ngg^{-1}, respectively. The highest concentration of Aroclors (140 ngg^{-1}) was found in samples from Aliaga, while the lowest concentration of Aroclors (35.1 ngg^{-1}) was found in fish samples collected from the Middle Bay (Table 3).

In general, a ratio of (DDE+DDD)/ΣDDTs is more than 0.5 shows long-term biodegradation of DDT to DDE and DDD whereas a ratio of less than 0.5 may indicate recent input of DDT. The ratios of (DDE+DDD)/ΣDDTs were 0.73 to 0.88 in fish in this study (Table 3). These results indicated aged DDT pollution and showed that there has been no recent input of technical DDT from the agricultural regions into the sampling regions. Ratios of DDD/DDE in fish less than 1 mean that *p,p'*DDT had been biotransformed to DDE under aerobic conditions in the all sampling sites.

Table 3. Total concentrations of DDTs, cyclodiens, Aroclors and the ratios of DDT concentrations in fish

Compounds/ Locations	Gediz	Uzunada	Gulbahce	Middle Bay	Aliaga
ΣDDTs (ng g^{-1})	1.93	6.05	7.74	1.18	0.93
∑Cyclodiens[1] (ng g^{-1})	13.43	19.85	20.7	3.84	4.96
ΣAroclors (ng g^{-1})	35.7	67	49.3	35.1	139.6
DDD/DDE	0.81	0.45	0.18	0.20	0.84
(DDE+DDD)/ΣDDT	0.77	0.88	0.74	0.81	0.73
DDT/ΣDDTs %	23.3	12.2	26.2	19.5	26.9
DDE/ΣDDTs %	42.5	60.5	62.5	66.9	39.8
DDD/ΣDDTs %	34.2	27.3	11.2	13.6	33.3

[1]Σcyclodienes: heptachlor + aldrin + dieldrin + endrin

According to this study, health risk assessment was performed for Aroclor1254 and DDTs due to consumed fish. Annual seafood consumption in Turkey is estimated to be about 25 kg per year [12]. Therefore, the daily dietary exposure estimation by an adult person was calculated on basis of an average 68.5 g of fresh fish muscle consumption per day in Izmir, Turkey [13].

Table 4. Estimated daily intakes of DDTs, Aroclor 1254 and OCs in the fish by human (average body wt. 70 kg) in Izmir and Candarli Bays (ng/kg body weight/day)

	Gediz	*Uzunada*	*Gulbahce*	*Middle Bay*	*Aliaga*	*ADI/TDI*
∑DDTs	*0.53*	*1.66*	*2.12*	*0.32*	*0.25*	*20,000*[a]
Aroclor1254	*5.8*	*10.4*	*9.0*	*4.4*	*12.1*	*20*[b]
∑OCs	*14.3*	*26.0*	*21.6*	*11.1*	*40.1*	-

[a]FAO/WHO (1996b)
[b]IPCS (2000)

Estimated Daily Intakes (EDI) of DDTs by the people were far below the acceptable daily intake (ADI) suggested by the FAO/WHO [14] proposing this intake would not pose adverse effect to inhabitants of Izmir at the present. The EDI of Aroclor1254 by the people was below the tolerable daily intake (TDI) for of 20 ng/kg body weight per day, proposed by IPCS [15] suggesting this intake might not pose a health risk in Izmir and Candarli today (Table 4).

4. CONCLUSIONS

Organochlorines were measured in the sediment and fish samples from Izmir and Candarli Bays. *p,p'*-DDE was the predominant DDT congener. ΣCyclodiens were generally predominant contaminants. Aroclors were found in noticeably higher levels than OCPs in sediments and fish. The highest levels of Aroclors, OCPs were found in sediments of Nemrut which can be attributed to industrial activities. According to SQG, DDTs were lower than the values that may cause adverse biological risk in sediment samples. Aroclor 1254 in sediments only exceeded the TEL value at Nemrut region. The maximum levels of ΣOCPs were found in fish collected from Gulbahce, while Aroclors were measured in Aliaga. According to selected ratios indicated no recent influxes of DDT in the sampling areas. The estimated daily intake of DDTs, Aroclor1254 in fish were below the acceptable daily intake level recommended by FAO/WHO.

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An Anatolian City on History-Future Pendulum; Kutahya-Eskigediz (Turkey) Historical City

Nurhan KOCAN[1], Omer Lutfu CORBACI[2]*

Abstract

Historical cities are placement including livability, identity and original values that have occurred as a result of cultural factors in harmony with nature from past to present. Historical cities expressed in time for visual and semantic features that including meaning in terms of living traditional cultural history and place. Because of these characteristics of such areas must be protected. Using protection is a valid approach in terms of sustainability. Uncovering of the importance of historical cities and ensuring the efficient use of these cities should be created to forefront of the tourism value of these cities, to include in the tour itinerary and/or to attract urban visitors and visitors to the city by highlighting the special factors of these places. In this study Kutahya-Eskigediz historical urban structure were investigated in terms of the quality of the natural and cultural landscapes. Concepts were developed within the protected areas for urban use strategies in the study. These strategies include proposed urban land use decisions, new functions, the maintenance, repair and urban design guidelines within the concept. The suggestions were presented in the form of the landscaping projects in the study. Autocad 2016, Photoshop CS5, Sketchup and Lumion software were used as well as hand drawings and sketches for creation of the landscape project. Recommendations and three-dimensional images have been presented in the form of plans. The projects produced results of the study can be an example for other historical cities of a similar nature.

Keywords: *Historical city, historical city protection, landscape planning, landscape design, Kutahya-Eskigediz City.*

1. INTRODUCTION

Cultural landscapes constitute parts of our common identity as mirror of the social development, creativity and spiritual richness of human beings. These areas connect the past with the present with their historical, artistic, documentary, functional etc. values so they need to be protected [1].

The physical qualities of the historical urban texture and the interactions of historical elements with each other should be evaluated with a holistic view. Restoration of cultural landscapes with sustainable uses and adaptation they to current living conditions will ensure preservation and continuity for future generations.

Eskigediz historical urban area is an important example for working because it has many examples of immovable cultural heritage, natural landscape and alternative tourism possibilities. In this context, the natural and cultural values of the study area has great importance in terms of the decisions on the preservation and use of historical urban areas for tourism purposes through sustainable usage principles and the presentation of the qualities of the historical urban area.

Traditional residential texture is the material culture document that enables continuity of society with its traditional character; constitute the memory of the place; connect the society's subjects to each other and to the geography where they live. The various dangerous such as changing social structure of the settlement, economic hardships, natural disasters as well as the lack of care in the traditional settlements and migration can negatively affect the development of traditional settlements [2].

[1*] [1]*Bartın University, Faculty of Forestry Department of Landscape Architecture Bartin/Turkey*. Email:nurhankocan@mynet.com
[2] *Recep Tayyip Erdoğan University Faculy of Fine Arts Department of Landscape Architecture Rize/Turkey*.
Email: omerlutfucorbaci@hotmail.com

1.1. Cultural Heritage and Historical City Protection

Historical cities and original constructions are very important in terms of our cultural heritage. The preservation and revitalization of these areas to meet requirements of contemporary life condition is accepted as conservation idea [2].

The urban places created by each society in the different phases constitute the cultural structure of that society. These qualities are characterized as old for the next stages and they have become historical because they are part of the cultural evolution of mankind.

A concept of conservation based on the understanding of the continuity of history which brought new interpretations by introducing new contents to the concept of contemporary developments is based on the necessity of preserving the historical structure as a whole. Also developing the protection approaches based on the constant change of the physical environment [3].

The best way in urban conservation is active use of these areas and change in the urban environment [4]. Understanding the threats that cultural beings face and carry their values and importance to future can only be achieved by sustainability. The protected traditional urban texture provides social and cultural integration with cultural and touristic attraction. The cultural assets of the area make it a touristic center [4].

The conservation studies that began with restoration of monuments in the past but they have developed in the present to the preservation of historical textures and cities. The conservation and renovation work is included in conservation studies of the horticulture, street and urban building elements which complement the historical buildings. The purpose of preserving and renewing of the historical structure is to ensure historical and cultural continuity, to revitalize the historical landscape in the direction of contemporary living conditions, to maintain its identity, to evaluate historical structures with current functions, to establish urban landscape and traditional settlement model [1].

1.2 Sustainability and Tourism Relations

In line with the differentiation of human needs and the development of technology and demands historical sites have changed and they are undergoing changes. This causes the disappearance of the cultural characteristics of the elements belonging to the locality. Within the changing urban dynamics, the natural and cultural landscaping elements of the city and the settlement texture must be re-evaluated and examined. The investigation of physical place, usage relations, user requirements and expectations will enable the planning and design of these places according to today's conditions [2].

People living in the intense and difficult living conditions of the cities prefer tourism movements towards natural and cultural areas and want to get away from these negative conditions for a while. Natural, cultural and historical areas have attracted people in recent years highly. However, the increasing interest in these areas makes it necessary for the preservation and renewal of qualities of these areas.

Historical environment; it has a special importance and feature because it is a part of the circumstance which is formed in the historical perspective and which will continue its formation [1].

It is necessary to protect and develop the natural and cultural values for the continuity of tourism activities which are important contributions to the economic, social and cultural values of our country. The natural and cultural environment constitutes the basis of tourism. Therefore the protection of the environment is of great importance for a sustainable tourism. The development of tourism based on environmental protection will bring an economic, social, physical and socially improved environment. Tourism can be a vehicle for supporting the preservation of traditional architectural characters in important natural and cultural areas. The environmental quality and value of the area rises, the infrastructure can be improved and the environmental consciousness can be formed in the local area thanks to the tourism [5]. The people participate in alternative tourism to get information about natural, cultural and traditional life, to gain experiences and to spend their vacation in alternative areas [6].

2. MATERIAL-METHOD

The main material of this work is the Eskigediz town of Kutahya Province. Preliminary research about the topic has been used as auxiliary material in the study for literature on the subject. The urban area boundary of the study area was drawn through the Google Earth image and the historical city settlement was shown via the Eskigediz zoning plan. Eskigediz city has been chosen as a study area due to its natural, cultural and historical values for tourism. The continuity of cultural values for tourism future in Eskigediz is very important. In this context in order to enable the development of tourism solutions for protection-utilization balance have been proposed in the study. Evaluation and suggestions were made under the titles of residential gardens, the surroundings of historical buildings, the streets, the preservation of natural resource values, conservation and plant regeneration.

3. FINDINGS

3.3.1. General Characteristics of the Study Area and the Surrounding Area

Eskigediz is a town center connected to Gediz District center in Kutahya Province in inner western Anatolia part of Aegean Region. Eskigediz is 7 km away from the north-east of Gediz district center. Eskigediz is 91 km away from Kutahya city center and 63 km away from Usak. It is surrounded by Hisarcik, Emet, Cavdarhisar in the north, Aslanapa, Altintas in the east, Usak in the south, Manisa in the southwest, Saphane in the west and Simav in the northwest. Mount Murat is in the east and Mount Saphane is in the west [8].

Figure 1. The location of the city in the country and city border

Gediz District was founded by the Phrygians in BC. After the battle of Malazgirt in 1071 Gediz met the Turks for the first time. Between the years (1075-1086) it joined to Turks and in 1233 it joined to the Anatolian Seljuks lands. He joined the Ottoman lands after 1428 and became the center in 1871 [7].

Since its foundation Gediz has faced frequent natural disasters due to its location and ground features. The floods that erupted in 1875, 1901, 1911 and 1945 caused significant damage. The especially the floods of 1875 caused the destruction of the tannery area and so lather craft settled down. The city survived great fires in 1911, 1918 [9].

Eskigediz survived major earthquakes in 1886, 1896, 1944, 1956 and 1970. Gediz has moved with the decision of the Council of Ministers No. 7/1164 on 05.08.1970 because it’s tectonic structure which causes the catastrophic events such as landslides and earthquake disaster. The residential area is 7 km distance to Eskigediz on the Simav highway. While Eskigediz was a neighborhood within the boundaries of Gediz Municipality in 1970-1988 it became a center of the province on 07.12.1988 [10].

The population of Gediz district center was determined as 5772 people in the first census of 1927. There are 10651 people in the 1970 census. After the 1970 earthquake there were 1452 people in 1975 census. 7307 people live in the Eskigediz according to the census conducted in 2000 [11].

Eskigediz was built in a valley where Gediz Creek partially collapsed. The topography around the town has a rugged structure. Because settlement area is located in a narrow valley so it cannot be enlarged in the horizontal direction. Horizontal expansion in the houses is only towards to the entry and exit points of the north and south of the valley. The placement on the risky area about earthquake prevented the vertical growth of dwellings [9]. Gediz River which in the south direction of Eskigediz collects the waters from Murat and Saphane Mountains, is important with a water collection area of 17500 km^2 [11].

Murat Mountain extends in the north-south direction in east of the district. Murat Dagi (2312 m) which is open to mountain tourism is covered with pine forests and ostriches. Murat Dagi has a very rich plant species, is attracting attention with this aspect the tourist especially in the spring and summer seasons with herbal and cold spring waters. Mount Saphane (Ulugedik Summit 2120m) is located to the west of Eskigediz [10].

Eskigediz was built on an undulating plateau with an average elevation of 1100-1200 meters. Mountains rising from the deep valleys opened by the rivers reach 2300 meters. The plains stuck between the mountains stretch along the river valleys in narrow strips [10].

The urban is influenced by the continental climate of inner western Anatolia. The average annual temperature value in the region is determined as 12.9 °C. The summers are usually set. The annual precipitation average is 565 mm. Rainfalls are generally seen in winter and the summer is droughty [11].

The widespread plant species are palm tree (*Quercus aegipolis*). Plants such as plane trees, cranberries, wild plants, roses, blackberries, walnuts, willow, poplar, spruce are spreading in area. (*Pinus nigra*) forests are spreading in there. The plants that adapt to the drought are on the southern slopes which are not very high. There are red pine trees (*Pinus brutia*) in this group. Herbaceous plant species are spread in pasture areas around the vineyards in the region. There are *Cistus laurifolius*, *Astragalus* sp., *Verbascum* sp., *Polypodium vulgare*, *Poterium spinosum*.

Due to its geological structure Gediz was founded on an area where fault lines are widespread. As a consequence of this situation hot waters in the region are much in the area. The Murat Mountain Thermal Spring is 30 km from the east of the Gediz District. The area is the center of tourism located on 1600 m where hot and cold water. The Ilica Hot Springs is 13 km far from the sea and 940 m high from the sea. It is a thermal tourism center established at the height. The thermal springs in 40-85 degrees have an important potential in terms of plateau as well as climate cures. The thermal springs are preferred due to the presence of forests and hot-cold waters around the springs in summer and winter. There are constructions for accommodation. There is no transportation problem on the roads connecting the area to the district and its surroundings [12].

Eskigediz's economic activity is composed of sectors such as trade, social services, construction, industry and agriculture. Due to the rugged nature of the Eskigediz agricultural activities are provided in a small part. Eskigediz is a town center that has not reached the desired development in economic terms. The economic struggle is pushing the townspeople migration [11].

The square kebabs made from the meat of animals thyme-fed in the mountainous region of Eskigediz and Gediz stew has a good reputation in the environment. The Gediz tarhana and Gediz hosmerim sweet are the other important food cultures that reflect cultural values.

3.3.2. The Historical Urban Texture of the Study Area

The character of a cultural landscape is defined both by physical forms such as roads, buildings, walls and vegetation as well as by forms of use that reflect cultural values and traditions [13].

The characteristics of the region are defined by elements such as traditional regional texture, streets, neighborhoods, open spaces, private home gardens, roads and structures that create important region character. Cultural landscape is a geographically can be limited and it gains value over time through the interrelationships between culture and the natural environment and identified by its natural, cultural, visual and semantic qualities [14].

Eskigediz is located in a valley extending in the north-east / south-west direction. The modern buildings in the town are seen in the areas of Sabirgazi and Camikebir in the north and south directions of the area. Park, Kurtulus, Hisar, Ismetpasa and Camikebir streets in Eskigadiz are important for the two-storey wooden carcass houses reflecting the Ottoman architectural style. The town is a rugged place. The streets are formed in a narrow structure [11].

The commercial activities are concentrated in the Kurtulus neighborhood. The modern industrial establishments such as socks factory, tire factory etc. are in the Camikebir district of Eskigediz. The marble factory is located in the Park district, the oil factory in Sabirgazi district. Within the borders of Park and Ismetpasa districts there are workshop type industrial establishments [11].

The city which attracted attention with its historical city texture became a member of the Union of Historic Towns in 2001. Eskigediz was included in the scope of urban, natural and archaeological site with its extraordinary identity. The Asarardi District where ancient Kadoi city remains is preserved as second and third degree archaeological site. 111

buildings were selected as examples of urban sites and architecture. In addition 10 fountains, 11 mosques, 4 bridges, 3 laundry facilities, 1 waterway, 1 aqueduct, 1 water depot and military buildings were protected under the same scope.

The Kursunlu Mosque built in 1540 in Eskigediz and the Ulu Mosque (Gazanfer Aga Mosque) built in 1553 are the oldest buildings in the city. The original states of the constructions were distorted in the earthquake of 1970 [10].

Figure 2. An old view from the city

Figure 3. A view from the city in now

The wooden houses located in the historical texture are the houses that best reflect the Ottoman architecture. The houses are usually two layers and made of stone base walls and upper floors are made by wood. The upper floor consists of sitting units and the lower floors consist of rooms, haystacks and stables. On the second floor there are lounges, rooms, kitchen and bay window. At the back of the house there is a courtyard. You can get out and watch the street from the side windows. The size of the house is the indication of the socio-economic status of the host. The historical buildings in the district are mostly covered with tiles also houses include windows with cages and bay window. The streets in the city have some cobblestone pavement which is traditional stone pavement in some streets while in some streets this feature is broken and the roads are covered with asphalt. The roofs of the houses are square-quadrangular folded roofs in Turkish architecture and roofing material is alaturka tile. The stone, soil and wood materials that are easy to find in the natural surroundings have been selected for construction of the houses.

The gardenless buildings provide direct street or street access to the building. The facade of houses is located in the street direction. The ground floor of the courtyard is covered with stone or compacted soil. The walls are made of stone or mud brick. Because of the small size of the residential gardens there are plants with vegetable horticulture, fruit trees and pine trees that have not been treated with excessive trees and trees.

The streets are of human scale and are curvy and featured to pass through staircases in places. The pavilions of the structures, the stone walls, the courtyards, the entrance gates and the bay windows constitute the vertical limit of the street. Because the roads are very narrow and have an organic structure and there are no pavement and road afforestation. The green places on the historical site are not enough. The small squares in the intersection of hilly and rocky areas, public areas, residential gardens and streets form open green areas.

The narrow roads between city centers and historical districts cause problems for vehicle and pedestrian circulation system because they are open to traffic. There is a parking problem in the city, vehicles parked on the side of the road so cause image pollution and traffic accidents.

The lack of restoration has led to the establishment of low-income families with low socio-economic, cultural and income levels. The new users of some traditional historical houses have damaged the original appearance of the structures and the originality of the building-structure.

4. CONCLUSIONS AND RECOMMENDATIONS

Despite the destruction of disasters such as fire, flood and earthquake in many times in the history of Eskigediz, it attracts attention with its fascinating historical urban texture, natural structure, hot springs and different cultural features. Today, Eskigediz is waiting for tourists as one of the outstanding historical cities of our country with its characteristic feature, its historical architectural texture as stopover place for tourism.

The area has different alternative opportunities for weekend and day trips and congress tourism thanks to its location and close proximity to many cities. The presence of services such as thermal spas makes the area attractive.

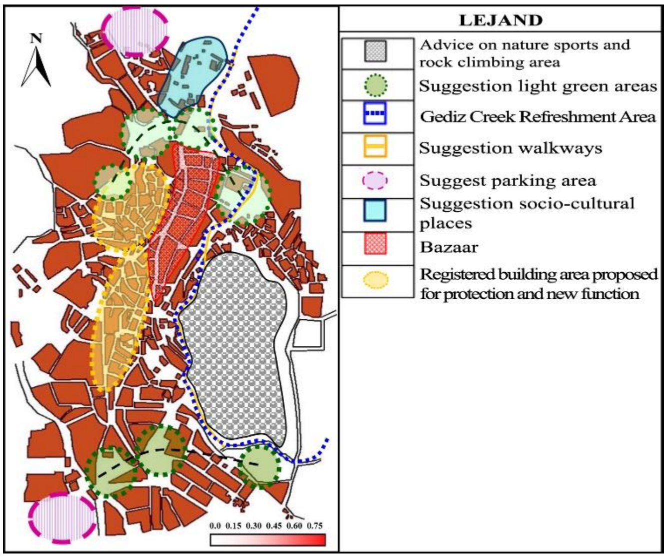

Figure 4. The map of proposal land use

The green spaces around the historical towns and structures should also be considered together in their conservation and development plans. The green spaces, parks, urban afforestation, children's playgrounds are needed to meet the physical and visual needs of the inhabitants and tourists in the region. In this context, gardens of historical houses, openings in the surroundings of structures should be taken into consideration. The materials, accessories and plant material of the active green areas should be in accordance with the original-natural structure and plants of the city. The development of forests and wooded areas around the city is important in terms of appreciation of the city together. The attractive natural visibility of the roadside can be achieved with the green belt system.

The maintenance of existing plants such as drug-pruning should be done and the plants that disturb the urban silhouette should be arranged and redesigned. The pruning of large trees that prevent the perception of housing patterns and overflowing public spaces must be met by the municipality.

The arrangement of some the buildings that have not lost their originality can be used as a museum. It will be an example for preservation. The creation of the creation of areas such as pedestrian areas, local sales products, living and recreation areas, walking paths, culture-information houses, exhibition areas and etc. where cultural activities will stimulate social life will make the historical city tourism center where will be more experienced. The new business opportunities and economic benefits will be provided to the public with tourism. The cafeteria, restaurant, tea garden, sightseeing, recreation, entertainment and needs oriented business are inadequate in the area. The rocky hill where the earthquake monument is located carries the view terrain feature dominated by the settlement. There should be resting places suitable for small and local architecture where visitors can spend more time for relax and they watch the city.

In the historical city, the use of vehicles and parking problems brought about by today's living conditions should be solved and parking lots should be designed in the access road. The routes should be considered in the form of traffic on a narrow road and certain service hours should be set for commercial use.

The suitable routes and paths for hiking and nature walk should be determined and wooden walkways should be provided for all seasons in the city. In the historical areas a standard should be introduced especially all kinds of objects such as canopy, tent etc. that can be seen in photographing.

The prevention should be taken from commercial workplaces to remove complex image because they scatter much of their products to image in the environment. The edge of the creek that passes through the settlement should be cleaned and rehabilitated by considering as a natural area.

The conservation should not only be physical protection but protection as well as socio-cultural structure. The city needs to organize and care for the infrastructure and physical environment when it is considered both for the living and for the sight. The sale of local products which local people can benefit from tourism should be provided.

The co-operation of universities, municipalities and non-governmental organizations with joint decisions will gain speed and the success of application of the protection measures will be provided for the area and the development of tourism. The counseling, guidance staff training and public education centers and tourism bureau should be established. In conservation and renewal studies protection should be taken to cover the entire city as well as areas such as streets, houses and gardens. These structures play a decisive role on the city identity.

For the integration of the research area into contemporary, economic and social life, it will be a good solution to convert traditional houses into different living spaces and acquire new functions. Eskigediz historical city has the potential of tourism with the potential of ecotourism as a source of cultural values, archaeological and historical places, structures, settlement texture, handicrafts and local culinary features. Providing the traditional Turkish experience and continuity of the characteristic features of the city will define the city as a more interesting place.

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Experimental study using reactive distillation column for biodiesel production

Suleyman KARACAN [1*]

Abstract

In this experimental studies, a reactive packed distillation column was used for production of fatty acid methyl ester (FAME) . The FAME considered as biodiesel was produced from transesterification reaction between sunflower oil and methanol by using packed heterogenous basic CaO catalyst. Steady-state and dynamic studies were investigated in the system. The effect alcohol-oil ratio on the system was investigated. Experiments have shown that the RD process can produce biodiesel at a production of %90 (%m/m) continuously with an alcohol-oil ratio of 6:1.

Keywords: *Reactive Distillation, Biodiesel, CaO*

1. INTRODUCTION

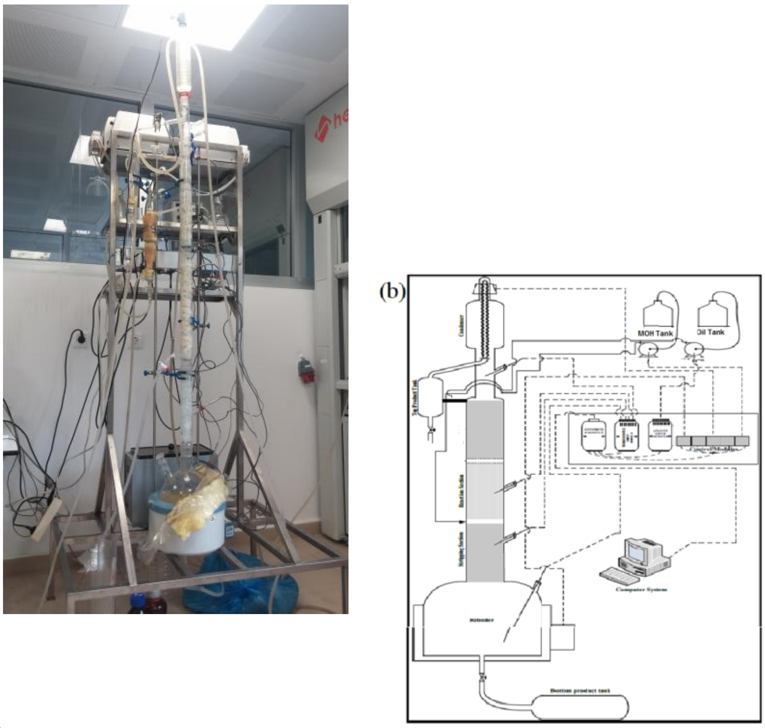
Biodiesel, as an alternative fuel, has many merits. It is derived from a renewable, domestic resource, thereby relieving reliance on petroleum fuel imports. It is biodegradable and non-toxic. Compared to petroleum-based diesel, biodiesel has a more favourable combustion emission profile, such as low emissions of carbon monoxide, particulate matter and unburned hydrocarbons. Carbon dioxide produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing). the impact of biodiesel combustion on the greenhouse effect [1-2].Base catalysts include homogeneous base catalysts and heterogeneous base catalysts . The commonly used homogeneous catalysts are NaOH, KOH and their alkoxides. Homogeneous alkali-catalyzed transesterification is much faster than acid-catalyzed transesterification [4]. However, a large amount of water is required to transfer the catalysts from the organic phase to a water phase after the reaction. Therefore, it is considerably more costly to separate the catalyst from the produced solution [3–4]. Heterogeneous base catalysts have many advantages: they are noncorrosive, environmentally benign and present fewer disposal problems. Meanwhile, they are much more easily separated from the liquid products and can be designed to give higher activity, selectivity and longer catalyst lifetimes [5]. Many researchers have studied calcium oxide (CaO) as a strong candidate for the heterogeneous catalyst, due to the commercial availability, the economical advantage and the relatively higher activity [6–7]. Heterogeneous catalytic transesterification reactions required higher methanol-to-oil molar ratio to forward the reaction toward product side which leads to increase the production cost of biodiesel. In order to reduce the methanol-to-oil ratio, an ideal system for continuous production of biodiesel is the application of reactive distillation (RD) technique. In the reactive distillation (RD) system, the excess/ unreacted methanol was completely vaporized by the reboiler and the vapors were recirculated in the RD column and utilized in the reactive zone. Hence, the methanol-to-oil ratio is reduced significantly [8]. Transesterification of palm oil with methanol in the presence of potassium hydroxide as homogeneous catalyst in reactive distillation (RD) column was studied by Prasertsit, Mueanmas, and Tongurai 2013. A maximum methyl ester conversion of 92.27% was reported under the optimal conditions of reboiler temperature at 90°C, methanol- to-oil ratio at 4.5:1 and KOH at 1 wt%. Agarwal et al. [9] studied continuous transesterification of karanja oil in the reactive distillation (RD) system and helical tube system using KOH as homogeneous catalyst. Therefore, a heterogeneous catalyst operated RD system is needed to check the feasibility of continuous production of biodiesel.
Niju et al.[10] investigated continuous flow transesterification of waste frying oil (WFO) with methanol for the biodiesel production in a laboratory scale jacketed reactive distillation (RD) unit packed with clam shell based CaO as solid catalyst. The effects of operating parameters on methyl ester conversion were investigated and discussed. In this work, the RD system packed with CaO was studied for the biodiesel production

[1*] *Correspounding aurtor: Ankara University, Engineering Faculty, Department of Chemical Engineering, Tandogan 06100, Ankara, TURKEY, E-mail:*karacan@)eng.ankara.edu.tr

to develop a continuous heterogeneous catalyzed process. The effects of operating parameters on methyl ester conversion were investigated and discussed.

2. MATERIAL AND METHOD

Sunflower oil and methanol were used as a feedstock for the biodiesel production. heterogenous basic CaO catalyst was used for the biodiesel production. Sunflower oil was supplied from an oil production plant. Methanol and CaO were purchased from Sigma–Aldrich. The process involved in this work was a transesterification reaction occurring simultaneously with distillation operation that were carried out in the reactive packed distillation column set up as shown pictorially in Figure 1a and schematically in Figure 1b. The column, excluding the condenser and the reboiler, had a height of 1.5 m and a diameter of 0.05 m. It consisted of a cylindrical condenser with a diameter and a height of 5 and 22.5 cm respectively. The main column section of the plant was divided into two subsections. The upper and lower sections sections were the reaction and the stripping sections respectively. The stripping section was packed with raschig rings while the reaction section was filled with small lumps ~3-20 mm of CaO solid. The reboiler was spherical in shape with a volume of 3 Liter. The column was fed with sunflower oil and Methanol at the top. All the signal inputs (reflux ratio (R), feed ratio (F) and reboiler duty (Q)) to the column and the measured outputs (top segment temperature (Ttop), reaction segment temperature (Trxn) and bottom segment temperature (Tbot)) from the column were sent and recorded respectively on-line with the aid of MATLAB/Simulink computer program and electronic input-output (I/O) modules that were connected to the equipment and the computer system. This block diagram was shown in Figure 2.



(a)

*Figure 1 Reactive packed distillation column: **.(a)**) Pictorial view; (b) Sketch view*

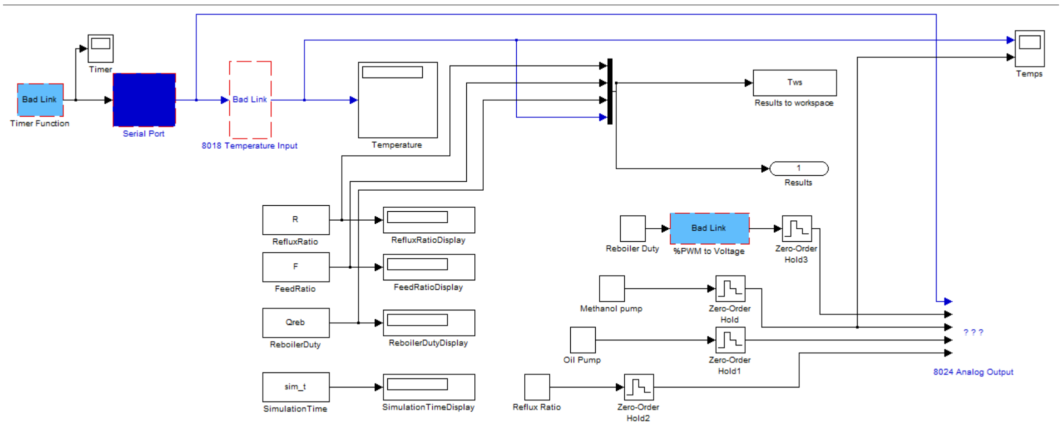


Figure 2 Block diagram in which experimental data are received and recorded

2.1.Transesterification Reaction

Transesterification of vegetable oils with alcohol is the best method for biodiesel production. There are two transesterification methods, which are: (a) with catalyst and (b) without catalyst. The utilization of different types of catalysts improves the rate and yield of biodiesel. The transesterification reaction is reversible and excess alcohol shifts the equilibrium to the product side [11-12]. Fig. 1 shows the general equation of transesterification reaction.

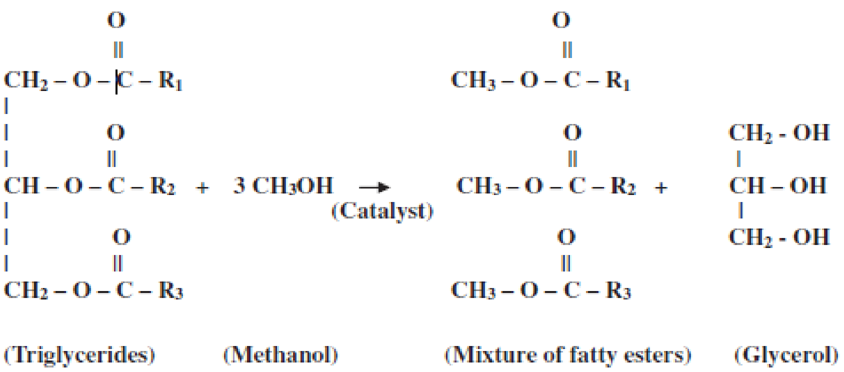
$$\underset{\text{Triglyceride}}{RCOOR^1} + \underset{\text{Alcohol}}{R^2OH} \xleftrightarrow{\text{Catalyst}} \underset{\text{Alkyl Ester}}{RCOOR^2} + \underset{\text{Glycerol}}{R^1OH}$$

Figure 3 General transesterification reaction equation.

Many different alcohols can be used in this reaction, including, methanol, ethanol, propanol, and butanol. The methanol application is more feasible because of its low-cost and physical as well as chemical advantages, such as being polar and having the shortest alcohol chain [11]. According to Figure 4, R1, R2, and R3 are long chains of hydrocarbons and carbon atoms called fatty acid chains. The reaction is based on one mole of triglyceride reacting with three moles of methanol to produce three moles methyl ester (biodiesel) and one mole glycerol.

Generally the transesterification reaction involves some critical parameters which significantly influence the final conversion and yield. The most important variables are: reaction temperature, free fatty acid content in the oil, water content in the oil, type of catalyst, amount of catalyst, reaction time, molar ratio of alcohol to oil, type or chemical stream of alcohol, use of co-solvent and mixing intensity.

The esterification reaction occurring in the column was an equilibrium type given as:



(1)

Figure 4. Methanolysis of triglyceride.

3. RESULTS AND DISCUSSION

Steady-state and dynamic studies were carried out in the system. The effect alcohol-oil ratio on the system was investigated. The reactant flow rate is one of the most important parameters in continuous flow RD system. At very low feed flowrates, liquid film formed on the catalyst surface enhanced the mass transfer resistance and lowered the methyl ester conversion. However, an increase in the feed flowrate reduces the mass transfer limitation and results in higher methyl ester conversion. Experimental studies was carried out in a reactive distillation column given in Figure 1. In order to see the effects of the feed flow rate ratio on the system, dynamic experimental studies were carried out by keeping the oil flow rate constant and positively affecting the methanol flow rate. In the steady state condition, the reboiler heat duty, Q value is 490 W, feed flow rates of methanol and oil were 4 ml/min at a 6:1 molar ratio of methanol to oil and reflux ratio was selected as 3. The reboiler temperature, the stripping zone temperature and the reaction zone temperatures were measured in the system. In order to bring the system into a dynamic state, firstly the flow rate of Methanol was increased from 4 ml / min to 5 ml/min for 600 second at a 8:1 molar ratio of methanol to oil. Later, the flow rate of Methanol was increased from 5 ml / min to 6 ml / min for 600 second and than increased from 6 ml / min to 7 ml/min for 760 second at a 10:1 molar ratio of methanol to oil. The experimental data obtained were given in Figures 5-7. As seen in the Figures, the positive effects on methanol flow rate were increased in the temperatures of the reactive distillation column

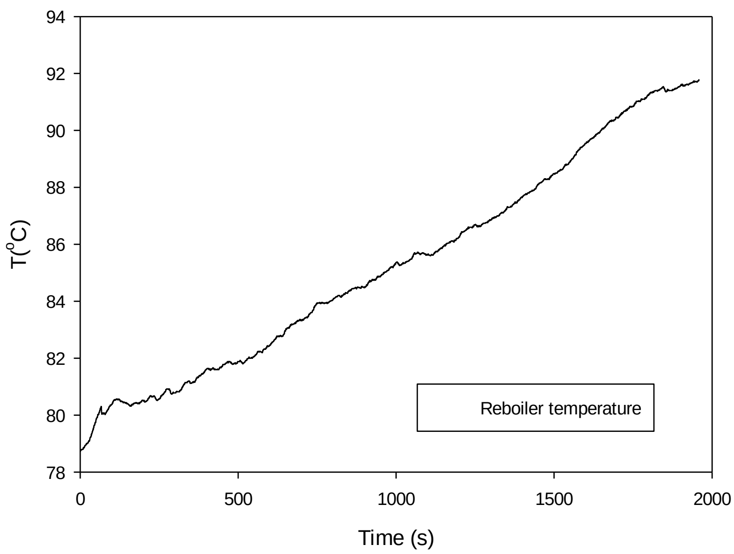


Figure 5 Effect of the flow rate of methanol on the reboiler temperature.

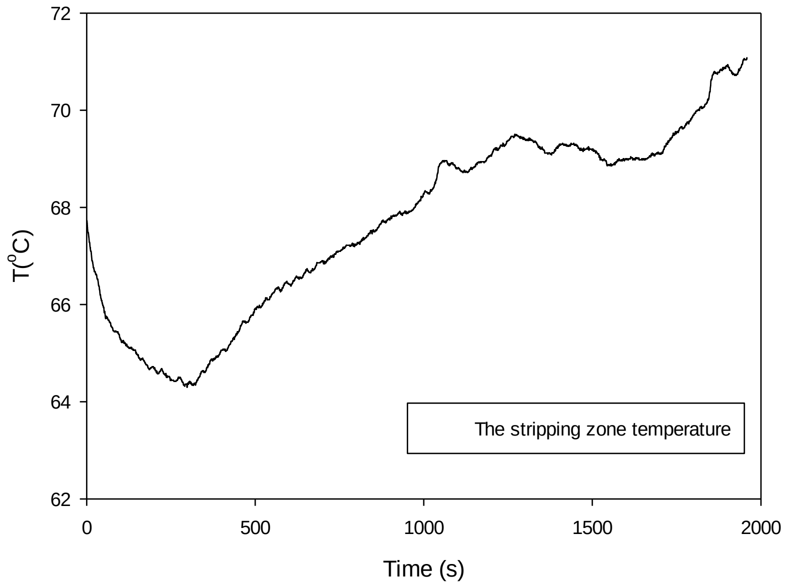


Figure 6 Effect of the flow rate of methanol on the stripping zone temperature

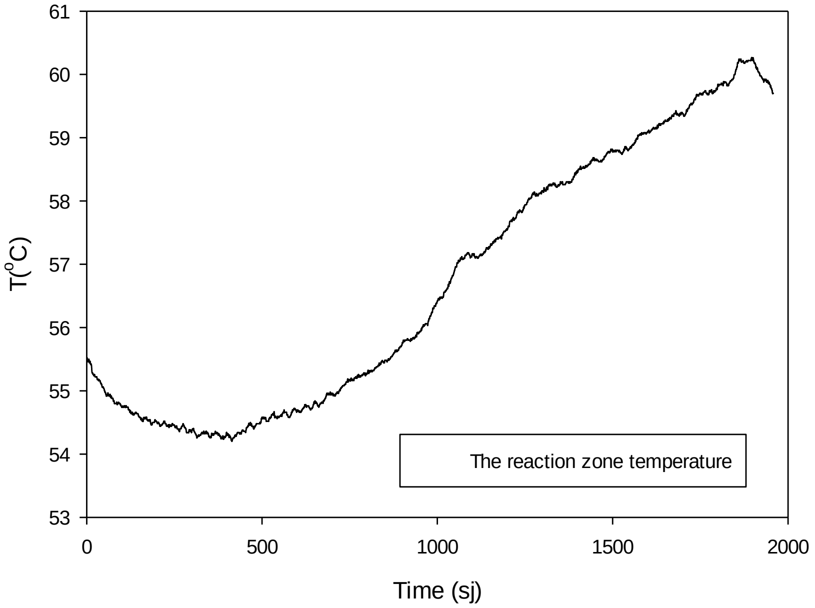


Figure 7 Effect of the flow rate of methanol on the reaction zone temperature

The biodiesel yield could be improved by introducing excess amounts of methanol to shift the equilibrium to

the right-hand side. The experimental results, illustrated in Figure 8, indicate the feed flow ratio of methanol to oil has a significant impact on the biodiesel yield. The biodiesel yields grew as the molar ratio increased, and the yield was 78.96 % at a 6:1 molar ratio of methanol to oil when analytical reagent methanol was used.

In comparison, the biodiesel yield increased from 74% to 93% when the molar ratio was increased from 4:1 to 10:1. However, the yields were slightly reduced when the ratio of methanol to oil was higher than 12:1, and the biodiesel yield was only 88% at 14:1. The reason is that the catalyst content decreased with increase of methanol content. Therefore, the optimum molar ratio of methanol to oil was 10:1.

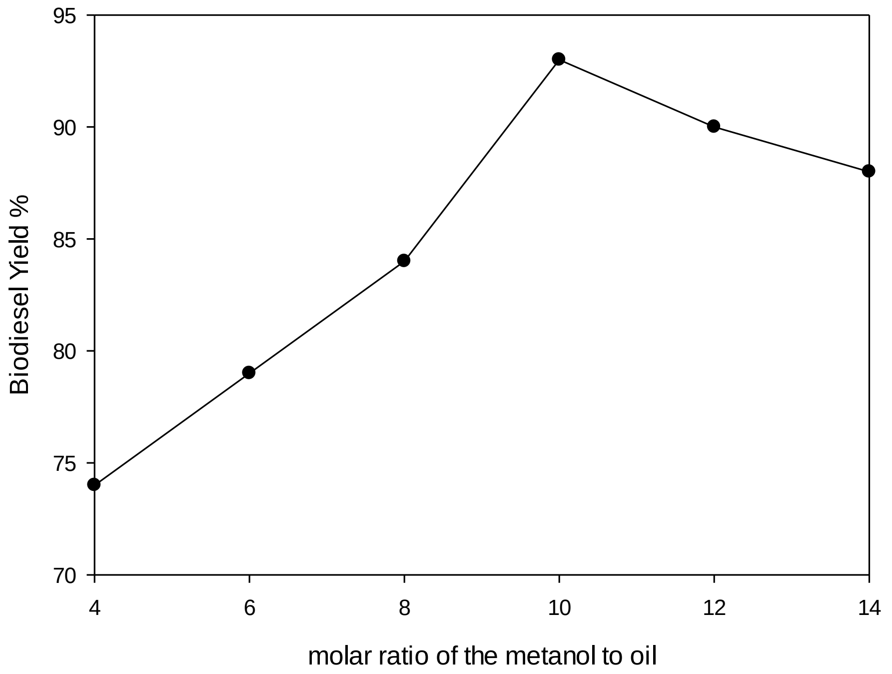


Figure 8 Effect of molar ratio of methanol to oil on biodiesel yield

4. CONCLUSIONS

In the present study, I developed Reactive Distillation system for the continuous production of biodiesel.

by using packed heterogenous basic CaO catalyst was successfully tested as a solid catalyst for transesterification of sunflower oil into biodiesel in the continuous process. A maximum methyl ester conversion of 93% was obtained at a reactant flow rate of 0.4 mL/min, methanol/oil ratio of 10:1 and the reboiler heat duty, 490 W. These results suggest that the RD system packed with CaO is a promising method for the continuous biodiesel production.

ACKNOWLEDGMENT

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Calorific Properties of Flowering Plants

Suryakant CHAKRADHARI[1*], Khageshwar Singh Patel[2]

Abstract

The aroma and coloring chemical compounds inherently present in the flowering plants are thrown in large scale as waste after the harvesting. In view of sustainable waste energy management, the combustion characteristics of 40 flowering plants grown in central India are described. The values of bulk density, moisture content, calorific value and ash residue of the flowering plants (n=40) was ranging from 560 – 1300 kg m-3, 1.6 – 4.8%, 4450 – 9500 kcal kg-1 and 3.7 – 17.6% with mean value (p = 0.05) of 953±56 kg m-3, 3.3±0.3%, 6657±352 kcal kg-1 and 11.4±1.3%, respectively are presented. The cluster analysis is used for grouping of the energetic plants.

Keywords: *Gross calorific value, proximate parameter, flowering plant*

1. INTRODUCTION

Flowering plants (angiosperms) are largest genera including > 250000 species, comprise 90% of the Plant Kingdom. They are seed-bearing vascular plants almost every habitat from forests to grasslands. Most flowers grow on receptacles, which are enlarged parts of the plant's stem. They usually have five sets of parts i.e. whorls, corolla, stamens, pistils and seeds. In addition, they survive in the various climatic stresses i.e. drought, cold, salt and low nutrient availability [1]. The calorific value of trees, agricultural and animal wastes was reported [2]-[13]. However, no data for fuel property of flowering plants which having high mass productions were reported in the literatures. In this work, gross calorific value and proximate parameters (i.e. bulk density, moisture content and ash residue) of 40 flowering plants are described for their uses as energetic biomass to meet urgent energy demand in the developing country.

2. MATERIAL AND METHODS

2.1. Study area and sampling

The name and family of plants selected for the proposed work is shown in Table 1. The flowering plants of Raipur city, central India (21° 15′ 0″ N, 81° 37′ 48″ E) were selected randomly. The composite sampling of the matured plant parts i.e. stem, leaf and flower was carried out during winter period i.e. February, 2016. The various plant parts (i.e. flower, leaf, stem and root) of the most energetic biomass: Sweet sultan was collected separately. The samples were stored in the cleaned plastic bag with drying in air by sun light for 2 days. They were grinded in the powder form by sieving out particles of size < 0.25 mm. The prepared sample was stored in the cleaned 100-ml glass conical flask and dried at 50 ^{o}C for one day in an oven.

2.2. Analysis of proximate parameters and calorific value

The compactness of the biomass affects remarkably the heat value and handling cost. The bulk density (BD) of the biomass was determined by dividing the mass with the volume of the capsule. The moisture content of the samples were analyzed by heating at 105 ± 2 °C for a period of 60 min [14]. The ash content of the materials was determined by heating the sample at 800˚C for 5 hr in a platinum crucible [15]-[16]. The ash extract was prepared by equilibrating 5 g of sample with 25 ml of deionized water in ultrasonic bath for 6 hr. The clear extract was decanted out for the pH measurement.

[1]Corresponding author: School of Studies in Environmental Science, Pt. Ravishankar Shukla University. Raipur, 492010, CG, India. suryachakradhari99@gmail.com*

[2] School of Studies in Chemistry, Pt. Ravishankar Shukla University Raipur, 492010, CG, India. patelkhageshwarsingh@gmail.com

The gross calorific value (GCV) was determined experimentally using a Digital Microprocessor Based Bomb Calorimeter UTS 1.34, Advance Research Instruments Co., New Delhi as described in the literature. A weighed wood sample was placed in the combustion capsule. The oxygen gas was flowed into the combustion cylinder. The power was then switched on to start the auto temperature adjustment and the stirring motor. The initial temperature was recorded after equilibrium attained i.e. after 5 min. The bomb content was then fired by using the ignition switch. The bucket temperature i.e. final temperature was recorded after stabilization. The difference between the original length and the new length was multiplied by 0.335 to obtain the number of calories liberated by combustion of the fuse. For every sample, gross calorific value in kcal kg-1 was calculated using the following equation [17].

$$GCV = [\{We.\ \Delta T\}-\{W_1(4.18) + (W_2(0.335)\}]/M$$

lorific value of species, water equivalent, weight of sample, weight of cotton thread, weight of fuse wire and rise in temperature, respectively.

2.3. TG-DGA Spectra

The content of volatile compounds, moisture, cellulose, lignin and residue of the biomass was analyzed by using a Metller Thermogravimetric Analyzer- TG-DGA-2 by heating at rate of 20ºC/min. The fixed carbon (FC) fraction was calculated by using following equation [18].

FC % = {W- (VC+AR)} 100/W

Where, W, VC and AR represent the initial content of the biomass, volatile organic compounds and ash residue, respectively.

2.4. Cluster analysis

The IBM SPSS Statistics 23 was used for the statistical and cluster analysis in the present work (IBM SPSS 2015) [19].

3. RESULTS AND DISCUSSION

The proximate parameters of the flowering plants are presented in Table 1. The physical and chemical properties of biomass affect the processing efficiency as well as logistical delivery and overall energy production cost. The whole process of thermal utilization of solid biofuels (i.e. fuel supply, combustion system, solid and gaseous emissions) is influenced by their nature, physical characteristics (e.g. particle size, bulk density, moisture content, calorific value) and chemical composition [20].

Table 1. Botanical characteristic, proximate parameters and calorific value of plants

S. No.	Local name	Botanical name	Family	Type	BD, kg m-3	MC, %	GCV, kcal kg-1	AR, %	pH of AR
1	Sweet sultan	Amberboamoschata	Asteraceae	Herb	1260	1.6	9500	8.4	13.5
2	Daisy	Bellisperennis L	Asteraceae	Herb	950	3	6850	14.8	13.2
3	Pot marigold	Calendula officinalis L	Asteraceae	Herb	1000	3.2	6350	15.2	12.5
4	Corn flower	Centaureacyanus	Asteraceae	Herb	1080	2.2	7930	11.2	12.3
5	Sevanti	Chrysanthemum sp.	Asteraceae	Herb	570	3.8	5630	16.5	13.5
6	Coloured cosmos	Cosmos bipinnatus	Asteraceae	Herb	830	3.4	6810	13.7	13.8
7	Yellow cosmos	Cosmos sulphureus	Asteraceae	Herb	1160	2.1	7940	13	13.5
8	Dahlia	D. variabilis	Asteraceae	Herb	900	2.4	6000	15	12.6
9	Indian blanket	Gaillardia pulchella	Asteraceae	Herb	800	3.8	5160	17.5	12.6
10	Sunflower	Helianthus annus	Asteraceae	Herb	740	4.8	5430	17.5	12.9
11	Beach sunflower	Helianthus debilis	Asteraceae	Herb	660	3.4	5340	7.9	14.4
12	Chandanigenda	Tagetespatula	Asteraceae	Herb	1000	3.4	6980	11.5	14.3
13	Genda	Tageteserecta	Asteraceae	Herb	890	3.2	5910	8.2	14.3

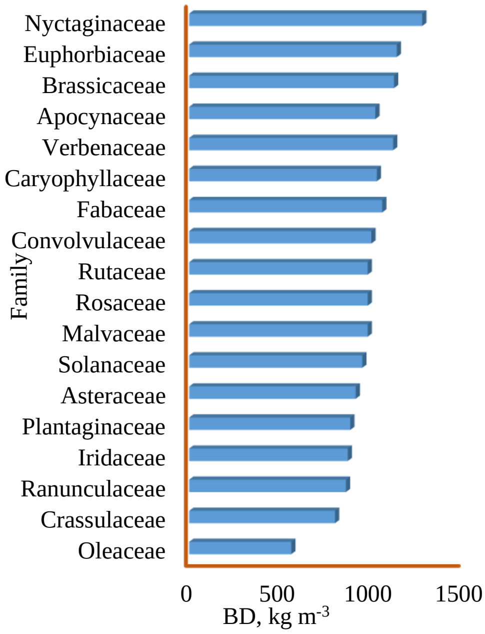
14	Tithonia	T. rotundifolia	Asteraceae	Herb	750	3.2	5630	17.6	13.7
15	Straw flower	Xerochrysumbracteatum	Asteraceae	Herb	1120	2.2	7830	11	13.3
16	Sadabahar	Catharanthusroseus	Apocynaceae	Herb	1200	2.6	7730	9.4	13.4
17	Mudra	Calotropis gigantean	Apocynaceae	Herb	890	4.1	6960	11	13.2
18	Yellow kaner	Cascabelathevetia	Apocynaceae	Shrub	870	4.2	6100	6.9	14.1
19	Chandani	Tabernaemontanadivaricata	Apocynaceae	Herb	1150	3.8	7470	11.8	13
20	Kaner	Nerium oleander	Apocynaceae	Shrub	1000	2.2	7890	6.9	13.2
21	Piliya	Tecomastans	Bigoniaceae	Shrub	1300	2.4	8320	5.6	13.3
22	Candytuft	Iberisamara L.	Brassicaceae	Herb	950	4.7	6270	8.2	13.9
23	Gudhal	Hibiscus rosasinensis	Malvaceae	Shrub	1120	3.8	7590	4.2	13.6
24	Hollyhock	Althea rosea	Malvaceae	Herb	840	2.6	6380	12.6	13.3
25	Poppy	Papaversomniferum	Papaveraceae	Herb	750	3.1	5740	15.1	14.3
26	Garden phlox	P. drummondii	Polemoniaceae	Herb	860	3.2	5460	14.7	13.3
27	Snap dragon	Antirrhinum majus L	Plantaginaceae	Herb	850	3.9	4930	15.2	13.7
28	Besharam	Ipomoea carnea	Convolvulaceae	Shrub	1000	3.6	6900	8.2	12.7
29	Flaming katy	Kalanchoeblossfeldiana	Crassulaceae	Herb	800	4.8	5030	17.6	11.4
30	Carnation	Dianthus caryophyllus	Caryophyllaceae	Herb	1030	2.6	7030	12.3	13.9
31	Crown thorns	Euphorbia milli	Euphorbiaceae	Herb	1140	4.1	6780	15.4	12.9
32	Red powder puff	Calliandrahaematocephala	Fabaceae	Herb	1060	2.6	8090	3.7	12.3
33	Sword lily	Gladiolus grandiflorus	Iridaceae	Herb	870	3.6	6220	7.1	12.8
34	Booganbel	Bougainvillea glabra	Nyctaginaceae	Shrub	1280	2.8	8660	8.6	13.3
35	Mogra	Jasminumsambac	Oleaceae	Herb	560	4.8	4450	16.4	13.4
36	Larkspur	Delphinium ajacis L	Ranunculaceae	Herb	860	4.4	5940	13.2	13.6
37	Rose	Rosa rubiginosa	Rosaceae	Herb	980	4	6150	9	14
38	Madhukamini	Murrayapaniulata	Rutaceae	Shrub	980	2.6	7520	4.4	14.2
39	Petunia	Petunia interifolia	Solanaceae	Herb	950	2.9	6190	14	13.6
40	Raimuniya	Lantana camara	Verbenaceae	Herb	1120	3.8	7170	4	14.2

3.1. Bulk density

The bulk density (BD) is an important parameter of harvested plant for the subsequent processing. It is related to the transport cost and energy production of biomass. The BD value of the plants (n=40) was ranged from 560 – 1300 kg m-3 with mean value ($p = 0.05$) of 953±56 kg m-3. The highest BD of plant of Nyctaginaceae family was observed, may be due to presence of higher combustible organics i.e. cellulose and lignin materials as shown in Fig. 1(a).

3.2. Moisture content

The moisture content (MC) in biomass presents as bulk and physically or chemically bound water. Low moisture content results in improved density and durability of the fuel [21]. Most compaction techniques require a small amount of moisture to "soften" the biomass for compaction. The MC value (i.e. physically and chemically bound water) of 40 plants was ranged from 1.6 – 4.8% with mean value (p=0.05) of 3.3±0.3%. The lowest MC for plants of three families i.e. Caryophyllaceae, Fabaceae and Rutaceae was recorded as shown in Fig. 1(b).



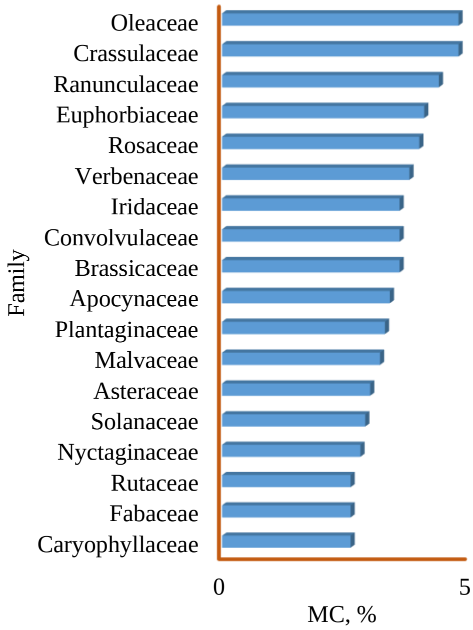


Fig. 1 (a). Bulk density (BD) of plants belonging to 17 family (b). Moisture content (MC) of plants belonging to 17 family

3.3. Calorific value

The most important fuel property of biomass is calorific or heat value [22]. The gross calorific value (GCV) was used to compute the competitiveness of a processed fuel in a given market situation. It represents the absolute value of the specific energy of combustion, in calorie, for unit mass of a biofuel burned in presence of oxygen in a calorimetric bomb under the conditions specified. The GCV of 40 dried plants was ranged from 4450 – 9500 kcal kg-1 with mean value (p = 0.05) of 6657±352 kcal kg^{-1}. Remarkably higher GCV for plants of family i.e. Fabaceae and Nyctaginaceae was marked as shown in Fig. 2(a). Among them, the highest GCV for Sweet sultan (Amberboamoschata) was recorded, may be due to presence of higher combustible carbons, Fig. 2(b). The GCV for various plant parts of Sweet sultan is shown in Fig. 3. The energy of different parts of Sweet sultan was found in following decreasing order: flower > leaf > stem < root, may be due to storage of energetic materials through foliage rather than root.

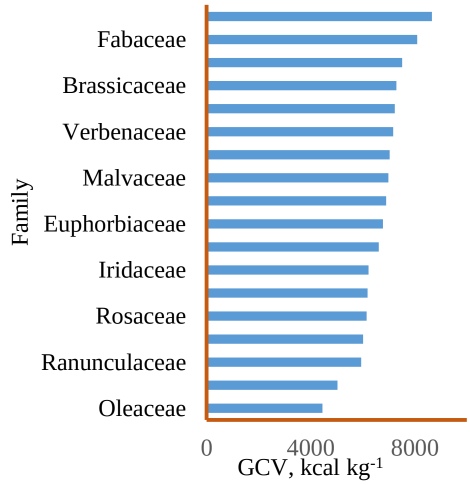


Fig. 2(a). Gross calorific value (GCV) of plants belonging to 17 family

Fig. 2(b). Image of Sweet sultan plant

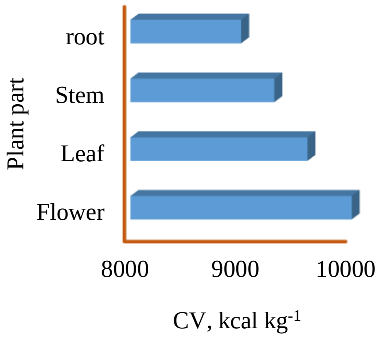


Fig.3. Energy variation of Sweet sultan's plant part

3.4. Ash residue

The fraction obtained from chemical break down of biomass by thermal process is known as ash residue. Inorganic constituents, such as organically bound cations, inorganic salts and minerals make up the ash present in or on the surface of biomass [23]. The ash content of biomass affects both handling and energy conversion cost. The value of ash residue of the plants (n=40) was found to be ranged from 3.7 – 17.6% with mean value ($p = 0.05$) of 11.4±1.3%. The lowest AR value of plants belonging to family i.e.Fabaceae, Verbenaceae and Rutaceae was recorded as shown in Fig. 4. The AR extract was found to be alkaline in nature, pH value ranged from 11.4 – 14.4 with mean pH value ($p = 0.05$) of 13.4±0.2. The ashes are usually composed of oxides and salts of Na, K, Mg, Ca, Al, Si, P, S, Cl and Fe [24]. These minerals present with the biomass at high temperature can agglomerate and deposit inside the thermal device leading to slag formation and fouling.

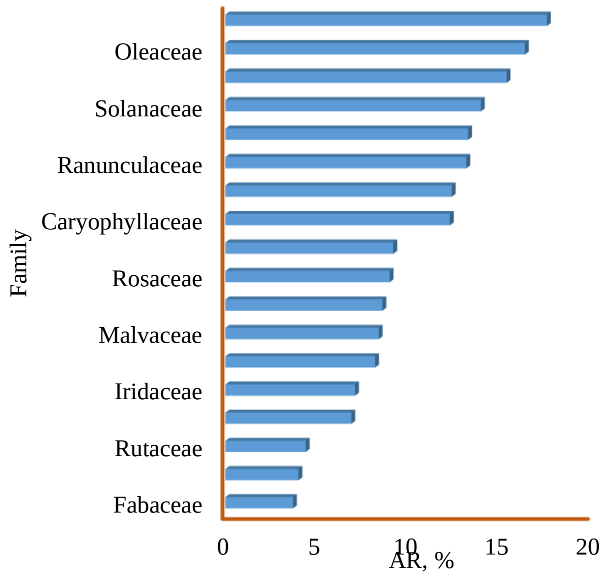
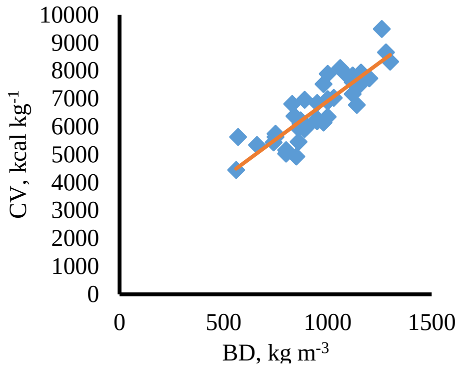


Fig.4. Ash residue (AR) of plants belonging to 17 family

3.5. Correlation of proximate parameters

The correlation analysis of gross caloric value (GCV) with proximate parameters is of tremendous importance for proper selection of biomass for specific purpose due to dependence of heat value on moisture content and chemical composition of biomass. The bulk density (BD) with the GCV had a fare positive correlation of 0.87 as shown in Fig.5 (a). In turn, the MC and AR with the GCV had fare negative correlation of 0.68 and 0.60, respectively as shown in Fig.5 (b-c).



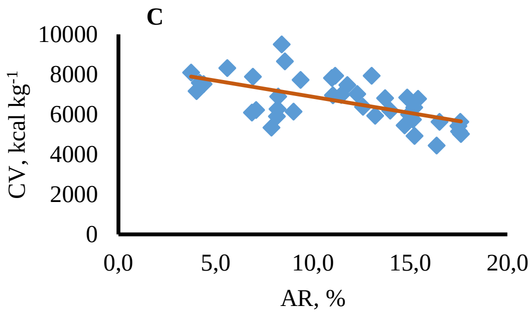
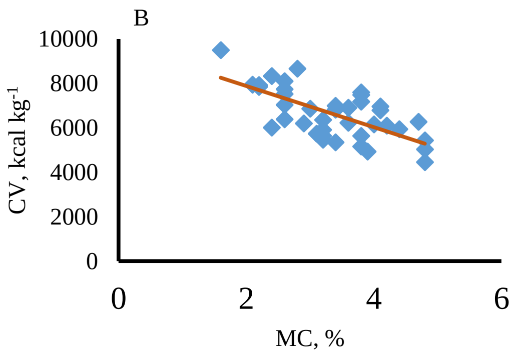


Fig.5 (a-c). Correlation of proximate parameters: (A = BD, B = MC, C = AR) with GCV



3.6. Cluster analysis

The elemental composition (i.e. C, H, N and O) of biomass is varied with respect to genotype of biomass, geographical and climate condition and harvesting methods. Hierarchical cluster analysis was employed to produce a dendrogram, using group-average linkage clustering, Fig. 6(a). The fuel characteristic of 40 plants was classified into two groups when proximate parameters i.e. BD, MC and AR are used as discriminating factors. In the I-group, 28 plants having GCV < 7030 kcal kg-1 was included. In II-group, 12 energetic plants having GCV value >7470 kcal kg-1 was categorized as shown in Fig. 6(b). These twelve energetic plants are herb and shrub of wild nature, commonly found to grow everywhere in India. Among them, four plants are belonged to Asteraceae family.

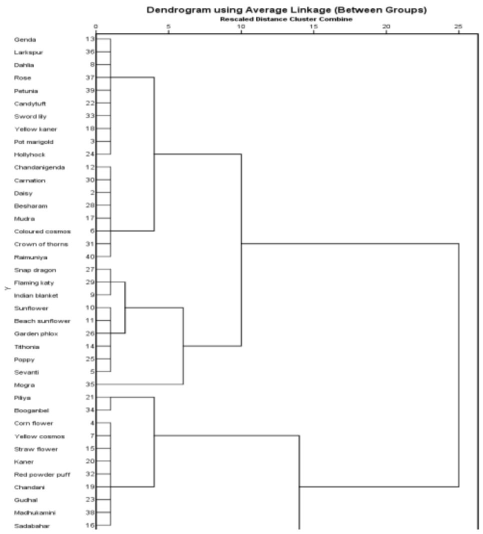


Fig.6 (a) Cluster analysis of energetic flowering plants

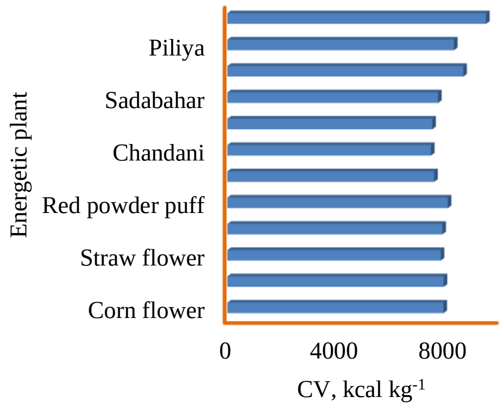


Fig.6 (b). Gross calorific value of energetic plants

3.7. Organics content of biomass

The biomass contains volatile organic compounds, cellulose and lignin materials which evaporate or oxidize at different temperature ranges by leaving fixed carbons. The TG-DGA chromatogram of Sweet sulton (SS) plant is shown in Fig. 7. The pyrolytic decomposition of the SS plant was occurred in six stages over temperature range of 50 – 1000^{o}C. In the first stage, a 7.5% weight loss was seen over temperature range of 50 – 100 ^{o}C, may due to evaporation of light volatile compounds including water. In the second stage, a large weight loss of 42.7% along with endothermic reaction was marked over temperature range of 150 – 400 ^{o}C, may be due to decomposition of hemicellulose materials. Similarly, 16.2, 10.4, 6.7 and 3.3% weight loss in the third, fourth, fifth and sixth stages were observed over temperature range of 400 – 600, 600 – 750, 750 – 850 and 850 – 950 ^{o}C, respectively, may be due to decomposition of cellulose and lignin materials of the SS plant. A residue of 13.1% was found to remain left belonging to fixed carbon and ash residue. The ash residue obtained by the oxidation method was found to be 8.4%. The computed value of fixed carbon was found to be 4.7%. The low fixed carbon content makes biomass tend to prolong cooking time by its low heat release (bake-oven effect) [25]. It also reduced the calorific energy of the briquettes by causing what is called fuel-saving effect. The higher the fixed carbon content the better the charcoal produced because the corresponding calorific energy is usually high [26].

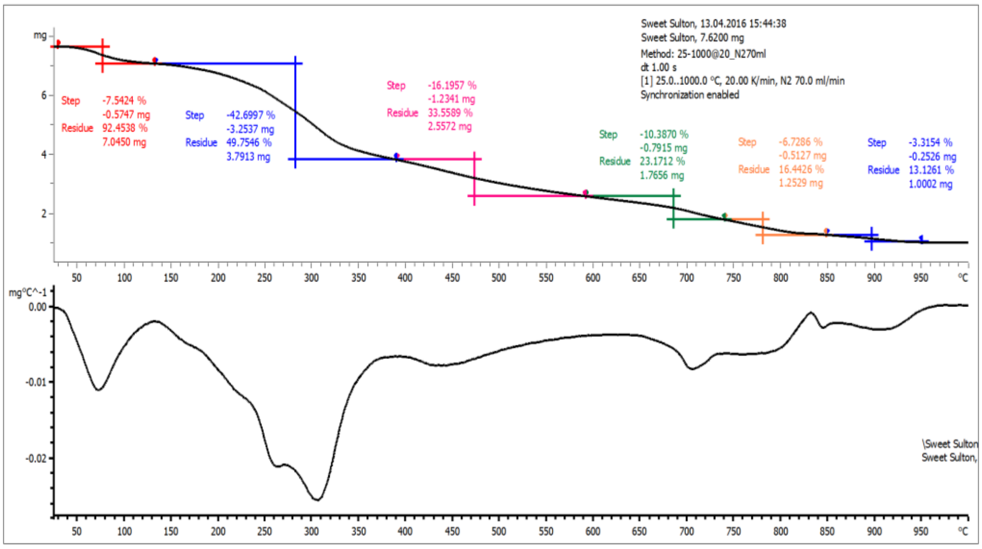


Fig.7. TG-DGA chromatogram of Sweet sulton plant

4. CONCLUSION

The wild plants having higher biomass productivity and climatic stresses adaptability seem to be good energetic biomass. The remarkable high fraction of hemicellulose was observed in the flowering plant. The most of energetic plants belong to economically important family Asteraceae.

ACKNOWLEDGMENTS

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The Effect of Air Pollution on Damages in Historical Buildings, the Case of Gaziantep, Turkey

Tulay KARADAYI YENICE[1*], Dilsat Deniz OLEKLI[2]

Abstract

Conservation of historical buildings and monuments and handing them down to future generations is one of the main issues of architecture. Contrary to popular belief, preserving these constructions for centuries may be difficult under the changing conditions in the world, in spite of the opportunities of the improving technology. Air pollution is one of the greatest protection issues for these structures to be preserved against. The major causes of air pollution may include the use of fossil fuels in transportation and electricity generation, burning of the solid waste, industrial and local use of fuel, and industrial activities. The aim of this research is to determine the impact of air pollution on the deformations at the historical buildings in Gaziantep's historical city center. The traditional monumental and civil architectural works made of stone materials constitute the basic material of the research. In the study, the effects of SOx and NOx, and particulate matters, the most important pollutants originating from the weather conditions and causing deformation at the stones, were evaluated and the harms were determined. As a result of this study, it is identified that the most important effect of air pollution on the stone material is the formation of crust. The crusting not only affects the structure of the stone but also it may cause exfoliation and stratification. Abrasion is another effect of air pollution on the stone. However, it has been seen that the importance of this effect is less than the other factors related to air pollution.

Keywords: *Conservation, restoration, air pollution, Gaziantep*

1. INTRODUCTION

Air pollution can be defined as the amount that will harm the health of living things in a general expression atmosphere and the coexistence of one or more of the pollutants in time. The main sources of air pollution are the use of fossil fuels in the production of transportation and electricity, solid waste incineration, industrial and local fuel use and industrial activities. The most important effect of air pollution on stone material is crust formation. This crust affects the structure of the stone as well as exfoliation and separation into plates. Air pollution on the surface of the stone is cleaned together with the products and rain of the layer rising without scaling. Therefore, air pollution-related crust formation and spillage can often be observed in areas protected from rainwater. Another effect of air pollution on the stone is erosion. However, this effect has less precautionary effects than other factors related to air pollution [1].

It is known that the air pollution that occurs due to human activities in the atmosphere structure of the cities and the high level of SOx (sulfur oxide) and NOx (nitrogen oxides) contained in the atmosphere forms a crust on the surface by reaching to the surface of the rocks in a gaseous form with wind effect in the absence of rain or snow. In this process, the precipitation rate, porosity and humidity of the surface are important factors as well as the climatic characteristics such as precipitation time, wind speed, relative humidity, and brightness of sunlight [2].

The researches indicate that in the last twenty years the deterioration of historic buildings and monumental stones has accelerated to a great extent in a dirty urban atmosphere. The main atmospheric pollutant that affects building materials is primarily SO_2, which is very reactive and corrosive. The main sources of sulfur gases are coal and crude oil [1]. The limestone, marble and travertine of various large-scale calcareous stones react more strongly with SO_2. The main part of the change observed in the structure of the reaction occurring in the field is the reaction that the sulfur dioxide

[1*] *Corresponding author: Hasan Kalyoncu University, Department of Architecture, 27100, Gaziantep, Turkey. tulay.yenice@hku.edu.tr*

[2] *Hasan Kalyoncu University, Department of Architecture, 27100, Gaziantep, Turkey. Dilsat.olekli@hku.edu.tr*

gas causes to form on the surface of the stone. The final product of chemical reactions; the calcium carbonate in the stone structure is the more soluble gypsum. The more soluble nature of the gypsum causes the structures to wear out more easily. Particularly, crust formation and breakup occur more rapidly in the rain water or the open areas of the buildings [1,3]. The degree of SO_2 accumulation on the stone and other building materials, or the degree of absorption and degradation, depends on the natural structure of the pollution density, wind speed, surface moisture and building material. However, it is known that daytime sunshine and temperature increase strengthens this effect [4,5].

The purpose of this research is to determine the effect of air pollution in historic buildings in Gaziantep's historical city center. It is believed that the research will contribute to the work to be done on preserving historical buildings and transferring them to future generations.

2. MATERIAL AND METHOD

Gaziantep is Turkey's sixth and Southeastern Anatolia is the largest city. The city, which has a population of about 2 million, has rich historical and cultural texture as well as industrial character. Gaziantep is one of the oldest settlements in Anatolia and is located at the intersection of Mesopotamia and the Mediterranean Region (Figure 1). The city has hosted many important civilizations in history such as the Ottomans, Seljuks, Byzantines, and Rome and maintained its importance in every period of history. Gaziantep has been added to the list in the gastronomy category of UNESCO's Creative Cities Network in 2015.

Figure 1. Gaziantep Historical City Centre and Khan's District

Besides all these, it can be said that the air quality of the city of Gaziantep is very dirty. This pollution is mainly based on three factors: fuels used in heating, industrial production and emissions from traffic. Nearly all of the current air pollution in the city is due to warming. The use of poor quality coals for heating in residential areas is the most important reason for air pollution. Particularly in the winter months, atmospheric pollutant gases and particulate matter are spreading considerably. Gaziantep has been identified as the fifth dirtiest city in Europe according to the World Health Organization's 2017 report.

The subject of this research is the traditional monumental and civil architectural examples made of stone materials located in the historical city of Gaziantep. In this context, traditional buildings affected by air pollution in the historical city center of Gaziantep are examined. In the study, a method was observed which came from two stages. In the first stage, various types of deterioration examples were found on the ceiling due to air pollution. These deteriorations are often seen as breaks, darkening, crusting. The second stage is to examine the factors that cause deterioration on the samples taken. In this frame, the solutions causing the deterioration are estimated by making solutions with various solutions.

3. RESULTS AND DISCUSSION

The basic construction material of the traditional buildings located in the historical city centre of Gaziantep is basalt and limestone, which are limestone based stones. Researchers, such as Harter [6] and Lipfert [7] do not put attention to the effects of air pollution especially on silica-based stones, however they draw attention to the dangerous effects of air pollution on travertine and limestone, which are limestone-based and extensively used in Gaziantep region. It can be observed that the deterioration of these stones due to air pollution is caused by the dissolution of $CaCO_3$ in their bodies. In particular, the effects of gaseous pollutants such as SO_2 and the effect of acid rain on the stone structure cause dissolution and break-offs in the stone. In various scientific studies, it has been seen that natural stones are separated by a size of up to 4 mm. pieces can break off from the body of natural stones due to air pollution [8]. One of the most important pollutants caused by weather conditions affecting the decay of stones in historical buildings in Gaziantep is SO_2. It can be said that the level SO_2 is very high in Gaziantep (Table 1).

Table 1: Annual and winter season average sulfur dioxide values in Gaziantep (µg/m³)

Annual average sulfur dioxide values (µg/m³)							
2004	2005	2006	2007	2008	2009	2010	2011
51	48	41	25	25	16	19	17
Winter seasons average sulfur dioxide values (µg/m³)							
2004	2005	2006	2007	2008	2009	2010	2011
58	86	68	46	47	23	32	30

*Data compiled from TURKSTAT Air Quality Statistics [12].

When the annual average SO_2 distribution of the last eight years is examined, it is seen that the average of the six years is above the threshold level set by the World Health Organization (Table 2). It can be said this value reached a high level for all years when examined during the winter season (Chart 1, 2).

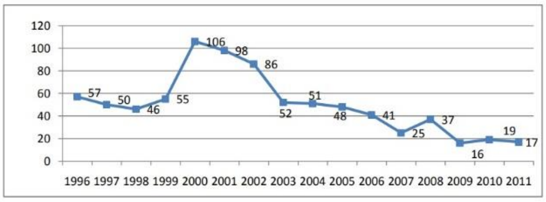

Chart 1. Annual average SO_2 change (1996-2011)

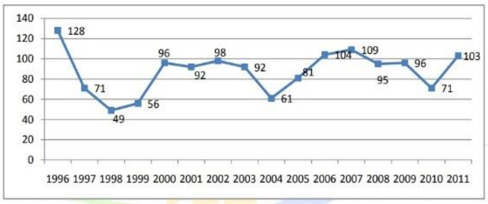

Chart 2. Annual average PM_{10} change (1996-2011)

Table 2: Accepted SO_2 upper values for air quality in the world and in Turkey

	EU Countries	WHO	USA (EPA)	Turkey
24 hours	125	125	365	400
Winter season	20	-	-	250
Annual	-	50	80	150

* Data compiled from Anonymous (2006), Anonymous (2011) [9,10]

In measurements made on 29.11.2011, it is seen that the sulfur dioxide value of Gaziantep is 122 µg / m³. These findings indicate that the value of SO2 increases especially in the winter months. The deterioration effects on the Gaziantep Historic Buildings due to air pollution can be seen in the form of color change, salt accumulation, crust formation and separation on the facades of the structures (Figure 2).

Figure 2. Examples of darkening - color change on the surface of a building

Liquid or solid materials in the atmosphere are particulate matters in air pollution [1]. It is known that particulate matter (PM10) acts as a catalyst in the oxidation of SO_2 on the surface of a stone and plays an active role in the formation of gypsum minerals, as well as causing the building surface to darken. When air the measurement values of the city of Gaziantep is analyzed according to the PM10 value, it can be said that it is quite high (Table 3). As a matter of fact, it is seen that the PM_{10} value of Gaziantep is 143 µg / m³ in the measurements made on 29.11.2011.

Table 3: Gaziantep annual and winter season average for Particulate matter PM_{10} values

Annual average PM_{10} values (µg/m³)							
2003	2004	2005	2006	2007	2008	2009	2010
50	57	46	59	79	60	67	83
Winter season average PM_{10} values (µg/m³)							
2002-2003	2003-2004	2004-2005	2005-2006	2006-2007	2007-2008	2008-2009	2009-2010
69	73	74	77	71	87	49	82

* Data compiled from TURKSTAT Air Quality Statistics [12]

These findings indicate that there is a high level of PM10 in the air structure of the city. When the average annual PM10 values of the city of Gaziantep are examined; according to the EU, World Health Organization and EPA norms (Table 4), this difference increases even more in winter. Deteriorations due to particulate matter in the buildings of the historical region of Gaziantep are seen as darkening on building facades (Figure 3).

Figure 3. Examples of darkening due to air pollution in building stones

Table 4. Accepted PM_{10} upper values for air quality in the world and in Turkey (µg/m³)

	EU Countries	WHO	USA (EPA)	Turkey
24 hours	50	50	150	100
Annual	20	20	50	60

* Data compiled from Anonymous (2006), Anonymous (2011) [9,10]

Another pollutant that causes deterioration due to air pollution in historical buildings is nitrogen oxides (NOx). Nitrogen oxides are soil and water based arising from traffic, agricultural activities and exhaust gases [1]. Compared to sulphur dioxide, the rapid cleaning of NOx from the surface of the stone due to the high solubility of calcium nitrate and other reaction products makes it difficult to detect their effects [2]. However, some research suggests that due to the increase of NOx sources, they may play a more important role in stone detoriation in the future [11].

It can be said that acid rain is another factor that brings deterioration due to air pollution on the historical Gaziantep constructions. A high level of sulphur and particulate matter causes deterioration. These pollutants, which can be suspended for 2-7 days in the air, bring acid when they react with water and this water comes down to the earth as acid rain. Water drops with a low level of pH value cause erosion on the exterior facades of buildings.

As a result, the surfaces where the rainwater is infiltrated and wetted the roofs, the wet areas formed by the water rising from the walls in regions where collecting the water around the building is insufficient, and the reaction and damage of the particulate matter and gases causing air pollution on the surface of the buildings can be seen in the historical buildings in Gaziantep. It is seen that dry surfaces are cleaner and healthier (Figure 4).

Figure 4. Wet areas on stone surfaces: color change, crusting, salt accumulation

4. CONCLUSIONS

As a result of the research, it has been observed that various distortions occurred in the traditional buildings in Gaziantep city historical urban fabric depending on the air pollution. Especially in the winter months, the deterioration effects on the Gaziantep Historic Buildings can be seen in the form of color change, salt accumulation, crust formation and separation in the fronts of the buildings. Another type of degradation is the formation of gypsum minerals by acting as a catalyst in the oxidation of SO_2 on the surface of the particulate (PM_{10}) matter. These minerals lead to the blackening of the building surface.

It is known that the main cause of air pollution in Gaziantep is caused by poor quality fuel used for heating especially in winter season. It should not be forgotten that the prevention of air pollution will be ensured by local governments with policies that are determined for the whole city in a short and long term. These policies can be based on large and small scale solutions, ranging from urban green space regulations and air circulation corridors to the development of the public transport system to reduce the use of individual vehicles, to the type of fuel used in buildings. The main target is to minimize the sources and elements that cause air pollution and to remove pollution from the urban atmosphere.

The widespread use of natural gas in the historic city center of Gaziantep will reduce the use of poor quality coal used for domestic heating. Therefore, it is thought that it will have a decreasing effect of air pollution caused by the use of fossil fuel for heating purposes. It is also important to reduce the traffic intensity around historic structures as air pollution, such as nitrogen and oxide, caused by intense pollution, accelerates the chemical reactions that sulfur dioxide gas and particles form on the surface of the stone. In this framework, the completion of the pedestrianization projects in the old city center will contribute to the preservation of historical buildings.

There are not enough researches and findings on the effect on the long-term structure of the surface-protective chemical substances, while reducing the deterioration effects of the short-term. For this reason, it is considered that the use of surface preservative chemical substances in reducing the deterioration due to air pollution in the Gaziantep buildings is not an appropriate approach in today's conditions. If air pollution is reduced, deterioration caused by air pollution will not progress. However, a separate investigation should be carried out to determine the protection methods applied to the degraded stones. It may be necessary to remove the salts that have affected the degradation of the stones. How to do such a study or how to clean the contaminated areas without damaging the stone should be determined by working with a material protection laboratory that conducts research on these matters.

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The Investigation of Fuel Properties of E-B Diesel Fuels At Different Blend Ratios

Fatih AYDIN[1*]

Abstract

In this study, biodiesel production was realized by converting raw oil obtained from safflower seed to Safflower Oil Methyl Esther (Safflower Biodiesel) by means of raw oil extraction with tempering at 90 °C and pressing after Vals process and consequently trans esterification process followed raw oil extraction. Experimental fuels were obtained as in D_{100}, $E_5B_5D_{90}$, $E_{10}B_{10}D_{80}$, $E_{10}B_5D_{85}$ and $E_5B_{10}D_{85}$ forms by mixing biodiesel fuel obtained from safflower with diesel fuel and bioethanol additives at a ratio of 5% and 10% and by mixing in volumetric ratio according to inversely proportion. Fuel properties of diesel fuel and the obtained fuel mixtures were determined with following tests; Kinematic viscosity (40 ⁰C and 100 ⁰C), Density, Water content, PH values, Color determination, Heating value, Flash point, Fogging, Pour and Freezing points, Copper rod corrosion test, CFPP (Cold Filter Plunge Point) and Cetane number tests. As a result of this study, the benefits of using the E-B diesel for the internal combustion engines can be explained as follows:

- *Biodiesel, which has a higher viscosity than the diesel, is reduced in viscosity when it is mixed with Bioethanol-Diesel, thus it is more usable in diesel engines.*
- *The cetane number has been increased by adding to the biodiesel diesel fuel which has a high cetane number.*
- *The cold flow properties of the diesel fuel were improved by bioethanol addition*

Consequently, it has been understood that the E-B Diesel fuel mixtures can be used in diesel engines.

Keywords: *E-B Diesel, Safflower biodiesel, Bioethanol.*

1. INTRODUCTION

Local resources should be used as much as possible in energy production. Besides, protection of the environment, increasing the productivity, diversity of resources and ensuring continuity are also important. The primary element in energy policies is to switch to reliable, quality, clean and economical energy types so as to meet the energy need in such a way that they support technological and social development [10].

After renewable energy sources have played a key role in the road to a reliable and sustainable energy, the introduction of green technologies within the scope of bio refinery technologies and the production and use of green products have become increasingly important. Bio refineries make it possible to obtain different industrial products such as biochemical, biomaterials and biofuels through various chemical and physical transformation processes [9].

The fuels that countries have obtained using their own herbal or animal sources are briefly called biofuels. Biofuels include all types of liquid and gaseous fuels obtained from vegetable or animal sources. There are alternative fuels such as biogas, bio methanol, bioethanol and biodiesel under the framework of biofuels. However, bioethanol is the most widely used of these [4].

Biodiesel is a mixture of fatty acid methyl esters produced from herbal and animal oil, oil waste and residues and conform to standard of TS EN 14213 and/or TS EN 14214 [5].

Although there are various methods of biodiesel production, the most widely used method today is the trans esterification method. Biodiesel is a nature friendly and renewable bio fuel that is released as a result of the trans

[1*] [1*]*Corresponding author: Necmettin Erbakan University, Eregli Faculty Of Engineering And Natural Sciences, Department of Energy Systems Engineering, 42310 , Eregli/Konya, Turkey.* fatihaydin@konya.edu.tr

esterification reaction of oils or animal oils, which are obtained from oil seeds such as colza (canola), sunflower, soybean and safflower in trans esterification method, with a short chain alcohol (generally methanol or ethanol) by means of a catalyzer [6].

The flash point of biodiesel is higher than diesel fuel. This makes biodiesel a more reliable fuel for use, transport and storage. Biodiesel can be thoroughly mixed with petroleum-derived diesel fuel at any rate, and this feature raises the quality of petroleum-derived diesel fuel. It reduces the emission values of harmful gases generated by combustion, increases the degree of lubrication on the engine [7].

There is biodiesel cycle in Figure 1.

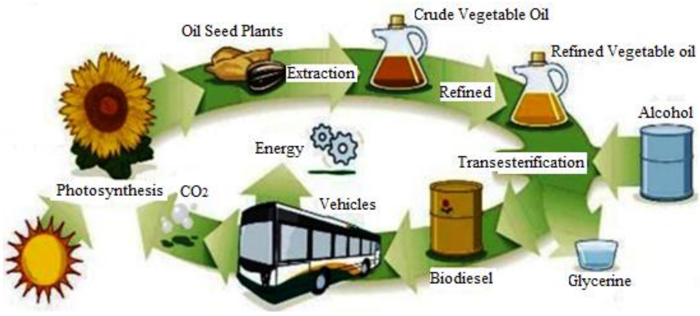

Figure 1. *Biodiesel cycle [1]*

Bioethanol is a biofuel that can be produced by fermentation of sugary and starchy plants or by acidic hydrolysis of cellulosic sources. The plants such as sugar beet, sugar cane, corn, wheat, potatoes; and also woody plants like stem, straw, bark; agricultural wastes and residues and molasses which are a by-product of sugar production can be used as raw material [2].

Considering that fuels that are easy to self-ignite and reduce ignition delay are preferred in diesel engines, the number of cetane numbers of the fuel becomes important [3].

The solubility of bioethanol in diesel fuel is limited. The phase separation of bioethanol-diesel mixtures and the amount of water in the mixture are important problems. However, the cetane number of bioethanol is extremely low [8].

These adverse effects of bioethanol-diesel fuel mixture are eliminated by the addition of biodiesel.

2. MATERIALS AND METHODS

Safflower seeds in this study were provided from Utek Agriculture Cons. Food Industry Co.ltd located at wheat market in Konya, Ilgin and oil production process was performed by Esen Oil Manufacturer in Ilgin County of Konya. To obtain the oils, the seeds were separately peeled in the peeling machines, then they were heated and annealed through the rolling process, fried at 90^0C and later they were squeezed in 200-ton hydraulic press. Biodiesels of these oils were produced at Energy System Laboratory of Energy Systems Engineering Department at Necmettin Erbakan University, Eregli Engineering and Natural Sciences Faculty. During the production, methyl alcohol was used as alcohol, NaOH was used as catalyser and trans esterification method was preferred. 99.8% pure bioethanol which was produced from molasses by Konya Sugar Industry and Trade Inc. is available in Energy System Laboratory. Diesel fuel was provided from BP Petrol Company in Eregli, Konya.

After biodiesel fuel (B_{100}), which was obtained from safflower, was mixed with diesel fuel at the rate of 5% and 10% together with the addition of bioethanol; and mixed volumetrically in inverse proportion, test fuels were obtained at the forms of, D_{100}, $E_5B_5D_{90}$, $E_{10}B_{10}D_{80}$, $E_{10}B_5D_{85}$ ve $E_5B_{10}D_{85}$. Kinematic viscosity, water content, color, heating value, flash point, cloud, pour and freezing point, copper rod corrosion, CFPP(Cold filter plugging point) tests of the mixture fuel were performed at Biodiesel Laboratory of Agricultural Machinery Department, Selcuk University Agricultural Faculty; density, pH amount and cetane number tests were carried out at Energy System Laboratory of Energy Systems Engineering Department at Necmettin Erbakan University, Eregli Engineering and Natural Sciences Faculty and fuel features were determined.

Mixture rates and names of the created fuels are given in Table 1.

Table 1. Names of the fuels and their volumetric constitution percentages

No	Fuels	Diesel	Bioethanol	Biodiesel
1	B_{100}	0	0	100
2	D_{100}	100	0	0
3	$E_5B_5D_{90}$	90	5	5
4	$E_{10}B_{10}D_{80}$	80	10	10
5	$E_{10}B_5D_{85}$	85	10	5
6	$E_5B_{10}D_{85}$	85	5	10

The results of the analysis are seen in Table 2. Standard values in the table belong to TS EN 590 for diesel fuel and to TS EN 14214 for biodiesel.

Table 2. Analyses results of the fuels

Characteristic Properties	Units	Raw Safflower Oil	B_{100}	D_{100}	$E_5B_5D_{90}$	$E_{10}B_{10}D_{80}$	$E_{10}B_5D_{85}$	$E_5B_{10}D_{85}$	Bio ethanol	Limiting Values	
										Diesel	Biodiesel
Density (15^{0}C)	g/cm^3	0,919	0,887	0,835	0,834	0,835	0,836	0,832	0,792	0.82-0.84	0.86-0.90
Kinematic Viscosity (40^{0}C)	mm^2/s	27,442	4,391	3,07	2,524	2,535	2,542	2,543	1,272	2- 4.5	3.5-5
Kinematic Viscosity (100^{0}c)	mm^2/s	7,389	1,921	1,438	1,381	1,391	1,397	1,398	0,699	——	——
Flash Point	^{0}C	170	121	60	——	——	——	——	——	55	101
Water Content	ppm	20,25	225,42	34,50	78,85	75,45	89,68	83,64	372,8	200	500
PH	——	3,98	4,12	4,01	4,94	4,89	4,79	5,50	6,24	——	——
Color	ASTM	2,2	1,8	1,4	1,4	1,4	1,4	1,4	<0,5	——	——
Calorific Value	kJ/kg	36340	39840	43207	40844	42484	42682	42031	29590	——	——
Cloud Point	^{0}C	-1,5	-2,5	-8,4	-8,7	-9,2	-10,1	-9,8	____	——	——
Pour Point	^{0}C	-16	-8	-15,1	-15,6	-15,8	-15,9	-15,7	____	——	——
Freezing Point	^{0}C	<-20	-10	<-20	<-20	<-20	<-20	<-20	<-20	——	——
CFPP	^{0}C	____	-8	-16	-19,4	-21,8	-22	-21	<-50	- 20	-15
Copper Strip Corrosion	——	1a	1a	1a	1a	1a	1a	1a	1a	No:1	No:1
Cetane Number	——	61,7	64,8	51,4	56,5	64,5	57,4	62,6	13	51	——

3. RESULT AND DISCUSSION

3.1. Density values of the fuels

Density values of the fuels are seen in Figure 2. When density test values were investigated, it was seen that density value of B_{100} fuel was higher than other fuels; however, it was within the standards. In mixture fuels, equivalent results to D_{100} fuel were obtained.

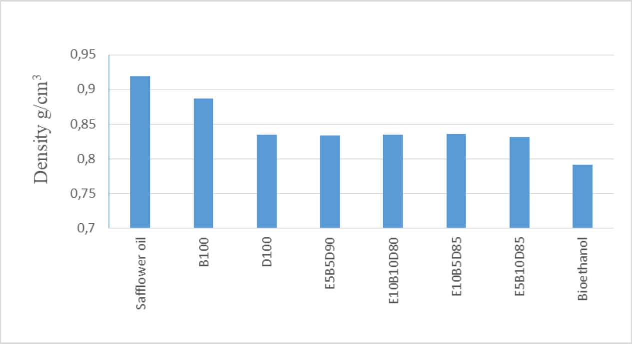

Figure 2. Density values of fuels

3.2. Kinematic viscosity values of the fuels at 40 ^{0}C

In Figure 3 kinematic viscosity values of the fuels at 40 ^{0}C are seen. When kinematic viscosity values at 40 ^{0}C were investigated, it was found out that kinematic viscosity value of B_{100} fuel at 40 ^{0}C was higher than other fuels but it was within standards; and in mixture fuels, lower viscosity values were obtained than in D_{100} fuel.

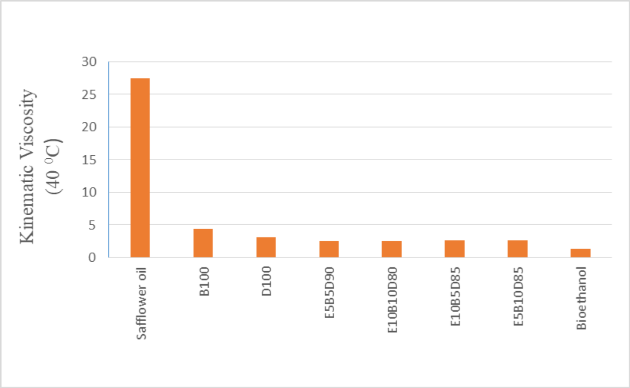

Figure 3. Kinematic viscosity values of the fuels at 40 ^{0}C

3.3. Kinematic viscosity values of the fuels at 100 ^{0}C

Kinematic viscosity values of the fuels at 100 ^{0}C are seen in Figure 4. When kinematic viscosity values at 100 ^{0}C were examined, it was found out that kinematic viscosity value of B_{100} fuel at 100 ^{0}C was higher than other fuels but it was within standards, and in mixture fuels, lower viscosity values were obtained than D_{100} fuel.

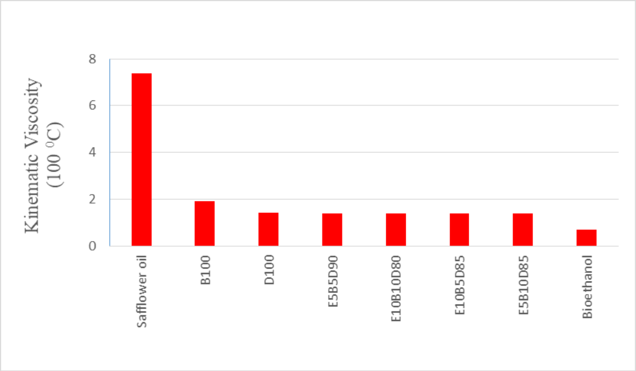

Figure 4. Kinematic viscosity values of the fuels at 100 0C

3.4. Flash point values of the fuels

In Figure 5, flash point values of the fuels are seen. When flash point values were investigated, it was seen that flash point values of B_{100} and D_{100} fuels were conforming to standards. For bioethanol-added fuels, the flash point values were not measured for safety reasons.

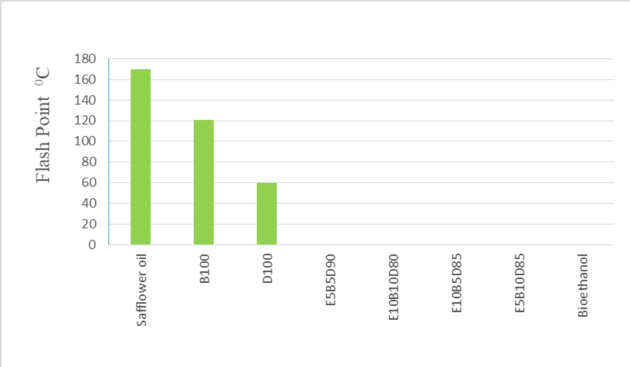

Figure 5. Flash point values of the fuels

3.5. Water content values of the fuels

In Figure 6, water content values of the fuels are seen. When water content values were investigated, it was discovered that water content values of B_{100} and D_{100} fuels were conforming to standards and no problems were encountered in mixture fuels**.**

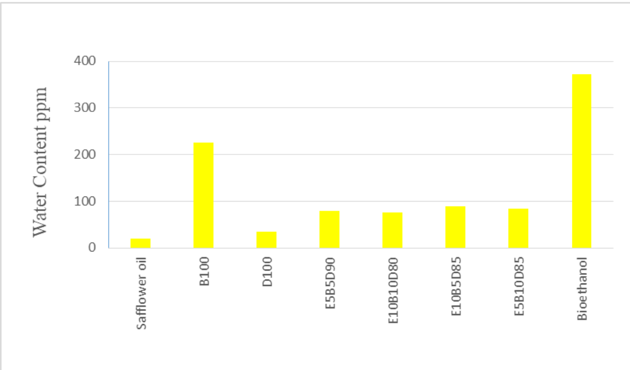

Figure 6. Water content values of the fuels

3.6. pH values of the fuels

pH values of the fuels are seen in Figure 7. When pH test values were investigated, equivalent results were obtained in all fuels.

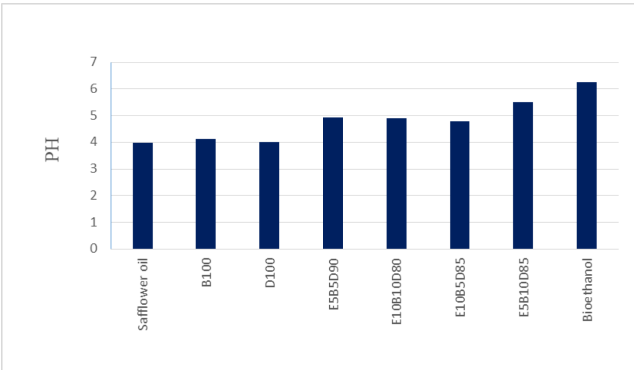

Figure 7. pH values of the fuels

3.7. Color specification values of the fuels

In Figure 8, color specification values of the fuels are seen. When color specification values were examined, equivalent results were obtained in all fuels. The result of color specification measurement of bioethanol does not appear in the graphic because the device gives <0.5 result.

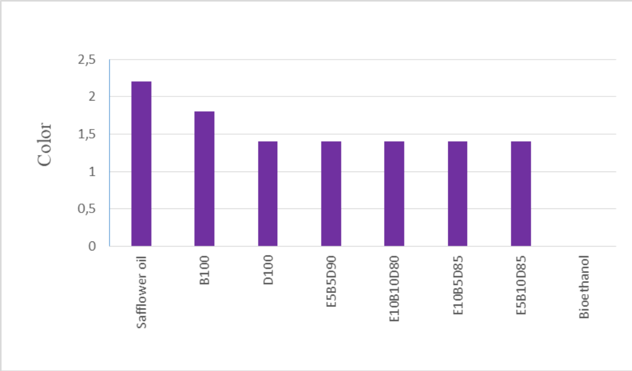

Figure 8. Color specification values of the fuels

3.8. Calorific values of the fuels

In Figure 9, calorific values of the fuels are seen. When calorific test values were investigated, it was seen that mixture fuels gave equivalent results to D_{100} fuel.

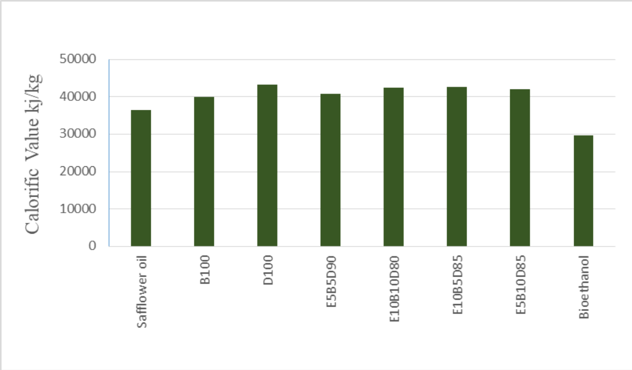

Figure 9. Calories values of the fuels

3.9. Cloud point values of the fuels

In Figure 10, cloud point values of the fuels are seen. When cloud point values were investigated, the values of mixture fuels were better than D_{100} fuel.

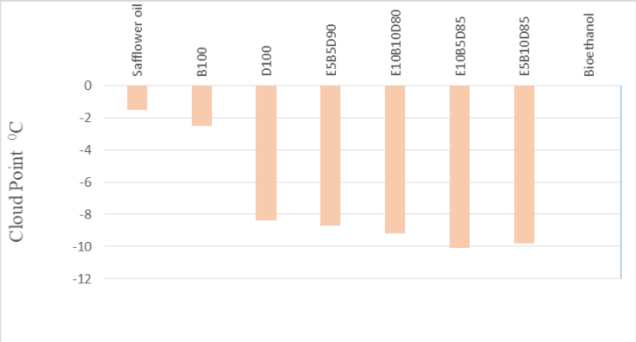

Figure 10. Cloud point values of the fuels

3.10. Pour point values of the fuels

In Figure 11, pour point values of the fuels are seen. When pour point values were examined, it was seen that the values of mixture fuels were better than D_{100} fuel.

Figure 11. Pour point values of the fuels

3.11. Freezing point values of the fuels

When the test values of freezing point were investigated, except for B_{100} fuel, other fuels gave equivalent results. The results could not be given in the graphic because of the fact that the device gave <-20 ^{0}C result for freezing point apart from B_{100} fuel.

3.12. Cold filter plugging point of the fuels

In Figure 12, Cold filter plugging point values are seen. When cold filter plugging point values were investigated, the values of mixture fuel values were better than D_{100} fuel.

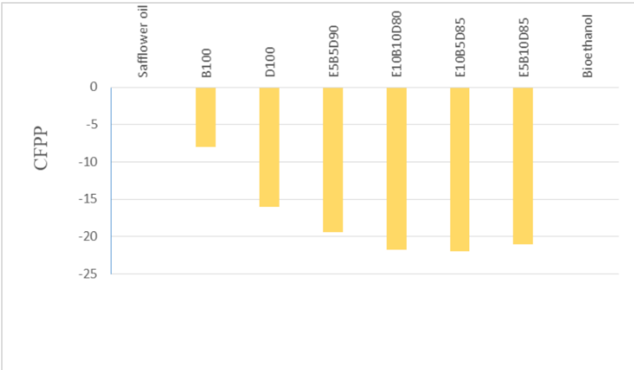

Figure 12. Cold filter plugging point values of the fuels

3.13. Copper rod corrosion values of the fuels

When copper rod corrosion values of the fuels were examined, 1a value was obtained in all fuels but it was not shown in graphic.

3.14. Cetane number values of the fuels

In Figure 13, cetane number values of the fuels are seen. When cetane number test values were investigated, the values of mixture fuels were better than D_{100} fuel.

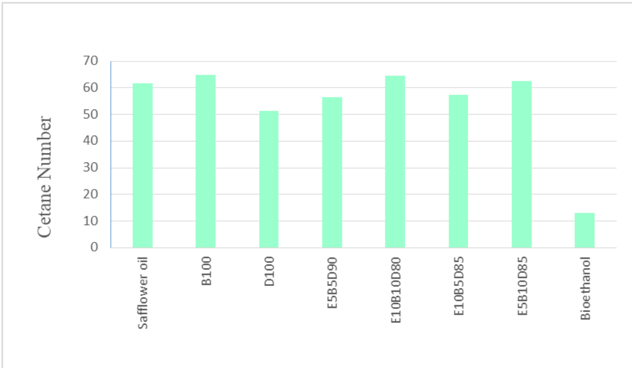

Figure 13. Cetane number values of the fuels

4. CONCLUSIONS

In this study, after biodiesel fuel (B_{100}), which was obtained from safflower by means of trans esterification method, was mixed with diesel fuel at the rate of 5% and 10% together with the addition of bioethanol; and mixed volumetrically in inverse proportion, test fuels were obtained at the forms of, D_{100}, $E_5B_5D_{90}$, $E_{10}B_{10}D_{80}$, $E_{10}B_5D_{85}$ and $E_5B_{10}D_{85}$. The tests were performed for kinematic viscosities of the obtained mixture fuels and diesel fuel at 40 ^{0}C and 100 ^{0}C; for density, water content, pH amount, color specification, heating value, flash points, cloud, pour and freezing points, copper rod corrosion, CFPP and cetane number; and then fuel properties were determined, the obtained data were given in graphics. As a result of this study, the benefits in internal combustion engines by using E-B Diesel can be explained as follows:

- Biodiesel, which had a higher viscosity than the engine, was reduced in viscosity when mixed with the Bioethanol-Diesel and its availability was provided.
- Biodiesel with high cetane number was added in diesel fuel and cetane number was increased.
- Bioethanol was added at a certain rate to the diesel fuel which poses a risk for Pour, Cloud point, CFPP which shows the temperature at which the fuel solidifies or melts and which shows rate of use of fuel in cold weather and the disadvantage of diesel fuel about this matter was eliminated.
- This disadvantage of Bioethanol and Biodiesel, which had lower energy values compared to fossil fuels, was prevented using E-B diesel fuel.
- As a result, it sheds light on the availability of E-B diesel fuel mixture in diesel engines.

ACKNOWLEDGEMENTS

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BIOGRAPHY

Fatih AYDIN was born in Konya in 01.01.1978 and he completed his undergraduate study at Gazi University, Technical Education Faculty, Department of Mechanical Education, Automotive Teaching Program; he did his master degree at Selcuk University, Institute of Science Mechanical Education Department; and he did his doctorate at Selcuk University Institute of Science, Agricultural Machinery Department. He still works as a assistant professor (asst. prof.) at Necmettin Erbakan University, Eregli Engineering and Natural Sciences, Department of Energy Systems Engineering.

Shear Flow of a Microstretch Fluid with Slip

Mehmet Sirin DEMIR[1*]

Abstract

In this study, the effects of slip boundary conditions on the shear flow of the microstretch fluids are investigated. The field equations of the microstretch fluids are solved under slip boundary conditions which are physically more realistic than no-slip boundary conditions. Exact analytical solutions are obtained for the velocity, microrotation, and microstretch fields for the case of a flow between two parallel plates. It has been shown that the previous solutions corresponding to pure Newtonian fluid and micropolar fluid appear as the special cases of the present analysis. Results are represented graphically for the velocity, microrotation, and microstretch for various values of the slip and micropolar parameters.

Keywords: *Microstretch fluid, Shear flow, Analytical solution, Slip boundary conditions.*

1. INTRODUCTION

Many modern engineering and industrial fluids exhibit certain microscopic effects due to local structures and microdeformation of fluid elements. In these situations the continuum assumption is not valid and the classical Navier–Stokes theory is not adequate for the description of such fluids since the fluid particles considered as material point and cannot support surface tractions and couples. In order to describe these fluids such as polymer melts, blood, suspensions, bubbly fluids, magnetic fluids, biological fluids, and many others Eringen[1,2,3] introduced the theory of microfluids in which the local effects arising from the local structure and intrinsic motions of the fluid elements are taken into account.

The most known subclass of microfluids is micropolar fluids in which the particles are rigid so that the microdeformation is only intrinsic rotational motions. Thus, the micropolar continuum possesses six degrees of freedom; three translational degrees (valid for the classical Newtonian fluid) of freedom and three additional degrees for microrotation. Another subclass is the microstretch fluids in which the fluid particles are considered to stretch (expand or contract) in addition to microrotation. Thus, the microstretch continuum possesses four extra degrees of freedom over the classical fluid dynamics. The most general case is the micromorphic fluids. Micromorphic continuum particles possess nine extra degrees of freedom for microrotation, microshear, and microstretch over the classical fluid dynamics.

Most of the studies on microfluids concern about the micropolar fluid flow problems, but very little work seems to have been done on applications of the theory of microstretch fluids to practical problems. Perhaps this is because of unknown viscosity parameters and the mathematical difficulties. Ariman [4] obtained the exact solution of the Poiseuille flow of a microstretch fluid between two parallel plates. In a subsequent study Ariman [5] analyzed blood flow in small arteries using the microstretch theory. Eringen [6] extended his theory of microstretch fluid to that of thermomicrostretch fluids and applied it to the problem of propagation of acoustic waves in bubbly fluids. In his subsequent study Eringen [7] modeled liquid crystals using the theory of microstretch fluids. Aydemir and Venart [8] solved the problem of unsteady flow of thermo microstretch fluid between two parallel and heated plates. In a following paper Aydemir [9] obtained the solutions for the problem of free convective boundary layer flow of a thermomicrostretch fluid. Electrodynamics of microstretch fluids developed by Eringen [10]. In a following paper Eringen [11] introduced electrodynamics of microstretch liquid polymers. Narasimhan [12] analyzed pulsatile flows of microstretch fluids due to varying pressure gradient in circular tubes. Recently, Moosaie and Atefi [13] analyzed the pipe flow of a concentrated suspension composed of spherical particles dispersed in a liquid by utilizing the theory of microstretch fuids.

It should be noted that the continuum assumption may not be valid in the case of flow problems in micro-nano channels since the characteristic length is too small. Experimental studies show that using no-slip boundary conditions can lead inaccurate results in micro-nano channel flows [14]. For more information about the slip boundary conditions the

[1*] *Corresponding author: Istanbul University, Department of Mechanical Engineering, 34320, Avcılar/Istanbul, Turkey.* demirms@istanbul.edu.tr

reader should consult the review studies by Neto et all. [14] and Shu et all. [15]. Sherief et all. [16,17] discussed the motion of a microstretch fluid by using the slip boundary conditions. In recent years there has been an increased interest in using the slip boundary conditions for micropolar fluids [18-22].

The present paper deals with the steady shear flow of an incompressible microstretch fluid between two infinite parallel plates. The slip boundary conditions applied for velocity and the spin boundary conditions applied for microrotation field. The exact analytical solutions of governing equations has been obtained. The expressions for the shear stress, couple stress, the microstretch force, and the difference between the normal stress and the micropressure have been calculated. The effects of flow parameters on the velocity, microrotation, and microstretch are presented graphically.

2. FIELD EQUATIONS

Following Eringen [3], for an isothermal microstretch fluid the field equations are written as:

$$\frac{D\rho}{Dt} + \rho\nabla\cdot \mathrm{v} = 0 \tag{1}$$

$$\frac{Dj}{Dt} - 2j\nu = 0 \tag{2}$$

$$-\nabla\pi + \lambda_0\nabla\nu + (\lambda_v + 2\mu_v + \kappa_v)\nabla\nabla\cdot\mathrm{v} - (\mu_v + \kappa_v)\nabla\times\nabla\times\mathrm{v} + \kappa_v\nabla\times\boldsymbol{\nu} + \rho(\mathrm{f} - \frac{D\mathrm{v}}{Dt}) = 0 \tag{3}$$

$$(\alpha_v + \beta_v + \gamma_v)\nabla\nabla\cdot\boldsymbol{\nu} - \gamma_v\nabla\times\nabla\times\boldsymbol{\nu} + \kappa_v\nabla\times\mathrm{v} - 2\kappa_v\boldsymbol{\nu} + \rho(\mathrm{l} - \mathrm{\sigma}) = 0 \tag{4}$$

$$\alpha_0\nabla^2\nu + \pi_0 - \lambda_1\nu - \lambda_0\nabla\cdot\mathrm{v} + \rho(l - \sigma) = 0 \tag{5}$$

where $\mathrm{v} = \mathrm{v}(\mathrm{x},t)$, $\boldsymbol{\nu} = \boldsymbol{\nu}(\mathrm{x},t)$, $\nu = \nu(\mathrm{x},t)$, and $j = j(\mathrm{x},t)$ are, respectively, velocity microrotation, microstretch, and the microinertia density that are unknowns to be determined under appropriate boundary and initial conditions. D/Dt material differentiation operator, ρ is the density, π the thermodynamic pressure, π_0 the inertial micropressure, f the body force density, l the body couple density and l denotes the microstretch body moment density. The spin inertia $\mathrm{\sigma}$, and the microstretch inertia σ are given by [3]

$$\mathrm{\sigma} = \frac{D}{Dt}(j\boldsymbol{\nu}), \qquad \sigma = \frac{1}{2}j(\frac{D\nu}{Dt} + \nu^2) - j\boldsymbol{\nu}\cdot\boldsymbol{\nu} \tag{6}$$

$\mu_v, \kappa_v, \lambda_v, \lambda_0, \lambda_1$, and α_0 are the viscosity coefficients for the translatory motions, α_v, β_v, and γ_v those for the rotatory motions. The stress tensor, the couple stress, the internal microstretch force density and the difference between micropressure s and $t = t_{kk}$ are respectively given by the following constitutive equations [3];

$$t_{kl} = (-\pi + \lambda_0\nu + \lambda_v\,\mathrm{v}_{m,m})\delta_{kl} + \mu_v(\mathrm{v}_{l,k} + \mathrm{v}_{k,l}) + \kappa_v(\mathrm{v}_{l,k} + \in_{lkm}\nu_m) \tag{7}$$

$$m_{kl} = \alpha_v\nu_{m,m}\delta_{kl} + \beta_v\nu_{k,l} + \gamma_v\nu_{l,k} + b_0\in_{mlk}\nu_{,m} \tag{8}$$

$$m_k = \alpha_0\nu_{,k} + b_0\in_{klm}\nu_{l,m} \tag{9}$$

$$s - t = -\pi_0 + \lambda_0\,\mathrm{v}_{m,m} + \lambda_1\nu\ . \tag{10}$$

where b_0 is a viscosity coefficient and $\in_{mlk}$ is the permutation symbol. Repeated indices denote summation over the range (1, 2, 3) and as index followed by a comma represents partial differentiation with respect to space variable x_m. In general, all material moduli may depend on ρ, j, and temperature. For linear approximation they are considered constants. As a second assumption, the flow is steady and the microstretch fluid is incompressible. In the case of incompressible fluids, π is replaced by an unknown pressure p, and equation of continuity (1) reduces to:

$$\nabla\cdot\mathrm{v} = 0. \tag{11}$$

In linear microstretch theory, $|\mathrm{v}|, |\boldsymbol{\nu}|$, and $|\nu|$ are considered to be small as compared to other term in Eq. (6) and the spin inertia $\mathrm{\sigma}$, and the microstretch inertia σ are approximated by [3]

$$\mathrm{\sigma} = j\frac{D\boldsymbol{\nu}}{Dt}, \qquad \sigma = \frac{1}{2}j\frac{D\nu}{Dt}. \tag{12}$$

Also, the flow is microisotropic in the sense that the microinertia tensor $j_{kl} = (1/3) j \delta_{kl}$. For the case of small microinertia j, the inertial micropressure π_0 can be expressed as [3, 12] :

$$\pi_0 = cj \,. \tag{13}$$

where c is a constant. Under these assumptions, and neglecting external body force, body couple and microstretch body moment, the field equations (2)-(5) reduce to:

$$\mathrm{v} \cdot \nabla j - 2 j \nu = 0 \tag{14}$$

$$-\nabla p + \lambda_0 \nabla \, \nu + (\mu_v + \kappa_v) \nabla^2 \mathrm{v} + \kappa_v \nabla \times \boldsymbol{\nu} + \rho \mathrm{v} \cdot \nabla \mathrm{v} = 0 \tag{15}$$

$$(\alpha_v + \beta_v + \gamma_v) \nabla \nabla \cdot \boldsymbol{\nu} - \gamma_v \nabla \times \nabla \times \boldsymbol{\nu} + \kappa_v \nabla \times \mathrm{v} - 2\kappa_v \boldsymbol{\nu} + \rho j (\mathrm{v} \cdot \nabla \, \boldsymbol{\nu}) = 0 \tag{16}$$

$$\alpha_0 \nabla^2 \nu + cj - \lambda_1 \nu + \frac{1}{2} \rho j (\mathrm{v} \cdot \nabla \, \nu) = 0 \;. \tag{17}$$

In the subsequent section, we shall obtain the exact solutions of the above equations for steady shear flow of a microstretch fluid.

3. SHEAR FLOW OF A MICROSTRETCH FLUID

Consider the flow of a microstretch fluid between two infinite parallel plates separated by a distance $2h$ as illustrated in Fig. 1. The plates are initially at rest and both plates are suddenly accelerated from rest and moves in their own planes with a constant velocity V to opposite directions. It is assumed that the flow is driven by motions of palates.

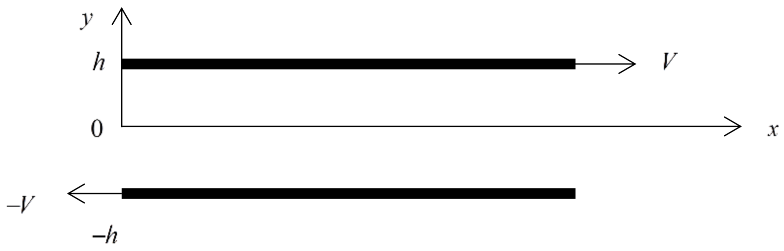

Figure 16. The geometry of the problem.

We seek solutions in which the velocity vector, microrotation vector, microstretch, and microinertia of the fluid are assumed to have the form

$$\mathrm{v} = \{u(y), 0, 0\}, \quad \boldsymbol{\nu} = \{0, 0, \psi(y)\}, \quad \nu = \nu(y), \quad j = j(y) \tag{18}$$

Substitution of Eq. (18) into Eqs. (14)-(17) gives

$$(\kappa_v + \mu_v) \frac{d^2 u}{dy^2} + \kappa_v \frac{d\psi}{dy} = 0 \tag{19}$$

$$\gamma_v \frac{d^2 \psi}{dy^2} - \kappa_v \frac{du}{dy} - 2\kappa_v \psi = 0 \tag{20}$$

$$\alpha_0 \frac{d^2 \nu}{dy^2} - \lambda_1 \nu + \pi_0 = 0 \tag{21}$$

The boundary conditions are as follows:

$$\begin{aligned} & u(-h) = -V + L \frac{du}{dy}(-h), && u(h) = V - L \frac{du}{dy}(h) \\ & \psi(-h) = -n \frac{du}{dy}(-h), && \psi(h) = -n \frac{du}{dy}(h) \\ & \nu(-h) = 0, && \nu(h) = 0 \end{aligned} \tag{22}$$

where, L is a slip parameter and n is spin parameter. $n=0$ indicates that a fluid particle does not rotate at boundaries which called strict adherence condition. $n=1/2$ indicates that a fluid particle rotation is equal to $(1/2)\nabla\times \mathrm{v}$. Introducing dimensionless parameter as;

$$\bar{y}=\frac{y}{h},\quad \bar{u}=\frac{u}{V},\quad \bar{\psi}=\frac{\psi}{V/h},\quad \bar{\nu}=\frac{\nu}{\pi_0/\lambda_1} \tag{23}$$

where, bars used to denote a dimensionless quantity. Throughout this paper, henceforth for convenience, unless stated otherwise, we shall drop the bars that appear over the dimensionless quantities.

Substituting Eq. (23) into Eqs. (19)-(22); the dimensionless governing equations and boundary conditions obtained as follows:

$$(1+\Delta_m)\frac{d^2u}{dy^2}+\Delta_m\frac{d\psi}{dy}=0 \tag{24}$$

$$\frac{d^2\psi}{dy^2}-\lambda_m^2\frac{du}{dy}-2\lambda_m^2\psi=0 \tag{25}$$

$$\frac{d^2\nu}{dy^2}-\lambda_n^2\nu+\lambda_n^2=0 \tag{26}$$

$$\begin{aligned} &u(-1)=-1+\beta\frac{du}{dy}(-1), && u(1)=1-\beta\frac{du}{dy}(1)\\ &\psi(-1)=-n\frac{du}{dy}(-1), && \psi(1)=-n\frac{du}{dy}(1)\\ &\nu(-1)=0, && \nu(1)=0 \end{aligned} \tag{27}$$

where, Δ_m and λ_m are micropolar parameters, λ_n is microstretch parameter, β is dimensionless slip parameter and they are defined as follows:

$$\Delta_m=\frac{\kappa_v}{\mu_v},\quad \lambda_m=\frac{\kappa_v h^2}{\gamma_v},\quad \lambda_n=\frac{\lambda_1 h^2}{\alpha_0},\quad \beta=\frac{L}{h} \tag{28}$$

Solving Eqs. (24)-(26) under the boundary conditions (27), velocity, microrotation, and microstretch obtained as follows, respectively.

$$u=\frac{\dfrac{\Delta_m}{(1+\Delta_m)}\dfrac{(N-1)}{\lambda\cosh(\lambda)}\sinh(\lambda y)+2y}{\left(\dfrac{\Delta_m(N-1)}{(1+\Delta_m)}\dfrac{\tanh(\lambda)}{\lambda}+\dfrac{\Delta_m(N-1)}{(1+\Delta_m)}\beta+2(1+\beta)\right)} \tag{29}$$

$$\psi=\frac{\dfrac{(1-N)}{\cosh(\lambda)}\cosh(\lambda y)-1}{\left(\dfrac{\Delta_m(N-1)}{(1+\Delta_m)}\dfrac{\tanh(\lambda)}{\lambda}+\dfrac{\Delta_m(N-1)}{(1+\Delta_m)}\beta+2(1+\beta)\right)} \tag{30}$$

$$\nu=1-\frac{\cosh(\lambda_n y)}{\cosh(\lambda_n)} \tag{31}$$

where,

$$N=\frac{n(2+\Delta_m)}{1+\Delta_m-n\Delta_m},\quad \lambda=\lambda_m\sqrt{\frac{2+\Delta_m}{1+\Delta_m}} \tag{32}$$

For the problem under consideration, it is important to find the shear stress and couple stress. Using the Eqs. (7), (23) , and (29), the shear stress τ_{wx} can be written in non-dimensional form as follows:

$$\tau_{wx}=\frac{t_{yx}}{\mu_v V/h}=(1+\Delta_m)\frac{du}{dy}+\Delta_m\psi=\frac{2-\Delta_m}{\left(\dfrac{\Delta_m(N-1)}{(1+\Delta_m)}\dfrac{\tanh(\lambda)}{\lambda}+\dfrac{\Delta_m(N-1)}{(1+\Delta_m)}\beta+2(1+\beta)\right)} \tag{33}$$

Using the Eqs. (8), (23), and (30), the couple stress m_{wz} can be written in non-dimensional form as follows:

$$m_{wz}=\frac{1}{\gamma_v V/h^2}m_{yz}=\frac{d\psi}{dy}=\frac{\lambda\dfrac{(1-N)}{\cosh(\lambda)}\sinh(\lambda y)}{\left(\dfrac{\Delta_m(N-1)}{(1+\Delta_m)}\dfrac{\tanh(\lambda)}{\lambda}+\dfrac{\Delta_m(N-1)}{(1+\Delta_m)}\beta+2(1+\beta)\right)} \tag{34}$$

Using the Eqs. (9), (23), and (30), the non-vanishing components of the microstretch force vector are given in non-dimensional form:

$$m_{w1}=\frac{1}{b_0 V/h^2}m_x=\frac{d\psi}{dy}=\frac{\lambda\dfrac{(1-N)}{\cosh(\lambda)}\sinh(\lambda y)}{\left(\dfrac{\Delta_m(N-1)}{(1+\Delta_m)}\dfrac{\tanh(\lambda)}{\lambda}+\dfrac{\Delta_m(N-1)}{(1+\Delta_m)}\beta+2(1+\beta)\right)} \tag{35}$$

Lastly, the difference between the normal stress and the micropressure can be expressed by

$$p_w=\frac{s-t}{\pi_0}=-\frac{\cosh(\lambda_n y)}{\cosh(\lambda_n)} \tag{36}$$

4. RESULTS AND DISCUSSION

In this paper steady shear flow of a microstretch fluid is studied theoretically. Exact analytical solutions for the system of coupled partial differential equations governing the velocity field, microrotation, and microstretch are obtained. The effects of the flow parameters have been presented graphically. To the best of authors' knowledge, the numerical values of relevant viscosity coefficients for microstretch fluid are not available in the literature. Therefore, the hypothetical values of flow parameters have been taken.

It should be noted that the velocity distribution corresponding to pure Newtonian fluid appears as the special case of present analysis. If one sets $\Delta_m=\lambda_m=\lambda_n=0$ in Eqs. (29)-(31), these are obtained as follows;

$$u_N=\frac{y}{1+\beta},\quad \psi_N(y)=\lim_{\lambda_m\to 0}[\psi(y)]=0,\quad \nu_N=0 \tag{37}$$

which is the solution of the same problem for a Newtonian fluid. The case $\lambda_n=0$ corresponds to case of micropolar fluid.

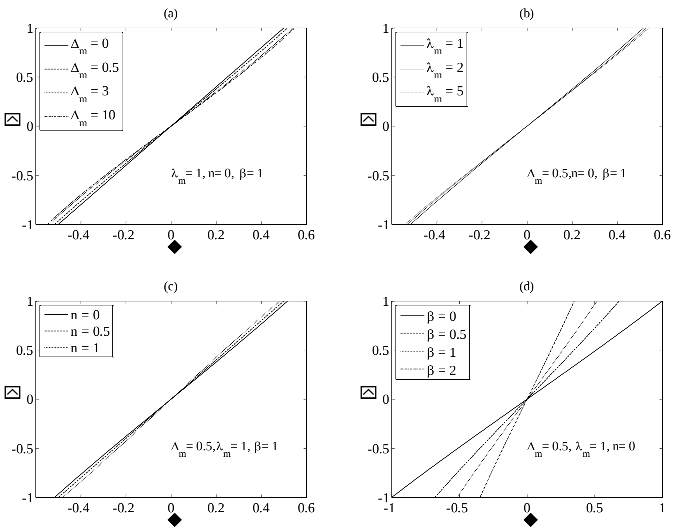

Figure 2. Variation of the velocity profile with flow parameters.

Figure 2 (a) and 2 (b) show that the velocity increases as both micropolar parameters Δ_m and λ_m increase. The line $\Delta_m=0$ corresponds to the classical case. This investigation of the flow of a microstretch liquid shows that while the behaviour of the microstructure has important effects upon the macroscopic flow.

From the Figure 2 (c), we observe that the velocity decreases as spin parameter increase. The effect of the slip parameter on the velocity is shown in Figure 2 (d).

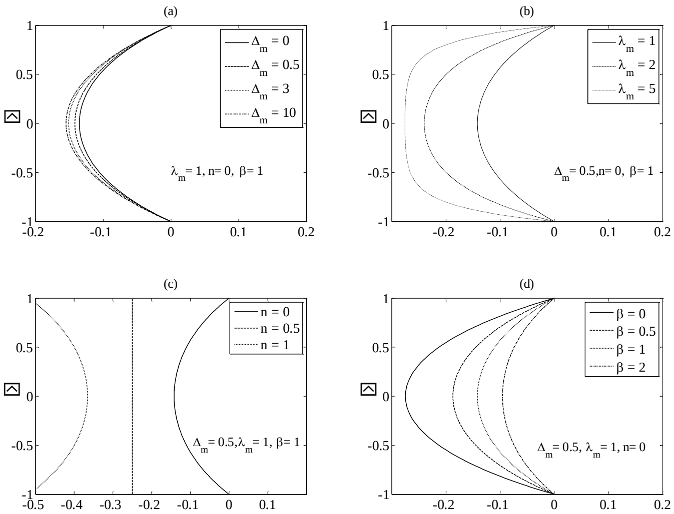

Figure 3. Variation of the microrotation profile with flow parameters.

Figures 3 (a) and 3 (b) illustrate the microrotation profiles for different values of the micropolar parameters. The numerical results show that the effect of increasing values of micropolar parameters result in an increase of the microrotation. Figure 3 (c) shows the variation of microrotation with spin parameter n . The case of $n = 0.5$ indicates that the microrotation is equal to z-component of rotation vector (w) of classical case. $\psi = (1/2)\nabla \times \{u_N, 0, 0\} = \{0, 0, 0.25\}$. Figure 3 (d) shows that the microrotation decreases as slip parameter β increase.

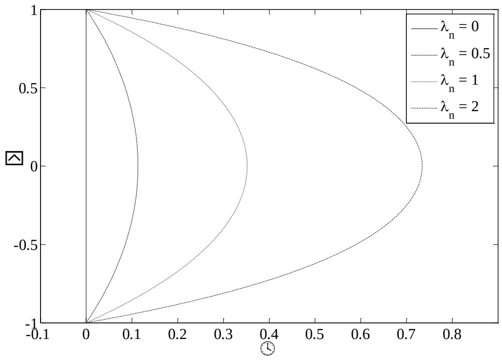

Figure 4. Variation of microstretch.

Finally, Figure 4 shows the variation of microstretch with microstretch parameter λ_n . Increasing values of λ_n result in an increase of the microstretch.

5. CONCLUSIONS

Exact analytical solutions to the shear flow of a microstretch fluid have been obtained. Passage to the classical case has been made. The effects of flow parameters on velocity field, microrotation, and microstretch are presented graphically. The results show that the microscopic behavior of fluid particles contribute the macroscopic behavior of fluid significantly. As a result, the local structure and intrinsic motions of the fluid elements should be taken into account in some cases where the continuum assumption is not valid.

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Determination of Combustion Properties of The Firetex Impregnated Scotch Pine

Cemal OZCAN[1], Rasit ESEN[1]*

Abstract

In this study, the effects of impregnation material and impregnation methods on combustion properties of Scotchpine (Pinussylvestris L.) have been investigated. The firetex was used for impregnation material. The four different methods were used for impregnation process. Combustion test was performed according to the procedure of ASTM-E 69 standards. The mass reduction, release of gasses (CO, NO, O2), and temperature differences of samples were determined for each 30 seconds during combustion.According to the test results, Firetex as an impregnation material was found to be the most effective after long-term dipping processing Scotch pine material.

Keywords: *Scotch Pine, Firetex, Dipping Method, Fire Retardant, Impregnation*

1. INTRODUCTION

Wooden material has a versatile usage area and it is a natural, recyclable and sustainable material. Considering its structure, which allow it to physical, chemical and mechanical modification, it is a very durable construction material. Moreover, this structure provides lots of unique properties to wood such as easy processing, color and pattern difference between species, insulation for noise and heat and makes it a high quality decorative material (e.g. [1], [2]).The combustion of wood relates to the fuel burn rate (or the reaction rate), the combustion product (or the emissions), the required excess air for complete combustion, and the fire temperatures. The processes are extremely complicated, principally, because the wood has a complex physical and chemical composition [3].

Important reactions to fire parameters in the full-scale fire are heat release rate and time of flashover [4].Flame retardant treated materials may have much better fire performance concerning these parameters than untreated wood products. Combustion of wood involves a complex series of physical transformations and chemical reactions that are further complicated by the heterogeneity of the substrate. Wood, and cellulosic materials in general, do not burn directly; under the influence of sufficiently strong heat sources they decompose to a mixture of volatiles, tarry compositions, and highly reactive carbonaceous char. Gas-phase oxidation of the combustible volatiles and tarry products produces flaming combustion. Solid-phase oxidation of the remaining char produces glowing or smoldering combustion, depending on the rate of oxidation [5].Wood coatings more often are designed to retard ignition and rate of burn rather than to provide the fire-resistive barrier which is more typical of steel coatings. Typically, coatings protective (or retardant) against cellulosic-type fires are applied in thin film coat sup to 1.5 mm (60mils) thick. These coatings are usually not very weatherable; so, for outdoor applications, a protective topcoat is needed [6]. Uysal et al. investigated the effects of finishing materials polyurethane, cellulosic, synthetic, polyester, and acid hardening varnish on combustion properties of Scotch pine. Cellulosic varnish was found to be the most successful varnish according to the CO amounts and mass reduction. According to their results, all of the varnishes used to in their study showed a low resistance against fire and high temperatures[7]. Uysal and Kurt studied the impregnation of the oriental spruce (piceaorientalis L.) with boron compounds, and the test samples were applied to the combustion test. A borax-boric acid % 10 solution was found to be the most successful fire retardant chemical[8]. Kurt and Uysal investigated the effects of fire retardant materials zinc chloride and di-ammonium phosphate were found to be the most successful fire- retardant chemicals in LVL. Since it diminishes combustion, the impregnation of LVL produced from walnut by using PF and PVAc adhesives can be advised to be impregnated by using the pressure-vacuum method[9].

[1] *Corresponding author: Karabuk University, Department of Industrial Product Design, 78600, Safranbolu/Karabuk, Turkey.* *cemalozcan@karabuk.edu.tr*

The aim of this paper is to investigate the combustion properties and emission testing of Scotch pine (Pinussylvestris L.), widely used in building construction and wooden materials. The samples were impregnated by using four different impregnatedmethod.

2. MARERIAL AND METHOD

Wood Material

Scotch pine (Pinus Sylvestris L.), wood was chosen randomly from timber supplier of Karabuk, Turkey. A special emphasis was put on the choice of the wood material. Accordingly, non-deficient, whole, knotless, normally grown (without reaction wood, decay, insect, or fungal infection) wood materials are selected.

Impregnated Material

Firetex is an effective, natural, non-toxic, ecologic and economic water based fire-retardant and fire-extinguisher. The properties of some physical are given in Table 1.

Table 1. Physical Properties of firetex

Boiling point	98 ºC
Freezing point	-3 ºC
pH	3,7
TDS	739 ppm
Evaporation (60°C / 24 h)	% 50

Preparation of Test Samples

The oversized test samples were acclimatized until they were stable at 20 ± 2 °C and 65 ± 3 % relative humidity in climate room. Later on they were cut with the dimensions of 9x19x1016 mm according to the procedure of ASTM E –69[10].Impregnation processes stated at ASTM D 1413-76, TS 344 and TS 345 were applied to the prepared test samples (e.g. [11], [12] and [13]). For this aim, the samples were dipped into the impregnation solution (having packing viscosity) for 2 min, 24 h,7 days and these samples were impregnated by brush, The peculiarities of impregnation were determined before and after impregnation processes. All processes were carried out at 20±2°C. The samples, oven dried before and after impregnation, can be calculated by the formula

$$R = \frac{GC}{V} \times 10^3 \ \mathrm{kg} / \mathrm{m}^3,$$

where R is the retention of impregnation material, G=T2−T1, T1 is the sample weight before impregnation (g), T2 is the sample weight after impregnation (g), C is the concentration (%) and V is the volume of the samples (cm^3). Impregnated test samples were kept at 20±2°C and at 65±3% relative humidity until their weights became stable.

Execution Test

The combustion test was carried out according to the principles of the ASTME –69. But some changes were made in the stand. For this purpose, a digital balance having 0.01 g sensitiveness has been used for determination of mass reduction of materials when they are burnt. Butane gas was used to make an ignition flame. The gas flow is standard as the high of flame is 25 cm, the temperature must be 1000 °C.The distance between the bottoms of the test samples, which were hanged inside of the fire tube and the top of the gas pipe must be adjusted as 2.54 cm. During the test, mass reduction, temperature and released gas (CO, NO, O_2) were determined in every 30 seconds. The test was made under a chimney where the flow of air blown was drawn with natural draft. At the beginning of combustion test flame source was used for 4 minutes then flame source was taken away and it was continued 6 minutes. Totally 10 minutes, the test was lasted.

Statistical Procedure

Descriptive statistics analysis was applied to determine both the amount of retention in the prepared natural and the effects of impregnation material on combustion with or without flame source.

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3. RESULT AND DISCUSSION

The air dry density (0. 480 gr/cm³) was obtained scotch pine wood. The proportion of impregnation material is given in Table 2.

Table2**.** Proportion of Retention

Test no	Impregnation Method	Retention (%)	
		$\overline{X}$	HG *
1	Finished with by a brush	3,7	A
2	Short-term dipping (2 min)	6,9	B
3	Middle-term dipping (24 h)	14,4	C
4	Long-term dipping (7 days)	24,8	D

$\overline{X}$: Average *HG: Groups of Homogeneity

The highest retention proportion was observed (24,8 %) in dipping method of long time, and the lowest (3.7%) in finished with a brush. The averages of mass reduction are given in Table 3.

Table 3. Average of Mass Reduction(%)

Measured of time	Control	Dipping method			with a brush
		2 min	24 hours	7 days	
1	2.23	2.55	1.95	2.24	2.29
2	5.08	6.48	3.95	3.54	3.21
3	9.45	8.38	5.44	5.16	6.62
4	16.18	10.17	7.28	6.60	8.24
5	24.12	13.04	10.29	7.21	11.14
6	31.21	15.59	11.03	8.10	13.94
7	40.68	18.06	12.26	10.13	15.94
8	48.23	21.76	13.58	11.06	17.57
9	55.23	25.60	16.24	13.54	19.09
10	64.57	27.87	18.53	14.80	20.20
11	76.41	29.51	20.52	15.86	21.67
12	81.57	32.18	23.66	16.94	23.59
13	85.79	32.71	25.39	17.49	24.74
14	91.84	34.14	25.83	18.06	25.69
15	94.02	35.79	26.18	19.81	27.05
16	96.33	36.36	26.54	20.53	27.45
17	97.49	37.10	26.90	22.10	27.93
18	98.13	37.56	27.32	22.40	28.37
19	98.53	38.83	28.02	22.83	29.49
20	99.15	39.07	28.61	23.18	30.36

The highest mass reduction was (99.15%) observed in control samples. the lowest value (28.61%) in the impregnated with firetex by middle-term dipping method. The averages of O_2 amounts are given in Table 4.

Table 4. Average of O2 amounts (%)

Measured of time	Control	Dipping method			With a brush
		2 min	24 hours	7 days	
1	20.75	20.47	20.10	20.11	20.36
2	20.51	20.31	19.73	19.73	19.86
3	20.19	20.15	19.59	19.54	19.61
4	19.95	19.98	19.51	19.35	19.27
5	19.65	19.76	19.43	19.08	19.25
6	19.32	19.58	19.35	18.78	19.28
7	18.95	19.35	19.27	18.66	19.43
8	18.60	19.28	19.25	18.90	19.67
9	18.25	19.03	19.38	19.14	19.85
10	17.95	18.84	19.51	19.53	20.37
11	17.67	18.89	20.11	20.13	20.67
12	17.41	19.13	20.39	20.32	20.84

13	17.32	19.64	20.55	20.48	20.92
14	17.55	20.19	20.60	20.62	20.94
15	18.17	20.56	20.61	20.70	20.97
16	18.76	20.73	20.63	20.85	20.98
17	19.76	20.91	20.63	20.88	20.98
18	20.56	20.94	20.71	20.88	20.98
19	20.86	20.96	20.86	20.89	20.98
20	20.94	20.97	20.99	20.90	20.98

The highest reduction of O_2 concentration (20.99%) was measured in the impregnated with firetex by middle-term dipping method. The lowest change of O_2-concentration (17.32 %) in scotch pine control samples. From the control samples it can be seen that the impregnation chemicals has the effect of fire retardant. Control samples gave the highest CO_2 concentrations.The averages of temperature are given in Table 5.

Table 5. Average of Temperature Values(°C)

Measured of time	**Control**	**Dipping method**			**with a brush**
		2 min	24 hours	7 days	
1	76.9	80.1	73.8	75.6	75.6
2	84.3	93.4	88.1	89.8	91.7
3	105.5	104.3	100.7	99.6	104.3
4	128.4	110.6	111.5	106.8	121.4
5	159.7	117.8	119.6	113.0	134.9
6	183.8	128.6	128.6	119.2	148.3
7	203.0	137.6	136.7	126.7	161.9
8	230.5	145.7	143.9	134.9	175.3
9	283.2	142.0	134.9	132.1	168.1
10	376.5	137.6	123.1	127.7	158.2
11	483.4	129.4	117.8	120.5	147.4
12	511.1	125.9	110.6	113.3	139.3
13	542.4	120.5	105.2	106.0	129.5
14	481.5	115.0	99.8	101.6	121.4
15	414.6	113.2	93.5	97.0	111.5
16	348.9	110.6	89.0	93.5	102.5
17	318.4	104.3	86.3	90.8	96.1
18	282.5	108.8	82.7	89.0	89.0
19	253.3	95.2	78.2	84.5	86.3
20	230.7	91.6	75.5	81.8	80.9

The highest averages temperature (542.4°C) variation was observed in the scotch pine control samples. The lowest (73.8°C) in impregnated with firetex by middle-termdipping method. The averages of variations of CO are given in Table 6.

Table 6. Variation of CO (ppm)

Measured of time	**Control**	**Dipping method**			**with a brush**
		2 min	24 hours	7 days	
1	11.76	61.23	74.06	65.25	54.40
2	27.34	111.89	115.37	117.98	125.06
3	48.74	125.40	141.55	145.91	151.19
4	75.06	137.24	155.32	184.47	175.44
5	117.3	152.07	167.84	242.28	199.24
6	156.6	186.51	169.09	294.66	211.31
7	188.5	195.95	177.82	347.06	194.54
8	247	198.84	176.23	366.81	171.47
9	296.6	203.45	187.22	336.04	140.08
10	355.68	220.96	186.49	315.60	114.64
11	410.92	245.31	166.94	224.71	101.77
12	494.46	203.28	143.82	173.41	86.87
13	500.62	193.42	124.61	110.31	74.29
14	449.85	157.66	122.68	67.86	50.83
15	335.04	123.42	103.64	44.26	38.98

16	269.52	77.61	85.90	28.84	27.54
17	199.04	47.52	73.44	20.33	14.45
18	146.53	29.31	51.45	14.59	9.46
19	101.37	20.49	37.51	8.75	6.46
20	61.85	15.20	17.00	6.02	4.19

The highest increase in CO concentration was (500.62 ppm) observed in the control scotch pine control samples and the lowest in (4.19 ppm) impregnated with firetex by with a brush samples. The averages of variation of NO are given in Table 7.

Table 7. Variation of NO (ppm)

Measured of time	**Control**	**Dipping method**			**with a brush**
		2 min	24 hours	7 days	
1	1.22	19.61	7.28	18.90	5.78
2	2.68	25.37	11.10	29.39	13.95
3	4.12	24.50	13.86	32.34	17.96
4	5.1	21.64	15.16	31.58	20.58
5	7.02	20.34	16.24	31.00	21.93
6	8.78	19.94	16.66	30.24	20.39
7	10.45	18.38	17.22	29.03	15.68
8	11.05	17.14	16.28	25.05	12.88
9	12.34	14.65	15.21	19.21	9.19
10	13.24	9.69	14.65	14.81	6.06
11	15.25	6.64	12.08	9.56	4.80
12	15.62	5.77	9.28	6.27	3.64
13	17.02	4.96	6.44	5.34	3.08
14	13.6	3.67	5.78	4.32	2.70
15	11.45	2.42	4.48	3.79	2.14
16	9.22	2.25	2.61	3.23	1.44
17	5.32	1.72	2.00	2.58	1.26
18	1.81	1.60	1.30	2.02	1.21
19	1.02	1.51	0.65	1.46	1.02
20	0.02	1.46	0.09	0.90	0.32

In this study. the highest increase in NO concentration was observed in the experiment of (32.34 ppm) impregnated with firetex by long-termdipping method samplesand the lowest in those of (0.02 ppm) non-impregnated control scotch pine samples.

4. CONCLUSION

According to Table 3. after taking the flame source from the fire tube. the highest mass reduction(99.15 %) was observed in the non-impregnated control samples. the lowest in the impregnated with firetex by middle-termdipping method scotch pine samples (28.61 %) at the second stage of combustion. It has been observed that impregnated with firetex by dipping method scotch pine samples decreases mass reduction values 71. 1 % in average.

According to Table 4. the highest O2 consumption was observed in the impregnated with firetex by middle-term dipping method (20.99 %). The lowest change of O2-concentration (17.32 %) in scotch pine control samples, impregnated with firetex samples decreases O2 consumption values 17.4 % in average.

According to Table 5. the highest temperature was observed in the non-impregnated scotch pine control samples (542.4°C). It been has observed that impregnated by middle-term dipping method samples impregnated with firetex samples decreases °C consumption values 85 % in average.

According to Table 6. the highest ratio of CO was observed in control samples (500.6 ppm). According to the averages values. it been has observed that impregnated by with a brush method scotch pine samples impregnated with firetex samples decreases CO ratio values 90 % in average.

According to Table 7. the highest ratio of NO was observed in the impregnated with firetex by long-term dipping method samples (32.34 ppm). According to the averages values. it been has observed that impregnated by long-term dipping method scotch pine samples impregnated with firetex samples increases NO ratio values 97 % in average. Consequently. fire retardant impregnated material was found to be the most successful according to the CO amounts and mass reduction.

It can be proposed that protecting by dipping method or with a brush firetex of historical wooden structure due to fire risk.

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Improvement of Fire-Resistance of Scotch Pine Wood Used On Historical Wooden Constructions

Rasit ESEN[1*], Cemal OZCAN[1]

Abstract

In this study, the effects of fire retardant finishing materials on combustion properties of 120-years in service historical wooden houseshave been investigated. Combustion test was performed according to the procedure of ASTM-E 69 standards. The mass reduction, release of gasses (CO, NO, O2), and temperature differences of samples were determined for each 30 second during combustion. According to the test results, fire retardant finishing material was found effective to preserve historical wooden structures against fire. Since fire retardant finishing material diminishes combustion, it is possible to advise using fire retardant finishing for varnishing to historical wooden structures.

Keywords: *Scotch Pine, Combustion, Historical Wooden Structures, Fire Retardant*

1. INTRODUCTION

Wood continues to play an important role as a structural material in today's high-tech society. In many countries, wood is widely used as a building material: in some areas as the main construction and decoration material [1].

The combustion of wood relates to the fuel burn rate (or the reaction rate), the combustion product (or the emissions), the required excess air for complete combustion, and the fire temperatures. The processes are extremely complicated, principally, because the wood has a complex physical and chemical composition [2].Wood material has a number of advantages such as good mechanical properties, but shows a low fire resistance. Wood is a naturally durable material that has been recognized for centuries throughout the world for its versatile and attractive engineering and structural properties(e.g. [3], [4] and [5]).

In our country and the world, the areas which form the best examples of ancient times' human settlements in their original environmental textures reflect the richness of our country. These wooden structures are the products of long-lasting history and culture and economical welfare gained during the strongest periods of Ottoman Empire. These structures still able to perform their duties are unique examples reflecting all the characteristics of traditional Turkish social life and serving their historical and cultural products to the whole world in their original atmosphere[6].

It is well known that there are possibilities to improve significantly the fire performance of wood by chemical treatment and to widen its application options. In general, the amount of flame retardant uptake to the wood is directly proportional to the improvement of reaction to fire characteristics [7]. Important reactions to fire parameters in the full-scale fire are heat release rate and time of flashover [8]. Flame retardant treated materials may have much better fire performance concerning these parameters than untreated wood products. Wood coatings more often are designed to retard ignition and rate of burn rather than to provide the fire-resistive barrier which is more typical of steel coatings. Typically, coatings protective (or retardant) against cellulosic-type fires are applied in thin film coat sup to 1.5 mm (60mils) thick. These coatings are usually not very weather able; so, for outdoor applications, a protective topcoat is needed [9].

The aim of this study to investigate combustion properties of fire retardant finishing materials on Scotch pine (Pinussylvestris L.) which 120-years in service historical wooden houses.

[1*] *Corresponding author: Karabuk University, Department of Industrial Product Design, 78600, Safranbolu/Karabuk, Turkey.* *resen@karabuk.edu.tr*

2.MARERIAL AND METHOD

Wood Material

Scotch pine (Pinus Sylvestris L.), wood was chosen randomly from timber supplier of Karabuk, Turkey. A special emphasis was put on the choice of the wood material. Accordingly, non-deficient, whole, knotless, normally grown (without reaction wood, decay, insect, or fungal infection) wood materials are selected.

Varnished Material

After a fire starts, any reduction in the propagation of flames can be decisive in saving lives. One of the purposes of fire retardant coatings is to reduce the rate at which the fire spreads and thereby retard it. As regards fire protection, most countries have very strict regulations concerning the performance of fire-resistant and fire-retardant coatings, especially for the treatment of bearing structures, coatings and wooden works. Wood exhibits an important aesthetic importance and fire retardant coatings for wood should combine fire protection with excellent aesthetic results. "Safety performance + Finish performance". When it is mandatory to conform to fire regulations, the architect/designer or authorizer issuer of the fire certificate may calculate the fire load (quantity of flammable material per square meter and relevant calorific power) for each room, assessing the class that each construction element falls into, based on emergency exits, firefighting systems, or internal permanent safety services. The technical specifications of the conventional varnishes are given in Table 1.

Table 1.Some technical properties of the conventional varnishes.

Technical Properties	Primer	Finishing coat
Density (g/cm^3)	1.220	1.150
Viscosity (second/DIN CUP 4 mm/20°)	140 sn	
Amount applied (gram/m²) 100	150 gr/m^2	150 gr/m^2
Drying type	Chemical	Chemical
Drying time (20°)	80 minute	90 minute

Preparation of Test Samples

The oversized test samples were acclimatized until they were stable at 20 ± 2 °C and 65 ± 3 % relative humidity in climate room. Later on, they were cut with the dimensions of 9x19x1016 mm according to the procedure of ASTM E – 69 [10] and finished with fire retardant finishing.10 samples were manufactured for each test sample 40 test samples were prepared in total.

Execution Test

The combustion test was carried out according to the principles of the ASTME –69. But some changes were made in the stand. For this purpose, a digital balance having 0.01 g sensitiveness has been used for determination of mass reduction of materials when they are burnt. Butane gas was used to make an ignition flame. The gas flow is standard as the high of flame is 25 cm, the temperature must be 1000 ^0C.

The distance between the bottoms of the test samples, which were hanged inside of the fire tube and the top of the gas pipe must be adjusted as 2.54 cm. During the test, mass reduction, temperature and released gas (CO, NO, O_2) were determined in every 30 seconds. The test was made under a chimney where the flow of air blown was drawn with natural draft. At the beginning of combustion test flame source was used for 4 minutes then flame source was taken away and it was continued 6 minutes. Totally 10 minutes, the test was lasted.

Statistical Procedure

Multi variance analysis was applied to determine both the amount of retention in the prepared natural and laminated samples and the effects of impregnation material on combustion with or without flame source. Concerning the Duncan test each significant test group was compared with one another and itself.

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3.RESULT AND DISCUSSION

The averages of density are given in Table 2. The air-dry density (0. 48 gr/cm³) was obtained in control scotch pine wood. The air-dry density (0.45gr/cm³) was obtained in scotch pine which 120 years of service of Scotch pine wood samples. Solid amounts of varnish types are given in Table 3.

Table 2. Average values of density (gr/cm³).

Control group	120year scotch pine wood
0.480	0.455

Table 3. Solid amounts of varnish types

Varnish Type	Primer	Finishing coat
Solid Amounts	% 76	% 59

The solid amounts of the varnish were measured. The highest solid amount of % 76 was obtained with primer varnish samples. The lowest solid amount of % 59 was obtained with finishing coat samples.

Table 4. Average of Mass Reduction (%)

Measured of time	120-year service and unvarnished	120-year service and varnished with fire retardant finishing	Scotch pine control and unvarnished	Scotch pine samples varnished with fire retardant finishing
1	3,89	3,15	2,19	2,79
2	6,98	6,23	4,98	4,09
3	10,92	8,58	9,26	5,59
4	16,10	11,22	15,86	8,81
5	26,97	13,93	23,64	13,15
6	36,68	17,31	30,59	16,46
7	45,77	22,40	39,87	18,58
8	50,47	24,89	47,27	22,37
9	59,09	27,76	54,13	23,49
10	65,04	27,97	63,28	23,60
11	75,17	28,71	74,88	24,59
12	81,71	29,13	79,94	25,19
13	85,75	29,60	84,07	25,62
14	89,40	30,59	90,00	25,87
15	95,36	32,14	92,14	26,32
16	96,18	32,67	94,40	26,87
17	96,57	32,79	95,54	28,39
18	97,55	32,89	96,17	29,78
19	97,83	33,13	97,56	30,37
20	98,45	33,25	98,17	30,74

The averages of mass reduction are given in Table 4. The highest mass reduction was (98.45%) observed in unvarnished scotch pine control samples, the lowest value (%30.74) in the 120-year service scotch pine samples with varnished fire retardant finishing. The averages of O_2 amounts are given in Table 5.

Table 5. Average of O_2 amounts(%)

Measuredof time	120-year service and unvarnished	120-year service and varnished with fire retardant finishing	Scotch pine control and unvarnished	Scotch pine samples varnished with fire retardant finishing
1	20,10	20,01	20,71	20,44
2	19,73	19,71	20,47	20,17
3	19,06	19,60	20,15	20,02
4	18,59	19,55	19,91	19,69
5	18,46	19,27	19,61	19,61
6	18,29	19,06	19,28	19,35
7	18,23	19,03	18,91	19,30
8	18,14	19,01	18,56	19,21
9	17,81	19,25	18,21	19,10
10	18,01	19,82	17,91	19,43
11	18,36	20,21	17,63	19,84
12	18,86	20,47	17,38	20,07
13	19,50	20,52	17,29	20,23
14	20,17	20,61	17,51	20,39
15	20,25	20,67	18,13	20,79
16	20,31	20,69	18,72	20,80
17	20,46	20,69	19,72	20,88
18	20,61	20,75	20,52	20,94
19	20,78	20,82	20,89	20,95
20	20,89	20,84	20,96	20,97

The highest reduction of O2 concentration (% 20,97) was measured in Scotch pine samples varnished with fire retardant finishing, the lowest change of O2-concentration (%17.29) in combustion of unvarnished scotch pine control samples.

Table 6. Average of Temperature Values(°C)

Measuredof time	120-year service and unvarnished	120-year service and varnished with fire retardant finishing	Scotch pine control and unvarnished	Scotch pine samples varnished with fire retardant finishing
1	56,19	91,31	68,10	82,46
2	76,76	111,47	85,82	96,71
3	99,87	128,88	107,40	108,93
4	126,03	150,16	130,71	124,20
5	155,65	168,28	162,57	144,56
6	182,12	184,77	187,11	159,83
7	205,03	202,79	206,65	167,97
8	232,92	211,54	234,65	180,19
9	257,55	210,93	288,30	187,31
10	286,97	193,11	383,28	190,37
11	347,65	176,52	492,10	198,51
12	453,42	162,27	520,30	209,71
13	476,22	150,36	552,16	222,94
14	406,59	141,60	490,17	208,69
15	353,76	133,77	422,06	201,56
16	315,27	126,54	355,18	187,31
17	285,65	119,00	324,13	175,10
18	262,44	113,41	287,59	163,90
19	243,91	108,11	257,86	147,61
20	228,44	104,35	234,85	134,38

The averages of temperature are given in Table 6. The highest temperature (552.1°C) variation was observed in the unvarnished and scotch pine control samples, the lowest (56.1°C) in unvarnished 120-year service scotch pine samples. The averages of variations of CO are given in Table 7.

Table 7. Variation of CO (ppm)

Measuredof time	120-year service and unvarnished	120-year service and varnished with fire retardant finishing	Scotch pine control and unvarnished	Scotch pine samples varnished with fire retardant finishing
1	46,05	59,40	9,94	33,80
2	81,12	93,20	23,10	94,64
3	99,79	108,08	41,19	141,12
4	107,40	122,78	63,43	182,52
5	140,19	148,97	99,12	215,48
6	267,70	199,42	132,33	243,36
7	428,58	204,15	159,28	256,88
8	490,69	203,31	208,72	288,15
9	476,58	199,50	250,63	306,74
10	408,73	196,55	300,55	291,53
11	245,47	175,25	347,23	266,18
12	221,47	148,13	417,82	231,53
13	198,41	95,74	423,02	219,70
14	169,93	63,71	380,12	204,49
15	152,86	51,63	283,11	177,45
16	142,89	45,46	227,74	158,86
17	128,10	40,81	168,19	97,18
18	86,27	17,58	123,82	65,07
19	52,47	9,97	85,66	41,41
20	43,69	6,59	52,26	21,97

The highest increase in CO concentration was (490.69ppm) observed in the unvarnished and 120 year service scotch pine samples and the lowest in (6,59ppm) varnished with fire retardant varnish and 120 year service scotch pine samples.

Table 8. Variation of NO (ppm)

Measured of time	120-year service and unvarnished	120-year service and varnished with fire retardant finishing	Scotch pine control and unvarnished	Scotch pine samples varnished with fire retardant finishing
1	1,56	2,34	1,59	1,04
2	2,73	3,64	3,48	3,64
3	3,64	7,15	5,36	4,68
4	5,59	9,49	6,63	7,80
5	6,37	13,00	9,13	10,92
6	8,71	16,51	11,41	13,78
7	11,31	17,68	13,59	14,82
8	12,48	17,68	14,37	15,60
9	13,52	16,51	16,04	13,78
10	14,56	17,68	17,21	11,44
11	11,05	20,02	19,83	9,36
12	8,71	20,02	20,31	8,06
13	7,41	9,49	22,13	6,50
14	6,76	5,98	17,68	5,46
15	3,77	3,64	14,89	4,68
16	1,69	2,47	11,99	2,73
17	1,17	2,47	6,92	1,43
18	1,04	1,56	2,35	0,91
19	0,52	1,43	1,33	0,65
20	0,52	1,30	0,03	0,39

The averages of variation of NO are given in Table 8. In this study, the highest increase in NO concentration was observed in the experiment of (22.13 ppm) unvarnished scotch pine control samples and the lowest in those of (0.03 ppm) unvarnished service scotch control pine samples.

4.CONCLUSION

According to Table 4, after taking the flame source from the fire tube, the highest mass reduction (98.45 %) was observed in the unvarnished control samples, the lowest in varnished with fire retardant finish and 120 year service scotch pine samples (30.74 %) at the second stage of combustion. It has been observed that while 120 – year service scotch pine samples finished with fire retardant samples decreases mass reduction values 68,77 % in average.

According to Table 5, the highest O2 consumption was observed in Scotch pine samples varnished with fire retardant finishing (20,97 %). It been has observed that while scotch pine samples finished with fire retardant samples decreases O2 consumption values 17,54 % in average.

According to Table 6, the highest temperature was observed in the scotch pine control and unvarnished samples (552.10C). It has been observed that while 120 – year service scotch pine samples finished with fire retardant samples decreases temperature values 89,83 % in average.

According to Table 7, the highest ratio of CO was observed in the 120 – year service and unvarnished samples (490.69 ppm). It has been observed that while 120 – year service scotch pine samples finished with fire retardant samples decreases ratio of CO values 98,6 % in average.

According to Table 8, the highest ratio of NO was observed in unvarnished scotch pine control samples (22.13 ppm). Consequently, fire retardant finishing was found to be the most successful according to the CO amounts and mass reduction. It can be proposed that protecting by varnishing fire retardant finishing of historical wooden structure due to fire risk.

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Religion And Environmentalism: A Search For The Religio-Philosophical Basis Of Environmentalism

Ali BAYER[1*] , M. Ali KIRMAN [1]

Abstract

One of the most important matters in today's world is the environmental problems. People believe is right and wrong environmental degradation such as environmental pollution, deforestation, global warming and source water pollution are arise from human's environmental worldview. Most of the environmental problems although scientists have warned us for decades about the potentially devastating consequences of climate change. The purpose of this study is examining the relationship between religious behavior and environmental worldview. People have customs, thoughts, philosophies, variety of life styles cultures, and beliefs. According to authors the religious world view of the people is their way of approach at environment. These approaches make different postulates about the world and create views that perceive the world differently. People really want to know the high being who holds this cosmos and controls human life. In understanding the role religion has, it can then be determined if religious social structures are a viable option to promote positive environmental behavior. Every religion or ideology has its own environmental purposes and functions. According to Islamic view man is responsible for protecting the environment that was delivered him. As a result if we are to reverse the deterioration of our environment then we have to make some hard choices and change our practices. In other words, ecological change calls for personal change.

Keywords: *Religion, change, environmentalism, worldview, philosophy*

1. INTRODUCTION

Environmental sociology is a relatively new area of inquiry that emerged largely in response to increased societal recognition of the seriousness of environmental problems. The growth of sociological work on environmental issues has been accompanied by a critique and reassessment of core sociological assumptions and practices.

In the 19th century, there have been fundamental changes such as great migration waves, world wars, famine, reform, renaissance, enlightenment, French Revolution and industrial revolution in the world. These events in social life changed the way people's view of the world, nature and environment. Environment is more than trees, water, land, and air. It is a sense of peace, an understanding of our place in our society. It sustains our satisfaction in life and our interest in caring for the life around us. Recognizing the sustaining forces that make up our environment sometimes requires a time of deep introspection. The world is undergoing accelerating change, with environmental stewardship lagging behind economic and social development. Environmental gains from new technology are being overtaken by increasing population and economic growth. It is still possible, however, to slow down trends towards environmental degradation by shifting economic activity to a more sustainable pattern (Wade-Benzoni, 2007: 166) The emphasis in the study is on consciousness because progress toward solving environmental problems is likely to depend on environmentally beneficial attitudes more so than on environmental behaviors (Pickett et al., 1993). According to Folz et al. (2003), no understanding of the environment is adequate without a grasp of the religious life that permeates the human societies which inhabit the natural environment.

[1*] *Corresponding author: Karamanoğlu Mehmetbey University, 7000, Yunus Emre, Karaman, Turkey:alibayer@kmu.edu.tr*

Early period environmental studies focused on personal background factors such as age, income, education, and so on that predispose individuals to environmental concern. Demographics provide only a limited explanation of environmental behavior, however (Granzin and Olson, 1991), and there are members of all demographic categories who are willing to participate in environmental activities. Diamantopoulos et al. (2003) provide a comprehensive review of the literature concerning socio-demographics in profiling green consumers and conclude that: (1) females are more environmentally concerned and participate in more pro-environment behaviors; (2) married people are more likely to participate in pro-environment behaviors; (3) there is a negative correlation between age and pro-environment attitudes; (4) larger families have more positive pro-environment attitudes; and (5) there is a positive correlation between education and all the components of the environmental domain knowledge, attitudes, and behavior (Brennan and Lo, 2002: 13).

2. DEVELOPMENT OF ENVIRONMENTALISM

Each person is born into a social and cultural environment. Humans, like other species, must also have a place to exist, and the environment provides our home-where we live, work, play, travel, and spend our lives. There are three functions of the environment. The environment provides us with the resources that are necessary for life, ranging from air and water to food to materials needed for shelter, transportation, and the vast range of economic goods we produce. Secondly, in the process of consuming resources humans, like all species, produce ‘‘waste’’ products; indeed, humans produce a far greater quantity and variety of waste products than do other species. Finally, the environment is to provide a ‘‘living space’’ or habitat for human populations. Humans, like other species, must also have a place to exist, and the environment provides our home-where we live, work, play, travel, and spend our lives (Dunlap, 2000: 800).

Environmentalism**,** political and ethical movement that seeks to improve and protect the quality of the natural environment through changes to environmentally harmful human activities; through the adoption of forms of political, economic, and social organization that are thought to be necessary for, or at least conducive to, the benign treatment of the environment by humans; and through a reassessment of humanity’s relationship with nature (Elliott, 2017). Environmentalism works to correct the damage as well as prevent future destruction. Environmentalism began as a movement in the 1960s and 1970s. However, humanity's relationship and dependence on the earth for survival has existed since the beginning of time. Beginning in the nineteenth century, the Industrial Revolution caused many changes; Western people realized their behavior had a negative impact on the environment. Although nature was the focus of much nineteenth and twentieth century philosophy, contemporary environmental ethics only emerged as an academic discipline in the 1970s. The questioning and rethinking of the relationship of human beings with the natural environment over the last thirty years reflected an already widespread perception in the 1960s that the late twentieth century faced a human population explosion as well as a serious environmental crisis. Lynn White (1967) argued that the main root of Judeo-Christian thinking had encouraged the overexploitation of nature by maintaining the superiority of humans over all other forms of life on earth, and by depicting all of nature as created for the use of humans. White’s thesis was widely discussed in theology, history, and has been subject to some sociological testing as well as being regularly discussed by philosophers. Central to the rationale for his thesis were the works of the Church Fathers and The Bible itself, supporting the anthropocentric perspective that humans are the only things that matter on Earth. Consequently, they may utilize and consume everything else to their advantage without any injustice. For example, *Genesis* 1: 27–8 states: “God created man in his own image, in the image of God created he him; male and female created he them. Likewise, Thomas Aquinas argued that non-human animals are “ordered to man’s use” (Brennan and Lo, 2002: 2).

The confluence of ethical, political and legal debates about the environment, the emergence of philosophies to underpin animal rights activism and the puzzles over whether an environmental ethic would be something new rather than a modification or extension of existing ethical theories were reflected in wider social and political movements. The rise of environmental or “green” parties in Europe in the 1980s was accompanied by almost immediate schisms between groups known as “realists” versus “fundamentalists” The “realists” stood for reform environmentalism, working with business and government to soften the impact of pollution and resource depletion especially on fragile ecosystems or endangered species. The “fundies” argued for radical change, the setting of stringent new priorities, and even the overthrow of capitalism and liberal individualism, which were taken as the major ideological causes of anthropogenic environmental devastation. It is not clear, however, that collectivist or communist countries do any better in terms of their environmental record (Brennan and Lo, 2002: 2).

3. CHANGING THE POINT OF VIEWS: ANTHROPOCENTRISM, BIOCENTRISM, ECO-CENTRISM

Anthropocentrism**,** philosophical viewpoint arguing that human beings are the central or most significant entities in the world. This is a basic belief embedded in many Western religions and philosophies. Anthropocentrism regards humans as separate from and superior to nature and holds that human life has intrinsic value while other entities (including animals, plants, mineral resources, and so on) are resources that may justifiably be exploited for the benefit of humankind. White (1967) believed religion was influential in determining how people view themselves in relation to their environment. In The Historical Roots of Our Ecological Crisis, argues that because the Bible provides guidance for people about how to view the environment, the Bible presents an anthropocentric view of Christianity, which was also a dominant environmental belief in Western society in the 1960s. White claims that Christianity is "the most anthropocentric religion the world has seen" and this anthropocentric view is the cause of the environmental crisis (White, 1967: 1025).

Aristotle argues that "nature has made all things specifically for the sake of man" and that the value of non-human things in nature is merely instrumental. Generally, anthropocentric positions find it problematic to articulate what is wrong with the cruel treatment of non-human animals, except to the extent that such treatment may lead to bad consequences for human beings. Immanuel Kant ("Duties to Animals and Spirits", in *Lectures on Ethics*), for instance, suggests that cruelty towards a dog might encourage a person to develop a character which would be desensitized to cruelty towards humans. From this standpoint, cruelty towards non-human animals would be instrumentally, rather than intrinsically, wrong. Likewise, anthropocentrism often recognizes some non-intrinsic wrongness of anthropogenic (i.e. human-caused) environmental devastation. Such destruction might damage the well-being of human beings now and in the future, since our well-being is essentially dependent on a sustainable environment (Brennan and Lo, 2002: 3).

Biocentrism emphasizes the natural integrity of ecosystems at the expense of human use. In contrast with anthropocentric orientation, which places emphasis on human benefits, bio-centric orientation means life-centered and, thus, stresses the value of both humans and nonhuman species. An American biochemist, Lawrence Henderson, coined the term biocentrism in 1913 to delineate that the universe itself was the originator of life. Deep ecologists later adopted this term to refer to the idea that all lives are equally important due to their intrinsic values, regardless of their usefulness to humans (Yu-Jen, 2002: 43).

The philosophical assertion that all things have inherent value is known as ecocentrism. Eco-centrism that emphasizes wildness value also puts a brake on alleged human improvements of nature through anthropogenic production of the properties in virtue of which we value nature. A stability and integrity based eco-centrism would have to judge human activity that enhanced ecosystem stability or integrity as value increasing. A highly humanized ecosystem could be more stable, integrated, and diverse than a natural ecosystem that it replaced Only an eco-centrism that puts its central focus on wildness value can prevent the unpalatable conclusion that such human manipulation of nature would, if successful, increase intrinsic value (Hettinger and Throop, 1999: 15). Ecocentric philosophies claim that the value or worth of a rock or a tree or water is not judged simply by the ways that humans can use it. Instead, it valuable because it plays a role in the greater environment. Ecocentrism is directly opposed to anthropocentricism, which claims that humans have more inherent value than other things (King, 1995: 458).

Although both anthropocentric and bio-centric individuals express environmental concerns and have an interest in protecting nature, they have different motives. Anthropocentric individuals care for the environment because they believe that everything in nature can be used to benefit humans. For example, they protect the rainforests because the destruction of rainforests may diminish the possibility of developing new medicines that could save human lives. Conversely, bio-centric individuals protect rainforests because they believe that everything in rainforests has value in itself, regardless of its purpose for human wellbeing. In other words, nature has a spiritual dimension and intrinsic value, both of which are reflected by their experience in nature (Yu-Jen, 2002: 1)

Other environmental ethicists have suggested that it is possible to value the environment without discarding anthropocentrism. Sometimes called prudential or enlightened anthropocentrism, this view holds that humans do have ethical obligations toward the environment, but they can be justified in terms of obligations toward other humans. For instance, environmental pollution can be seen as immoral because it negatively affects the lives of other people, such as those sickened by the air pollution from a factory. Similarly, the wasteful use of natural resources is viewed as immoral because it deprives future generations of those resources. Consequently, this is the view that all the moral duties we have towards the environment are derived from our direct duties to its human inhabitants. The practical purpose of environmental ethics, they maintain, is to provide moral grounds for social policies aimed at protecting the earth's environment and remedying environmental degradation (Brennan and Lo, 2002: 7).

4. FEMINISM AND THE ENVIRONMENT

By the mid-1970s, feminist writers had raised the issue of whether patriarchal modes of thinking encouraged not only widespread inferiorizing and colonizing of women, but also of people of colour, animals and nature. Sheila Collins (1974), for instance, argued that male-dominated culture or patriarchy is supported by four interlocking pillars: sexism, racism, class exploitation, and ecological destruction. From this point of wiev, human exploitation of nature may be seen as a manifestation and extension of the oppression of women, in that it is the result of associating nature with the female, which had been already inferiorized and oppressed by the male-dominating culture (Brennan and Lo, 2002: 7). Feminism represents a radical challenge for environmental thinking, politics, and traditional social ethical perspectives. It promises to link environmental questions with wider social problems concerning various kinds of discrimination and exploitation, and fundamental investigations of human psychology. However, whether there are conceptual, causal or merely contingent connections among the different forms of oppression and liberation remains a contested issue. The term "ecofeminism" (first coined by Francoise d'Eaubonne in 1974) or "ecological feminism" was for a time generally applied to any view that combines environmental advocacy with feminist analysis. However, because of the varieties of, and disagreements among, feminist theories, the label may be too wide to be informative and has generally fallen from use (King, 1995: 462).

5. CRITICAL SCHOOL AND NEO-MARXIST VIEW

While classical Marxists regard nature as a resource to be transformed by human labour and utilized for human purposes, Horkheimer and Adorno saw Marx himself as representative of the problem of "human alienation". At the root of this alienation, they argue, is a narrow positivist conception of rationality-which sees rationality as an instrument for pursuing progress, power and technological control, and takes observation, measurement and the application of purely quantitative methods to be capable of solving all problems. According to the critical theorists, the oppression of "outer nature" (i.e., the natural environment) through science and technology is bought at a very high price: the project of domination requires the suppression of our own "inner nature" (i.e., human nature)-e.g., human creativity, autonomy, and the manifold needs, vulnerabilities and longings at the centre of human life. To remedy such an alienation, the project of Horkheimer and Adorno is to replace the narrow positivistic and instrumentalist model of rationality with a more humanistic one, in which the values of the aesthetic, moral, sensuous and expressive aspects of human life play a central part. Thus, their aim is not to give up our rational faculties or powers of analysis and logic. Rather, the ambition is to arrive at a dialectical synthesis between Romanticism and Enlightenment, to return to anti-deterministic values of freedom, spontaneity and creativity (Brennan and Lo, 2002: 16)

6. RELIGION AND ENVIRONMENT

In general, religion teaches the concept of a God or gods that created the Cosmos and everything in it. They created man in their image and likeness. Man is upon the earth to learn about himself, attain to a certain high level of spiritual development and return home from whence he came – to God and the heaven life, there to stay for all eternity. Most religions in the world emphasizes on human interactions with the environment in various perspectives. Jewishs, for instance, celebrate a special new year for plants and crops known as Tu Bishewat. Similarly, Christians are always exposed to fish, birds and wildlife (as per The Genesis) while Christmas and Easter songs are always related to animals and plants. Sikhs, on the other hand, believe that their God lives on the tree, dreams of animals and wakes amongst humans. Meanwhile, Buddhists celebrate several celebrations by praying for a harmonious environment (A. R. Agwan, 1997). This in a way reflects the close interaction between humans and the environment as the content of most religions in the world. In Islam itself, human interaction with the environment is mentioned multiple times in the Holy Quran, supported by Hadith and further explained in detail by companions and scholars. The verse in the Holy Quran regarding the assignment of humans as the Caliph started with the general interaction between humans and the earth, and supported by many other verses.

In affluent developed nations, the rise in environmental concern at both the government and business levels occurred because environmental risks were perceived by the public and this led to popular demand for corrective and preventive action. Religious environmentalism is a post-materialist environmental philosophy that has emerged from the West and has its roots in the eighteenth century European "Romantic Movement. Religious environmentalists argue that religious traditions teach that the Earth is sacred and that this has traditionally served to exert control over how people interact with the natural world.

7. ISLAM AND ENVIROMENT

Islamic beliefs, traditions and values provide an effective and comprehensive solution to the current environmental challenges faced by the human race. Islam has a rich tradition of highlighting the importance of environmental protection and conservation of natural resources. According to Islamic law, the basic elements of nature-land, water, fire, forest, and light-belong to all living things, not just human beings. Environment protection is an important aspect of Islam. The main schools of Islamic theology did not pay much attention to a "theology of nature" which would be of significance in the present-day environmental crisis. By contrast, numerous works of Islamic philosophy provide not only an Islamic philosophy of nature, but what in the West would be called a "theology of nature." This is also true of Sufism, which contains the most profound expressions of an Islamic "metaphysics and theology of nature." Certain Sufi texts bring out the most inward meaning of the Qur'anic doctrine concerning the cosmos and human beings' relation to the world of nature. Scientific tradition has much to offer in the process of formulating a contemporary language expressing Islamic views of the relation of human beings and the natural environment. This contemporary Islamic view, in conjunction with various forms of technology developed in Islamic civilization, could help find a way out of the impasse created by the current environmental crisis (Nasr, 2003: 94).

Being stewards of the Earth, it is the responsibility of Muslims to care for the environment in a proactive manner. There is a definite purpose behind the creation of different species, be it plants or animals. Muslims are encouraged to reflect on the relationship between living organisms and their environment and to maintain the ecological balance created by Allah. Protection of the environment is essential to Islamic beliefs and mankind has the responsibility to ensure safe custody of the environment. Human being is one of the entities created by Allah in the whole ecological system. Hence, its existence is always correlated to other environmental entities. This indicates that the perfection of Islam hinges on application of the whole interaction between humans and the environment; physics and metaphysics (Al-Banna, 2016)

Philosophers of Islam, such as Farabi, Ghazālī, Shāṭibī, and Shāh Walīullāh explain that the aim of Shariah is to promote human welfare. This is evident in the Qur'ān, and teachings of the Prophet (s). The scholars explain that the welfare of humans is based on the fulfillment of necessities, needs, and comforts.

Necessities are matters that worldly and religious life depends upon. Their omission leads to unbearable hardship in this life, or punishment in the next. There are five necessities: preservation of religion, life, intellect, lineage, and wealth. These ensure individual and social welfare in this life and the hereafter.

From the (earth) did We create you, and into it shall We return you, and from it shall We bring you out once again. (Taha: 55)

According to the details by previous Muslim scholars, human interaction with the environment can be concluded into a more specific interaction; such as interaction between humans and the God (as worshippers), interaction amongst humans (as human beings in a society) as well as interaction between humans and other entities (as caliphs). This interaction concept is ongoing in every mukallaf and it is carried as amanah. It is not merely an ethic or an alternative task, but an obliged duty of human beings

Plants or flora is substantial entities that always interact and have a big contribution in human's life. In the Holy Quran, flora is given a special attention and there is even a surah named after a plant, At Tin (the fig tree). Furthermore, there are numerous verses that mention about human interaction with flora; e.g An Nahl: 12, Al An'am: 141, Al Anbiya'; 78 and etc. Islam also stresses on several principles related to human interaction with flora; for instance: • Protecting and conserving flora and derivates in its natural forms; flowers in their colourful hues and leaves in their green tones. This world is beautiful and green and Allah has made you His representatives on it and He sees (all things). (Narrated by Muslim) • Avoid cutting, shearing or causing the plants to die without a reasonable excuse • Make use of the plants appropriately (Al-Banna, 2016).

8. RESOURCE CONSERVATION AND WASTE

The Islamic perspective on environment protection reflects a positive image about Islam and how it embraces every single matter the humans face on earth. The Islamic attitude towards environment and natural resource conservation is not only based on prohibition of over-exploitation but also on sustainable development. The Holy Quran says:

"It is He who has appointed you viceroys in the earth … that He may try you in what He has given you." (Surah 6:165)

"O children of Adam! … eat and drink: but waste not by excess, for Allah loves not the wasters." (Surah 7:31)

Islam has always provided the keys to a harmonious life in which humans refuse to take more from nature than they need for their sustenance and enjoyment. Islam has repeatedly warned about the imbalances and inequalities that would arise if one were not to follow its recommendations. According to the Holy Qur'an, environmental conservation is a religious duty as well as social obligation, and not an optional matter. The exploitation of a particular natural resource is directly related to accountability and maintenance of the resource.

Today, with the increasing awareness of the dangers facing our planet and the great interest in green ideas, a reflection on the guidance of the religion in this area proves helpful and relevant.

The modern environmental theory by western scientists did not come up with a holistic solution. In short, the philosophy of Islamic environmental ethics theory as discussed by scholars five rationales (rukun) namely tauhid, khilafah, amanah, wasatiah and tawazun. These five rationales can be further explained into simpler guidelines and should be the pre-requisites to construct the codes of Islamic environmental ethics. Amongst the criteria that should be the fundamentals and emphasized in the Islamic environmental ethics are:

Understanding of the environment, hierarchy, roles and of the attitude of the consumers must be based on the main reference. The personal interests of humans, animals or other ecosystem should not be in the agenda at all. Islamic environmental conservation should frame the importance of wahyu as the primer guidance or in simpler terms, as a God-oriented interaction. The tauhidic concept based on the God as the Creator like this actually ensures total environmental conservation in a more balanced way.

Humans are assigned by Allah as the caliph, with the responsibility (amanah) to manage and administer the environment. The environment acts as the realm for humans to conduct the assigned tasks before being evaluated by Allah. However, humans are not left alone to bear the important duties, instead they are guided by syariat via wahyu. A caliph with strong belief on tauhid will not find difficulties in performing the syariah tasks. Humans who hold strongly and realize their obligation towards Allah when accepting the trust and stewardship (amanah khilafah) will never commit harms on any environmental entities under their stewardship (khilafah). This is mentioned in the Holy Quran:

We did indeed offer the Trust to the Heavens and the Earth and the Mountains; but they refused to undertake it, being afraid thereof, but man undertook it, He was indeed unjust and foolish (Al Ahzab: 72)

Therefore, it is concluded that whatever theories and ideologies applied in the context of environmental science, as long as it is based on the concept of stewardship (khilafah) that carries the responsibilities (amanah) assigned by Allah in implementing the syariah application, it is undoubtedly leading to sustainable environmental management and conservation.

The environment is created with functions to contribute and serve the human beings. This is understandable by many evidences, as one of them explained: And they (the animals) carry your heavy loads to lands that you could not (otherwise) reach except with souls distressed: for your Lord is indeed Most Kind, Most Merciful. (An Nahl: 7)

In today's modern world, commercial values are unreasonably worshipped to the extent that entities in the environmental ecosystem are also valued based on their commercial status. In Islam, social and general welfare should be given a priority more than personal interests or minority entities. Furthermore, in fighting for the rights specified for environmental entities, especially humans as the administrator or manager, the values of responsibility should come before the rights. In the cycle of environmental entity, the interrelated interaction will be harmonious and balanced when each entity performs their roles and responsibilities respectively, hence completing each other. Each entity that cares for and gives priority on other entities will create a mutual respect thus leading to a better interaction amongst them (Fazlun, 2010: 13).

The Islamic theory and philosophy never accentuate on opposites because of the moderation in constructing them by the same main references in harmony of the environmental philosophy. The theory or philosophy in Islam does not incline to opposition due to its moderation in constructing the philosophy and theory that suit the same main reference, contemplating a harmonious environmental philosophy that compiles all views and applications. Theories like anthropocentrism, egocentrism, animal rights, ethnocentrism or any otherwise created by Western extremists are philosophies accepted by Islam moderately, without bias on any and not totally against any.

The environment is readily created balanced and of the best measure specified by Allah. There are numerous verses in the Holy Quran that discuss and explain the balance and measures that Allah has fixed in the creation of the universe. The tawazun concept should steer the actions and decisions in the protection and interaction with the environment. The pairing concept, for instance, should be assimilated so as to hinder the wrongdoings on the environmental entities. The harmonious balance in the ecosystem cycle has been intelligently and perfectly created by Allah. Anything lacking or excessive in the ecosystem cycle may lead to continuous harm and spread to other entities in the cycle.

(Allah) Most Gracious! It is He Who has taught the Qur'an. He has created man: He has taught him speech (and intelligence). The sun and the moon follow courses (exactly) computed; And the stars and the trees - both (alike) bow in worship. And the Firmament has He raised high, and He has set up the Balance (of Justice), (Ar Rahman: 1-7)

The same applies to the balance in other contexts such as in evaluating the hierarchy of environmental entities based on material and non-material values. The values of each entity should be made in a reality context without prejudice on any. Another factor to be considered is the balance of concern on environmental conservation; physically and spiritually and the balance to acquire short term (duniawi) and long term (ukhrawi) returns.

Understanding of the balance in the environment created by Allah should be apprehended and utilized as the core in the application of environmental theory, especially in today's world that sees human greed for their insatiable personal interests that blindfolds them from the real perspective. This consequently leads to opposition, negative competition and fatality in some circumstances. The balanced Islamic concept is in agreement with the moderation concept, hence it should be enhanced based on the fundamentals of tauhid as well as the awareness of trust and stewardship (amanah khilafah)

With the theory application based on the five abovementioned rationales (rukun), environmental philosophies should be inferred more efficiently and effectively in any flexible ways possible. Islam has fixed various guidelines in rules/orders, prohibitions, suggestions and even fundamental principles to be deliberated with research and innovation based on human intellectual for environmental development. As the only perfect (syumul) religion in all aspects, it is undeniable that the evidences in the Holy Quran and Al Hadith are the principal reference that has summarized diverse principles for us to obey. Even the previous Muslim scholars have substantially contributed to the growth, research and the arrangement of guidelines regarding human interactions with the environment as well as in the aspect of environmental management

9. CONCLUSION

Environmentalism has focused the importance of a clean and healthy environment for human existence. Beyond our physical dependency on the environment are the intangible and emotional connections people feel with nature and these connections contribute to overall happiness in life. Environmentalism seeks to protect and preserve the earth for present and future generations; the intangible and emotional connections with nature are at risk. Environmental awareness and protection of natural resource is an integral part of Islamic beliefs. A major objective of Islamic teachings and Prophet traditions is to build and maintain a healthy and clean environment which is devoid of any source of pollution and misuse.

Islam views the attitude of interaction in the environmental ecosystem as a big issue when the trust and stewardship (amanah khilafah) are granted to humans as an important appointment to manage and administer the environment.

As Bryan Norton puts it, the world faces a global challenge to see whether different human groups, with widely varying perspectives, can perhaps "accept responsibility to maintain a non-declining set of opportunities based on possible uses of the environment".

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Biography: Ass.Prof. Ali Bayer is head of Sociology of Religion at the Faculty of Divinity, University of Karamanoglu Mehmetbey, Karaman/Turkey. His research interest are family, domestic violence, secularization, modernization, religious literacy. He has contributed articles to some journals. He has participated to some national and international conferences.

Biography: Prof.Dr. M. Ali Kirman is head of Sociology of Religion at the Faculty of Divinity, University of Cukurova, Adana/Turkey. His research interests are centered on the modernization, the secularization, the new religious groups in the West and modern Turkey, and related subjects, i.e. religious conversion and family. He is author of five books in Turkish. He has contributed articles to some journals. He has participated to some national and international conferences.

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Determination of Noise Levels At Central Balikesir Hospitals

Atilla MUTLU[1*]

Abstract

In this study, our goal was to determine of noise sources and emission levels from very sensitive environments, such as hospitals, at downtown of Balikesir. In the city centrum, it was also aimed to create noise pollution maps as the first time for those full-scale hospitals in Balikesir by carrying out of this scientific study. According to the study results, it was determined that the noise level in Balikesir State Hospital, where is located to closer to the city center, was higher than the noise level in Ataturk State Hospital. In general, the predicted noise values at Balikesir State Hospital were as high as about 9% (or approximately 7dBa) than the actual measured values. The modeling process was not performed at ASH, because the noise levels in the Ataturk hospital did not exceed the legal limits.

Keywords: *Balikesir, CadnaA, Hospitals, Noise*

1.INTRODUCTION

It is known fact that noise affects human health. Full-scaled hospitals where locate in the city downtown are assessed within sensitive areas by the environmental noise regulations [1]. Therefore, hospitals are one of the most sensitive spots in terms of noise. During the health service hours, traffic-related noise arises on the on the main streets. Patients and medical staff are adversely affected psychologically, biologically and physiologically due to existing noise levels. This situation affects the quality of the health care services [2], [3], [4]. For this reason, it is necessary to identify sources of noise emissions in which hospitals are exposed and it is also required to prepare noise distribution maps in that sensitive areas [5], [6], [7].

In a previous study, correlations between air pollution and traffic related noise levels were examined. As a result of the study, it was determined that there was a positive interaction between air pollution and noise levels caused by traffic [8]. In another study, the noise level of the traffic was defined as the degree of impact. The net noise level from the source and the number of repetitions that occurred during the traffic activities were consider the main parameters of the noise impact [9]. The another study reports that tires, which are the most important component of the running mechanism of the vehicles, should be produced in relevant qualities in order to reduce potential asphalt noise [10].

In this study, which was made for the first time in Balikesir downtown, it was aimed to determine the noise levels that the hospitals were exposed during the service hours. It was also intended to prepare noise distribution maps for those full-scaled hospitals.

2. MATERIALS AND METHODS

a. Study Area

In this study, noise level measurements were made at Balikesir State Hospital (BSH) and Ataturk State Hospital (ASH) in Balikesir's downtown. Balikesir State Hospital has been serving since 1954 and has a capacity of 200 beds [11]. Ataturk State Hospital, has been serving since 1965 and has a capacity of 521 bed [12]. In the scope of the study, the first stage measurements were made at the main entrance where human and traffic activities are highly intensive (see Figure 1).

[1*] *Corresponding author: Balikesir University, Department of Environmental Engineering, 10145, Cagis/Balikesir, Turkey.* *amutlu@balikesir.edu.tr*

(a) (b)

Figure 17. Balikesir state hospital (a) and Ataturk state hospital (b)

b. Study Plan and Data Collection

Measuring points for noise levels were selected in order to represent daily activities, Rush hours were determined as morning hours (work starts, beginning of school and patient admission) and evening hours (work off, school day). Measurements were made, on Monday and Wednesdays at the BSH with 3 days a week; only on Fridays at ASH, between 07:30 AM - 6:00 PM.

3. RESULTS AND DISCUSSIONS

c. Results of Noise Measurement at Hospitals

The measurement results of the study and the general descriptive statistical parameters of the obtained data are presented in Table.1 and Table.2.

Table 7. Environmental noise levels of Balikesir state hospital

Dates	**Minimum**	**Maximum**	**Means**	**Std.Dev.**
8 April	54.0	79.8	**65.9**	4.0
10 April	53.0	81.2	63.8	4.8
15 April	52.1	78.7	62.4	4.6
17 April	49.9	85.9	62.3	4.7
22 April	53.2	82.3	63.2	4.7
24 April	49.9	84.6	63.6	4.4
29 April	42.5	78.4	57.7	5.4
1 May	43.2	78.7	58.2	5.9
6 May	42.5	78.0	58.5	5.5
8 May	53.5	83.1	62.8	4.2
13 May	48.4	88.6	62.2	5.9
15 May	49.6	80.8	61.6	5.0
20 May	50.7	79.5	62.4	4.5
22 May	48.5	83.0	62.3	4.7
27 May	50.9	79.3	61.9	4.7
29 May	51.0	83.5	**65.9**	5.1
3 June	53.0	82.1	63.0	4.7
5 June	42.9	78.4	59.0	5.5
10 June	48.7	83.5	62.3	4.5
12 June	49.20	80.40	61.2	5.0

As a result of the measurements that performed in BSH, a total of 21 individual measurements were conducted at the BSH's main entrance. The lowest noise level during measurements was recorded as 42.5 dBA, while the highest level was recorded as 88.6 dBA in BSH. According to statistical analysis results, the morning noise levels were higher than evening noise levels in those collected 21 data sets. The results also show that mean noise levels of 8 April and 29 May exceeded the legal limits (65 dBA).

Daily noise levels in ASH were also measured and the measurement results are presented in Table.2.

Table 2. Environmental noise levels of Ataturk state hospital

Dates	Minimum	Maximum	Means	Std.Dev.
5 April	49.5	74.1	55.9	3.0
12 April	49.5	75.3	55.9	2.9
19 April	52.6	72.4	59.3	3.4
26 April	49.9	73.3	59.4	5.4
3 May	51.2	77.0	57.6	2.9
10 May	49.0	74.8	55.4	2.9
17 May	49.7	69.3	55.4	3.4
24 May	50.5	71.4	56.2	3.9
31 May	49.1	73.8	54.8	2.6
7 June	49.9	69.0	55.3	2.8
14 June	49.9	73.4	56.9	3.7

A total of 11 individual measurements were conducted at the ASH's main entrance. The lowest noise level during measurements was recorded as 49 dBA, while the highest level was recorded as 77 dBA in ASH.

d. Modeling and Mapping of Noise Levels

Nowadays, the first step to be taken for the environmental noise problem is to determine the current noise level and create noise level maps [13]. Noise maps are considered as a way of numerically and visually expressing distributions of environmental noise from related sources [14]. In this method, the changes in the potential noise levels from physical factors in the environment are illustrated and also animated on a map. Noise mapping is done by including several preliminary information such as detailed map, road information and population density. Traffic (route) plans, vehicle numbers, vehicle speeds, vehicle types, road features as inputs are transferred to the noise map program in compute [15]. The noise levels, for a specific area, obtained from the noise maps are compared to the official limit values that are found in the legislation [16].

In the second part of the study, noise measurements were conducted at BSH (Balikesir State Hospital), where local traffic activities are more intense, to ensure the validity of the modeling results. In order to determine noise levels that the BSH may be exposed, a total of 15 measurement points are selected around the hospital (See Figure.2).

Figure 2. Measurement points at BSH (Balikesir state hospital)

A software named CadnaA (Computer Aided Noise Abatement, DataKustik, 2016) was used to visually express the change in environmental noise levels in study area [17]. In this program, the number of vehicles (normal and heavy vehicles) passing through the near streets, the coordinates of the hospital, all the transportation lines of the hospital area, the technical specifications (one way / two way, lane width) of the roads are used as input parameters. Also, details of receptors to figure out noise levels of hospital has been exposed are indicated on the map. Estimated and Modeled environmental noise distributions for BSH are presented in Figure 3.

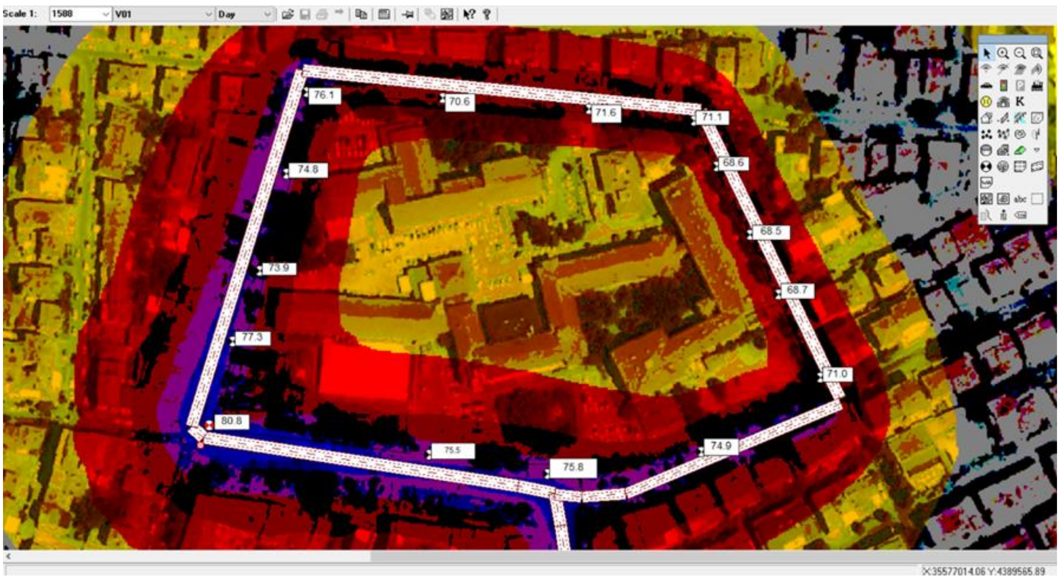

Figure 3. Environmental noise map of BSH (Balikesir state hospital)

After mapping, measurements were made at precisely specified receptor points in the model to investigate the validity of the predicted environmental noise levels. For this process, on-site measurements were held regularly on Mondays, Wednesdays and Fridays as three times a week. The overall results of the measurements are presented in Table 3.

Table 3. Environmental noise levels of Balikesir state hospital

Measurement Points	**Minimum**	**Maximum**	**Means**	**Std.Dev.**
Point1	47.0	111	68.7	6.4
Point2	49.9	114.9	68.2	6.6
Point3	48.7	98.9	67.4	6.7
Point4	51	84.6	66.7	5.2
Point5	44.3	84.3	68.3	5.7
Point6	49.6	105.1	66.6	5.8
Point7	50.9	88.4	65.2	5.1
Point8	48.2	89.9	65.6	5.2
Point9	51.2	98.2	64.8	6.4
Point10	50.3	89.9	66.2	5.3
Point11	49.1	102.1	64.1	5.7
Point12	52.2	90.6	66.1	5.1
Point13	51.1	94.5	66.4	6.2
Point14	51.8	92.4	68.0	5.3
Point15	48.5	101.2	67.7	5.7

In the last part of the study, the modeled and also the measured environmental noise levels were compared and the results are presented in Figure 4. Generally, it is determined that the modeled values were higher than the measured values by about 9% (in other words about 7dB) in BSH. The modeling process was not performed at ASH, because the noise levels in the Ataturk hospital did not exceed the legal limits.

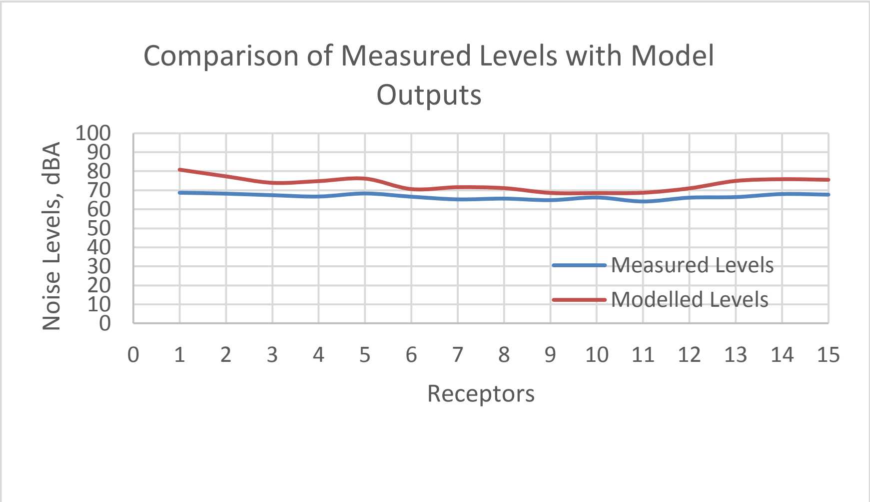

Figure 4. Measured and modeled environmental noise levels of BSH (Balikesir state hospital)

In a similar study in Greece stated that environmental noise levels were measured as 52.6 (± 8.2 dBA) and 59 (± 2.2 dBA), respectively, in two different hospitals [18]. It might be concluded that the measured noise levels at BSH (Balikesir State Hospital) were about 10% higher than those measured hospitals in Greece. This difference may be occurred that due to the fact that our hospital has more traffic density.

4.CONCLUSIONS

The following results were obtained as a result of the studies that carried out in full-scale hospitals in downtown Balikesir City;

- ✓ The equivalent noise levels in BSH (Balikesir State Hospital) where is located in Downtown Center were found to be statistically higher than ASH (Ataturk State Hospital) where is located in the West side of the Downtown,
- ✓ The equivalent noise levels of BSH were found to be higher in morning time than in other time periods for that hospital,
- ✓ It was determined that the equivalent noise levels in the Ataturk hospital did not exceed the legal limits,
- ✓ When the measurement results are taken into consideration, it was determined that the level of noise in BSH, which is located in the downtown, was higher than the noise level in ASH,
- ✓ As a result of the environmental noise levels obtained from the noise maps, it was understood that the values modeled in BSH, in general, were as high as about 9% (in other words about 7dBA) than the actual measured noise levels.

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BIOGRAPHY

Atilla Mutlu is an Assistant Professor of Environmental Engineering Department at Balikesir University. He received Ph.D. in Biogolical and Agricultural Engineering from the Texas A&M University, Texas, USA. He has been active in the area of pollution from agricultural and industral operations. He has also intended to study in noise pollution from traffic activities in local scales. His international experience includes education and academic areas in United States, South Korea, Turkey. His current research involves study of air pollution monitoring and modeling from industrial sites, greenhouse gases emissions from agricultral sites and also mapping environmental noise in local areas.

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Analysis of Air Pollutans Level In Balikesir Using Advanced Level Air Dispersion (AERMOD) And Long-Term Meteorological Data Processor (AERMET) Models

Atilla MUTLU[1*]

Abstract

It is a known fact that air pollutants have adverse effect to human health and to environment due to rapid development in industrial sites and increasing population density more likely in downtown of cities. In this unsuitable conditions, any protection approaches for controlling air pollutants within their standard limits have more importance than ever before. Nowadays, the major air pollutants are being emitted in downtown sites of cities. In particular, high level air pollution episodes occur in Balikesir during both cold and warm meteorological conditions that may cause severe asthma and allergic symptoms.

The main effect of industrial, commercial-residential sites and mobile sources on the related air pollutant levels will also be evaluated by using both AERMOD (AMS/EPA Regulatory Model) dispersion model and long-term meteorological data processor (AERMET). The output of AERMOD and AERMET models will be expected to understand how to disperse long term pollution levels in the city.

Keywords: *AERMOD, AERMET, Air Pollution, Balikesir, PM*

1.INTRODUCTION

The World Health Organization (WHO) published a risk assessment report in 2006 and the report emphasizes “fresh air is the most basic necessity for human health and well-being" in the introduction citation. The report has once again demonstrated the importance of clean air for living beings that form human and ecosystem [1]. Globally, the main anthropogenic air polluters are concentrated in urban areas. For instance, traffic, industry and residential heating systems are considered as the main sources of urban air pollution. Meteorology, topographic structure and urban settlements are important factors affecting the dispersion, storage and chemical conversion processes of air pollutants. Clinical studies on humans have been reported to increase respiratory tract diseases of pollutants such as ozone (O_3), sulphur dioxide (SO_2), particulate matter (PM), nitrogen oxides (NO_x), and biogenic antigens such as pollen. [2], [3], [4], [5], [6]. Similar studies have shown that there is a relationship between air pollution level and increased symptoms of respiratory tract, and increased incidence of death [7], [8]. It has been found in other studies that there is a relationship between air pollution levels and adults/children as of increased respiratory tract complaints or hospital and in some cases emergency admissions due to exacerbation of asthma [9], [10], [11].

Particulate matter, especially PM_{10}, emission sources are considered as industrial (especially cement plants), heating, coal and mine, excavation areas, particles from vehicle exhausts, dust from tires and roads [12], [13].

American Meteorological Society/Environmental Protection Agency Regulatory Model (AERMOD) is an atmospheric dispersion modeling software for air pollutants. AERMOD contains three separate components: AERMOD (AERMIC Dispersion Model), AERMAP (AERMOD Terrain Preprocessor), and AERMET (AERMOD Meteorological Preprocessor) [14]. AERMOD was first presented by USEPA as a new dispersion model that also included ISCST3 (Industrial Source Complex Short-Term model version 3) model in April-2000. The new model has the basic differences and innovations of the old model ISCST3. The differences are as follows; the way that the polluted gas cloud follows is characterized more realistically under different factors, more detailed and comprehensive meteorological data entry, new meteorological data format, more

[1*] *Corresponding author: Balıkesir University, Department of Environmental Engineering, 10145, Cagis/Balıkesir, Turkey.* amutlu@Balıkesir.edu.tr

detailed data entry on surfaces with contaminant distribution, more detailed PBL (Planetary Boundary Level) theory, advanced MLH (Mixing Layer Height) prediction, elaboration of topographic surfaces (detailed elevation parameters and surface characterization features etc.) [15], [16], [17]. Air quality dispersion programs such as AERMOD are employed to predict ground level concentrations of the air pollutants that exists in the atmosphere under different scenarios such as meteorological conditions, topographic properties and time zones [18], [19], [20], [21]. Air quality dispersion models are an alternative method when air pollutants from industry and also livestock are not technically feasible to measure on site or near source [22], [23]. AERMOD is used to determine the dispersion and effects of short and high-level (chronic) contaminant concentrations, and has also shown high performance in long-term (monthly or yearly) epidemiological studies [24].

In this study, the possible dispersion of PM_{10} emissions from an industrial operation in downtown Balikesir were investigated taking into account the existing meteorological and surface topography characteristics. The aim of this study is to show possible the temporal and spatial variability of the PM_{10} emissions affecting the air quality in the city center. The use of model such as AERMOD is beneficial in determination of risky areas of the city that may occur due to atmospheric pollution, contributing to the public awareness, it is aimed to present proposals in decision making process to the local authority.

2.MATERIALS AND METHODS

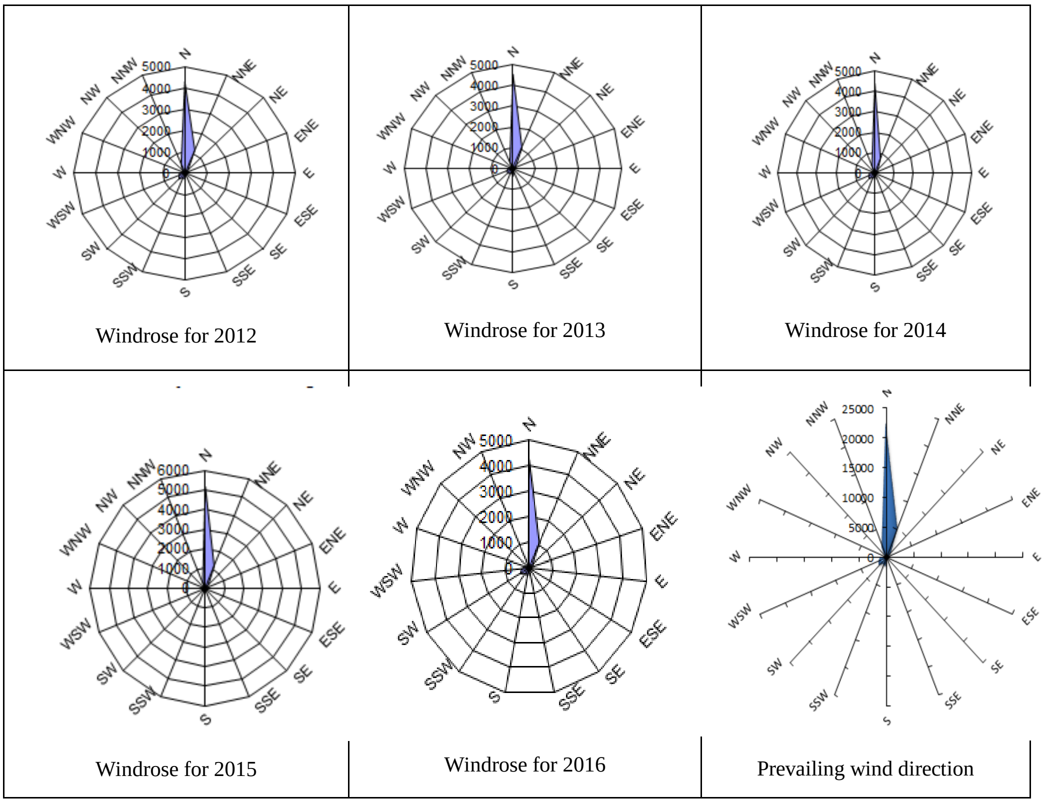
2.1.Study Area

In the study, one of the industrial site that was located nearby the downtown was selected. Industrial site, which are close to downtown, operates in the Organized Industrial Zone, which is located in the south-western region of the city. Location of the industrial site is shown in Figure1. The source is approximately 5 km to the downtown city.

Figure 18. PM_{10} sources in Balikesir

2.2.Study Planand Data Collection/Analysis

In this modeling study, the PM_{10} emission data and the physical properties of the stack were taken from the Provincial Environmental Agency within the scope of the "Balikesir Clean Air Action Plan" carried out by Balikesir Governorship. Within the scope of the Clean Air Action Plan, other meteorological data such as hourly wind speed/ direction/ frequency, temperature, precipitation, pressure and cloudiness required for air quality modeling were obtained from Provincial Agency of Meteorology. In the present study, it is important to obtain the representative meteorological and terrain data for the modeling study. The definition of "representative year" must be made for the modeling process. The obtained wind data set for the last five years are used for this purposes. When the wind data of the last five years are examined, the "representative year" was determined as the year of 2016 in terms of wind direction and frequency. For this reason, meteorological values such as hourly wind data, temperature, pressure, precipitation, cloudiness and mixture height of the year of 2016 were used in our study. The latest five-year wind data and the prevailing wind direction are presented in Figure 2.



Windrose for 2012 | Windrose for 2013 | Windrose for 2014

Windrose for 2015 | Windrose for 2016 | Prevailing wind direction

Figure 2. Wind data and prevailing wind direction of the last five years in the study area

All meteorological data of the representative year (2016) were comprehensively arranged and prepared as two separate databases, Surface and Upper meteorological data for the modeling process. Two separate meteorological data bases were then transferred to the AERMET meteorological data processor. The AERMET processor transforms the data into * .sfc and * .pfl files and sends them to the AERMOD processor. The modeling steps are illustrated in Figure 3.

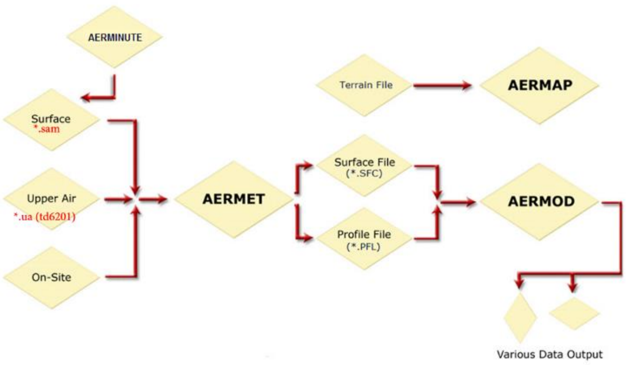


Figure 3. The AERMOD modeling process steps

The AERMOD generates the air quality dispersion maps using the characteristic surface data of the study area and PM_{10} emissions of the source.

3.RESULTS AND DISCUSSION

3.1.Modeling Results

As a result of the analysis, air quality dispersion maps were created for the maximum average values of three different time periods as in 1 hour, 24 hours and annual. As a result of hourly modeling, it shows the highest mean of PM_{10} downwind concentration value within the whole year.

The daily (24-hour) PM_{10} concentration data are averaged over a day and the highest mean concentration is used for the downwind dispersion value. The maximum daily mean of PM_{10} modeling results from the source are presented in Figure 4.

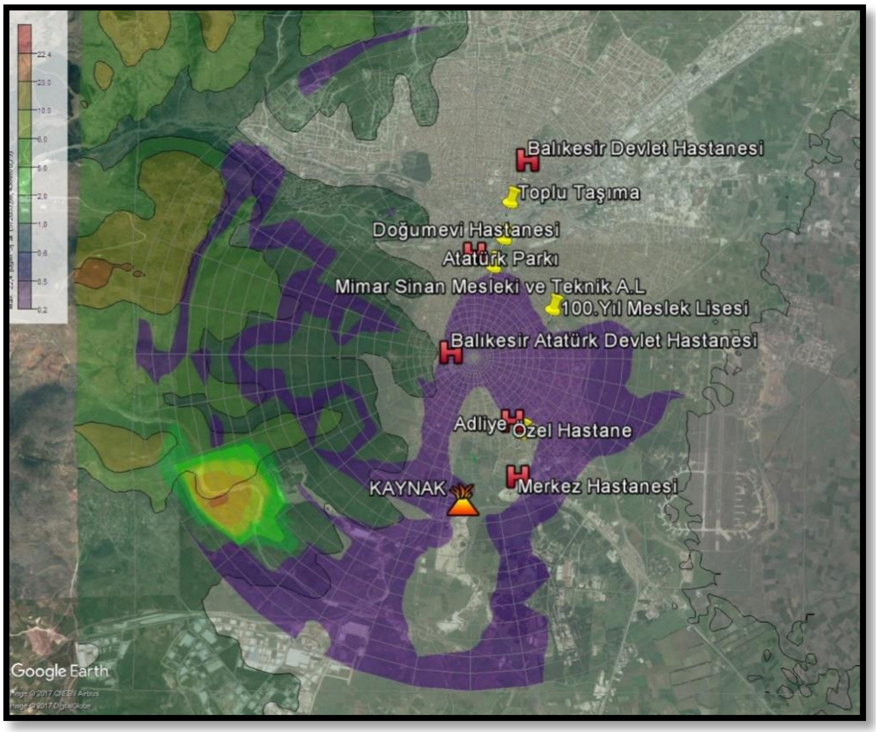


Figure 4. Maximum hourly means of PM_{10} dispersion from the source

The hourly PM_{10} concentrations emitted from the source changes with time as the wind direction changes. According to the modeling result, the maximum hourly mean downwind PM_{10} concentration was estimated to be 66.13 $\mu g.m^{-3}$ at 6 pm on February 29, 2016. It has been determined that the estimated maximum hourly average PM_{10} emission is effective in the southwestern part of the downtown and did not exceed the limit values of the regulation and it was also understood that it did not constitute any risk for the city.

The mean of the daily (24-hour) PM_{10} concentrations are estimated and the highest daily mean concentration is used for the downwind dispersion value. The maximum daily mean PM_{10} modeling results from the source are presented in Figure 5.

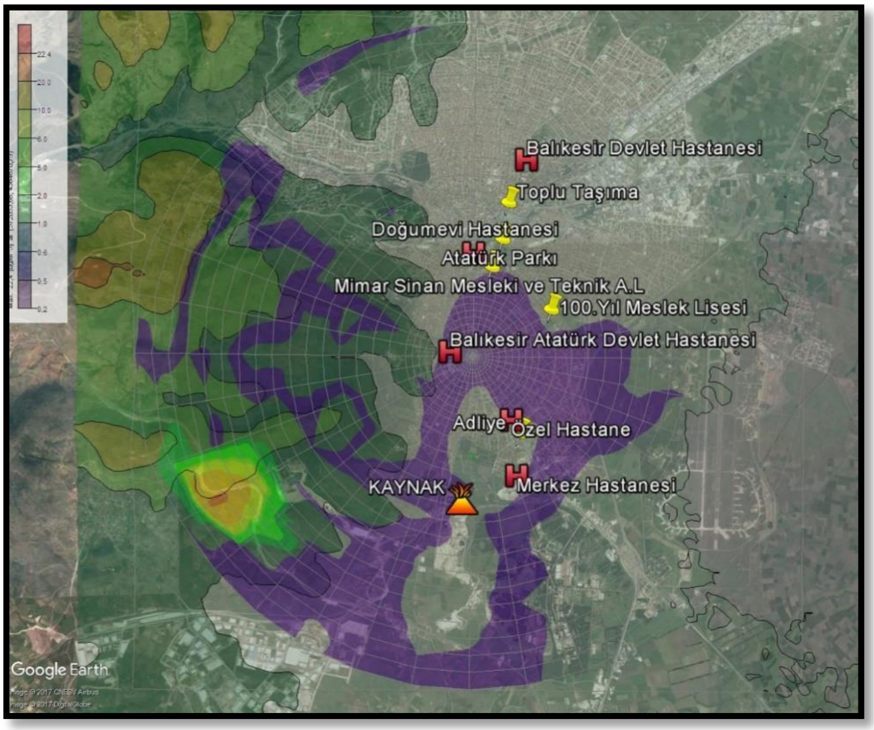


Figure 5. Maximum daily means of PM_{10} dispersion from the source

The daily PM_{10} concentration was influential in the southwest part of the downtown. The estimated PM_{10} downwind concentration from the source was estimated as 22.4 $\mu g.m^{-3}$ at the midnight on February 29, 2016. Considering the modeling result, it was understood that the estimated maximum daily means did not exceed the Short Term Limits (STL-24 hour) specified in the National Air Quality Assessment and Management Regulation (70 $\mu g.m^{-3}$ for 2017).

The maximum annual mean of PM_{10} concentration was estimated to be approximately 1 $\mu g.m^{-3}$ as a result of modeling. Thus, the estimated maximum annual means did not exceed the Long Term Limits (LTL-Annual) specified in the National Air Quality Assessment and Management Regulation (48 $\mu g.m^{-3}$ for 2017).

The source used in the modeling is approximately located southwest of the downtown. Considering the source effect, it was understood that the downtown was in the background of the source, and therefore, the PM_{10} emissions emitted from the source were propagated in the south-south west direction, which was opposite direction to the downtown based on the prevailing wind direction.

The effect of the modeled PM_{10} emissions that released from the source were also examined comparatively with measured PM_{10} emissions from the Air Quality Monitoring Station (AQMS) of the Ministry of Environment, located in the downtown of Balikesir.

The annual mean of measured PM_{10} from the AQMS was determined as 42 $\mu g.m^{-3}$ while the modeled annual mean of PM_{10} concentration at the same location was estimated to be about 1 $\mu g.m^{-3}$. The reason for the difference of the PM_{10} concentration measured by the AQMS at the downtown was thought to be caused by residential heating and transportation-related activities rather than industrial releases.

4.CONCLUSIONS

The following results were achieved in this study, which was made as the first step to contribute to the "Clean Air Action Plan" in Balikesir City;

Considering the long-term average, the prevailing wind direction for Balikesir province was determined as north-direction (N) winds.

The source used in the modeling is approximately located southwest of the downtown. Considering the source effect, it was understood that the downtown was in the background of the source, and therefore, the PM_{10} emissions emitted from the source were propagated in the south-south west direction, which was opposite direction to the downtown based on the prevailing wind direction.

No exceeding release of PM_{10} concentration from the source has been observed in the downtown. This is considered to be a negative risk for the residents of the city, especially considering the long-term meteorological data including particularly wind speed, wind frequencies, and prevailing wind direction.

The annual mean of measured PM_{10} from the AQMS was determined as 42 $\mu g.m^{-3}$ while the modeled annual mean of PM_{10} concentration at the same location was estimated to be about 1 $\mu g.m^{-3}$. The reason for the difference of the PM_{10} concentration measured by the AQMS at the downtown was thought to be caused by residential heating and transportation-related activities rather than industrial releases.

Only one source has been used for this modeling study and the number and types of the source data must be increased in the subsequent studies in future.

ACKNOWLEDGMENT

I wish to express my sincere gratitude to the Balikesir University, the Provincial Environmental Agency and Balikesir Governorship for their support in order to complete this study.

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Microemulsion-Based Biofuels from Rice Bran Oil and Ethanol: Production and Fuel Properties

Sakonwan PHOEMBOON[1], Atthaphon MANEEDAENG[1*]

Abstract

Due to environmental concerns and current fossil fuel situations, liquid biofuels have been increasingly explored and vegetable oils are the option of choice. Apart from their renewability and biodegradability, they have high oxygen but have no sulfur and aromatics, which is the main advantage of better fuel quality over the fossil fuel. However, the limitations of their use are the operation problems from low volatility and high viscosity of vegetable oil. The viscosity of vegetable oils can be reduced by a number of ways. However, microemulsion-based biofuel is an effective alternative energy which produced by using natural substances. This study aims to investigate the new microemulsion of rice bran oil and ethanol as main constituents emulsified by Tween 80 and Span 80 together with co-emulsifier of 1-Octanol, at different molar ratios of 1:5, 1:10, 1:20, and 1:30. Ternary phase diagrams of rice bran oil, ethanol, and emulsifier/co-emulsifier revealed that Span 80 exhibits an excellent emulsification as single phase microemulsion region is larger than obtained from Tween 80. This is due to the lower Hydrophilic-Lipophilic Balance (HLB) of Span 80 thus, it can greatly emulsify when a large amount of oil present in the mixture. In addition, 1-Octanol assisted and is capable working with both Tween 80 and Span 80. The increase in amount of 1-Octanol significant increases the single phase microemulsion region. In an aspect of fuel properties, the kinematic viscosity, higher heating value, and emission test of microemulsion-based biofuels were investigated in this work. It can be observed that the high amount of emulsifier, the higher viscosity obtained while higher ethanol amount could decrease the kinematic viscosity. The higher 1-Octanol and rice bran oil content resulted in larger value of higher heating value. The higher heating values increases with increasing molar ratios of emulsifier to co-emulsifier. The emission test revealed that NOx release is less than of commercial diesel while HC and CO are relatively higher.

Keywords: *Biofuel, Microemulsion, Rice bran oil, Surfactant*

1. INTRODUCTION

Most of the current energy and fuel are deried from the natural resources. As the energy depletion is concerned, it makes the world aware of new energy alternatives to replace the natural fuels that are gradually run out. The ways to finding renewable energy have been of interest is to develop of biofuels which are energy derived from plants or animals i.e. oil from animal fat, oil from various plants such as oil, palm oil, oil, rice, oil, sunflower etc [1].

In Southeast Asia, palm oil is another source of energy that is of interest in the production of biofuels. However, due to the desire to find alternative energy sources or alternative energy, palm oil is popular in the production of biofuels that maked palm oil has been very much needed and more expensive [2]. In 2011 – 2016, research was carried out to find other sources of biofuel, and rice bran oil may be an interesting alternative for Thailand [3] since Thailand is able to produce 31 million tons of paddy per a year. Most of the rice produced is processed and then consumed domestically or exported. But, rice price is expected to grow slowly [4]. With the ability to produce rice if the paddy is extracted into rice bran oil, it will be another way to increase rice value. However, if rice bran oil is used directly in the engine may cause problems with the engine due to its high viscosity, low evaporation, and become a wax when the temperature drops.Hence, it is important to improve the fuel properties of rice bran oil before use. There are four methods to lower the vegetable oil viscosity and improve fuel properties: 1. Mixed vegetable oil with diesel; 2. Pyrolysis; 3. Transesterification reaction and 4. Microemulsion.

Even the most popular method of biofuel production is transesterification reaction, however, the transesterification will produce glycerin as a by-product. The separation of glycerin from biofuels is further required which is a difficult and costly processes. Hence, the production of biofuels by microemulsion has received attention. Because there is no chemical reaction, no more glycerin and this method reduces the cost of biofuel purification. Microemulsion is a mixture of two insoluble liquids that can be homogeneous by the use of emulsifier which is surfactants together with co-surfactant which is a short hydrocarbon chain alcohol. Surfactant and co-surfactant will cause very small size of colloidal particles (ranged in 10-100 nm). The mixture will become homogeneous and transperent.

In this research, the biofuels from rice oil and ethanol by microemulsion was investigated using different nonionic surfactants (Tween 80 and Span 80) and co-surfactant (1-Octanol). The microemulsion phase behavior was examined from ternary phase diagram. The fuel properties of biofuel was studied through the kinematic viscosity, higher heating value, and emission test.

2. MATERIAL AND METHODS

a. Material

The materials used for biofuel production were: Rice bran oil (commercial food grade) and absolute ethanol 99.8% (ACS reagent grade) from Carlo Alba. Surfactants used are Span 80 (Sorbitane monooleate) from Sigma Aldrich and Tween 80 (Polyoxyethylene (20) sorbitan monooleate) from Acros Organics. Co-surfactant used is 1-Octanol 99.0% from Apex Chemical Co., Ltd.

The research focused to use the individual surfactant with different molar ratios of surfactant (S) to co-surfactant (C) of 1:5, 1:10, 1:20, and 1:30. The solubilization of S/C was found to completely dissolve in each other in all molar ratios.

b. Construction of ternary phase diagram of biofuel

The 5-mL Microemulsion biofuel was prepared with different compositions of three components of S/C, rice bran oil, and ethanol by v/v basis. Biofuel was formulated in 36 different fomulars according to the composition points in ternary phase diagram. Then, All of 36 test tubes were added in the constant-temperature sharking water bath at 40 ºC for 72 hr to allow the mixtures reach equilibrium. Monitoring the phase behavior (single or separate phase) in every 12 hr until 72 hr, and then the ternary phase diagrams were obtained.

c. Investigation of fuel properties of biofuel

After the ternary phase diagram was constructed, some microemulsion-based biofuel samples were collected to measure kinematic viscosity and higher heat value as seen in Figure 1 to investigate the effect of S/C ratios, types and amount of surfactant, types of microemulsion (water in oil, w/o and oil in water, o/w).

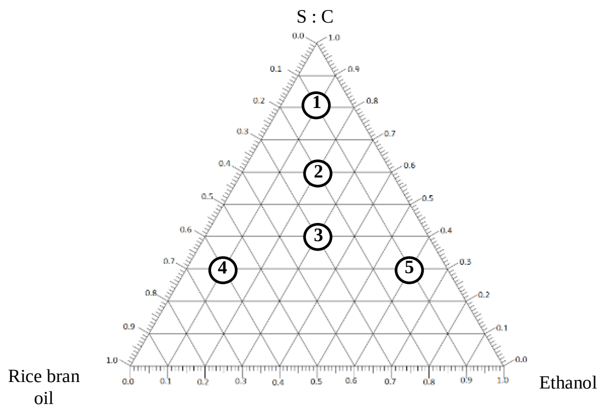


Figure 1. Selected points to sampling for further analysis on Ternary phase

d. Analysis of exhaust gases from a diesel engine

The samples from ternary phase diagram were chose to investigate the exhaust gas from the combustion in a single cylinder diesel engine. The ternary composition at the point number 3 in Figure 1 in Tween 80 and Span 80 with 1-Octanol at molar ratios of 1:10 and 1:30 were used for this analysis. The microemulsion-based biofuel combusted in a single cylinder engine (Fuel analyzer TESTO 350 at ambient temperature of 27 ºC) produced the exhaust gases of CO, CO_2 and NOx together with the exhaust temperature and amount of HC residue.

3. RESULTS AND DISCUSSION

a. *Microemulsion phase behavior*

Effect of surfactants and co-surfactant

Tween 80

Ternary phase diagrams of microemulsion-based biofuels using Tween 80 with varing S/C molar ratios of 1:5, 1:10, 1:20, and 1:30 were observed in Figure 2. The single phase region (the areas of shaded region) in all four various systems are larger than their separate phase region where two or three phases were observed. The increase amount of 1-Octanol promotes solubilization of rice bran oil and ethanol and thus, single phase microemulsion increases as seen in Figure 2 (a) – (d). In addition, as observed in Figure 2. (a). when S/C molar ratio is 1:5, the ability of Tween 80 itself could not solubilize to homogeneous mixtures when rice bran oil is the main composition with less S/C amount, the separate phase areas in lower left edge in ternary phase diagram is relatively large. This is due to the hydrophilic-lipophilic molecular structure in Tween 80 (HLB = 15.0) which indicates that Tween 80 favors to solubilize in polar phase (ethanol). However, when the molar concentration of 1-Octanol increased, the HLB of Tween 80 decreased and thus, it promoted solubilization of rice bran oil and ethanol, and can be seen in Figure 2. (c) – (d) that the separate phase areas in lower left edge in ternary phase diagram become smaller and smaller. The promotion effects of 1-Octanol on ternary phase diagram of microemulsion-based biofuels are in good agreement with previous researches [5]

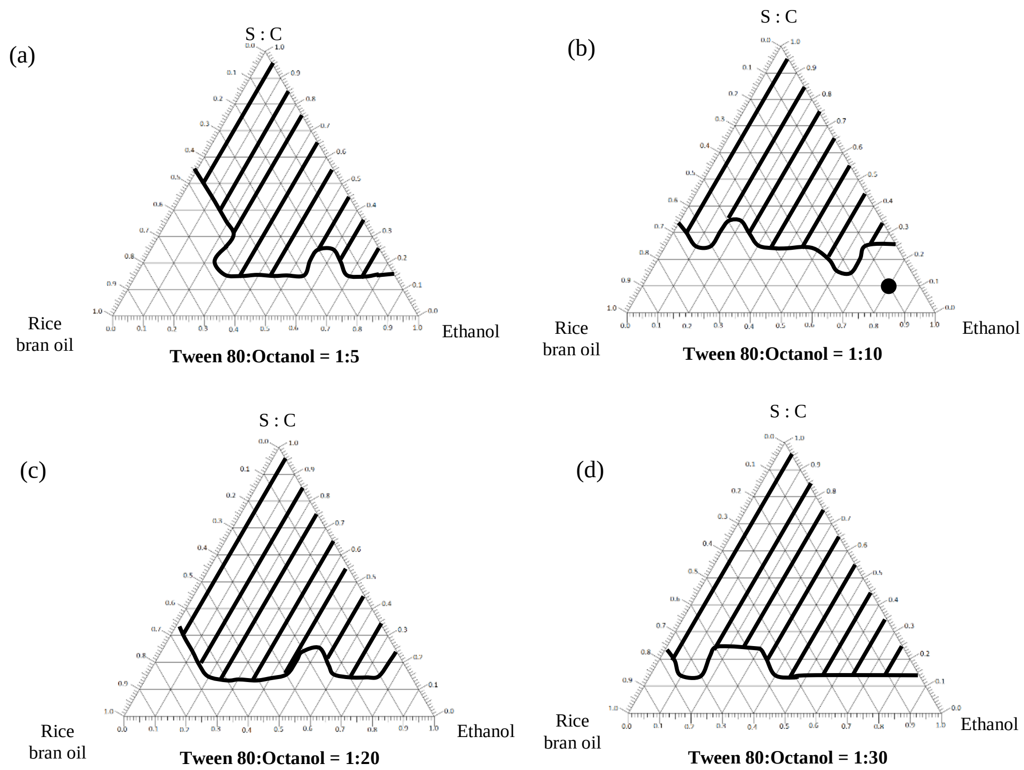


Figure 2. Ternary phase diagrams of microemulsion-based biofuels using Tween 80 with S/C molar ratios of (a) 1:5, (b) 1:10, (c) 1:20, and (d) 1:30

Span 80

Ternary phase diagrams of microemulsion-based biofuels using Span 80 with varing S/C molar ratios of 1:5, 1:10, 1:20, and 1:30 were observed in Figure 3. The single phase region (the areas of shaded region) in all four various systems are larger than their separate phase region as similarly seen in Tween 80 systems in Figure 2. However, the increase amount of 1-Octanol slightly assists to promote solubilization of rice bran oil and ethanol and thus, single phase microemulsion slightly increases as seen in Figure 3 (a) – (d). This is because of Span 80 capability to solubilize in rich-oil mixture by itself (HLB = 4.3) thus, the increase molar concentration of 1-Octanol is slightly significant. This indicates that Span 80 is more capable to produce microemulsion-based biofuels with slightly amount of 1-Octanol co-assistance.

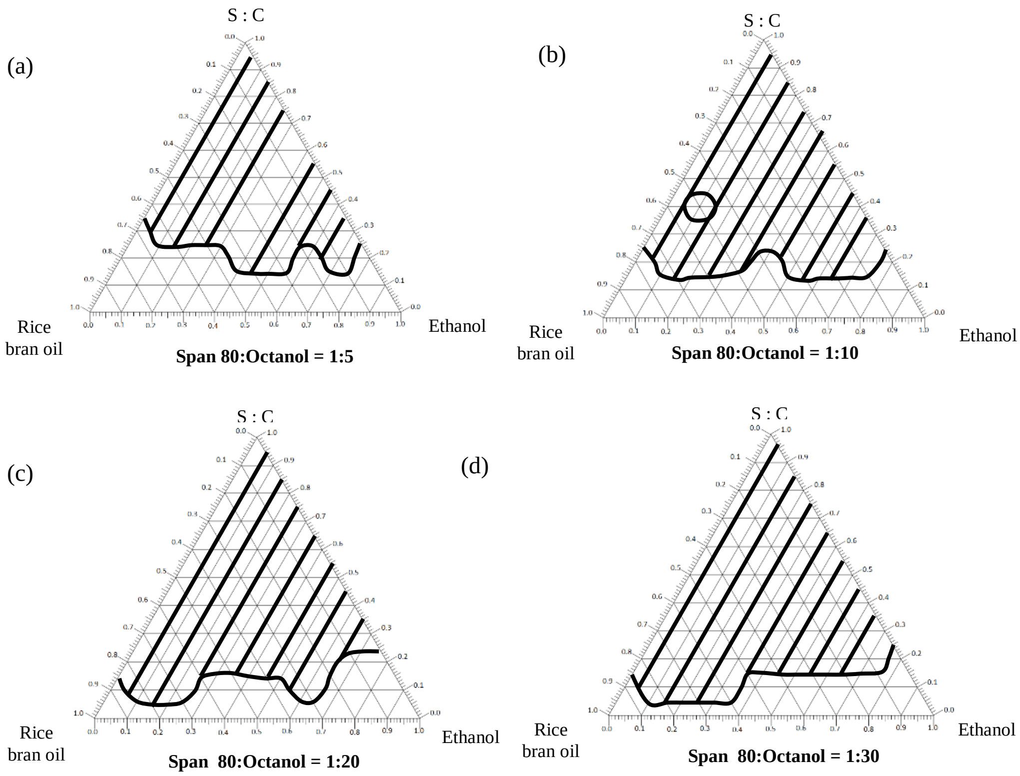
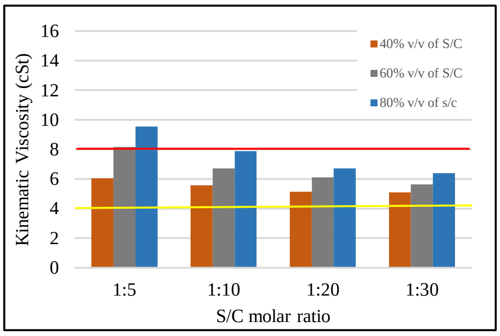


Figure 3. Ternary phase diagrams of microemulsion-based biofuels using Span 80 with S/C molar ratios of (a) 1:5, (b) 1:10, (c) 1:20, and (d) 1:30

b. Kinematic viscosity of microemulsion-based biofuels

Effect of surfactant and co-surfactant on kinematic viscosity

The kinematic viscosity of biofuels for selected systems from Figure 2-3 (point no. 1-3) with varying molar concentration of 1-Octanol and different types of surfactant are shown in Figure 4 (a) Tween 80 and (b) Span 80, respectively. It can be observed that the kinematic viscosity of microemulsion-based biofuels using both Tween 80 and Span 80 decreased as 1-Octanol molar concentration increased. This is because 1-Octanol has a lower viscosity compared to the used surfactant viscosity. Considering the kinematic viscosity in either Figure 2. (a) or (b) as v/v percent of S/C varied, the results showed that the kinematic viscosity increased with percent v/v of S/C increased. When the v/v percent of S/C increased, it means the amount of Tween 80 or Span 80 increased and thus, the influence of surfactant viscosity resulted in higher viscosity values. The standard of commercial biofuel (produced from transesterification method) and commercial diesel are approximately 8.0 and 4.0 cSt, respectively [6]. As can be seen in Figure 4.(b), the kinematic viscosity of biofuels from Span 80 systems are relatively close to the standard of commercial biofuel value while the kinematic viscosity of biofuels from Tween 80 systems could be tuned to be close to the standard value when the molar concentration of 1-Octanol increased.

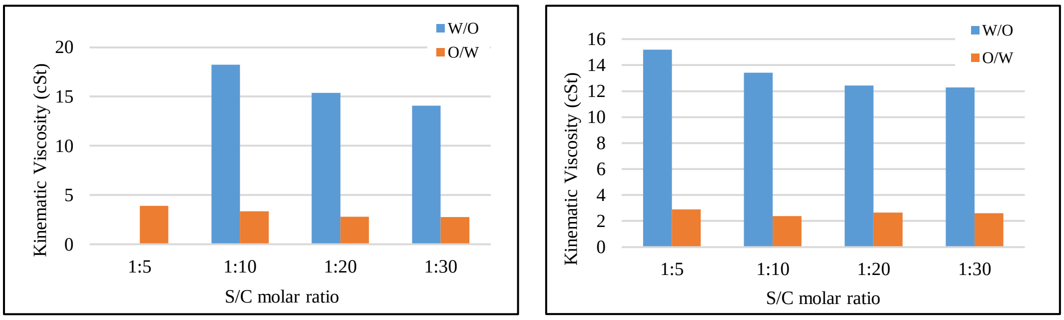


(a) (b)

Figure 4. The kinematic viscosity of biofuels for selected systems from Figure 2-3 (point no. 1-3) with varying molar concentration of 1-Octanol and different types of surfactant (a) Tween 80 and (b) Span 80. The red and yellow lines indicate the standard value of commercial biodiesel from transesterification and diesel, respectively

Effect of w/o and o/w on kinematic viscosity

The kinematic viscosity of biofuels for selected systems from Figure 2-3 (point no. 4 (w/o) and 5 (o/w)) with varying molar concentration of 1-Octanol and different types of surfactant (a) Tween 80 and (b) Span 80 is shown in Figure 5. For the prepared biofuels with o/w microemulsion type in both Tween 80 and Span 80 systems, the kinematic viscosity were observed to be similarly and no significant difference because the amount of ethanol is more influent on the viscosity value of the mixtures. The kinematic viscosities of biofuels with w/o microemulsion type were observed to be very higher than the biofuels with o/w microemulsion type because of the existence of rice bran oil as a rich phase which has high viscosity. As can be seen in Figure 5. (a), the kinematic viscosity of microemsulion-based biofuels with w/o microemulsion of S/C molar ratio at 1:5 in Tween 80 system does not show up since this point appears two separate phases from lack of enough 1-Octanol.



(a) (b)

Figure 5. The kinematic viscosity of biofuels for selected systems from Figure 2-3 (point no. 4 (w/o) and 5 (o/w)) with varying molar concentration of 1-Octanol and different types of surfactant (a) Tween 80 and (b) Span 80

c. Higher heating value

Effect of surfactant and co-surfactant

The higher heating value of biofuels for selected systems from Figure 2 (at point no. 1-3) using Tween 80 at different molar concentration of 1-Octanol of 1:5 and 1:10 with varying S/C volume percent are shown in Figure 6. It can be seen that the more amount of 1-Octanol in the biofuels, the larger higher heating value obtained. It is due to 1-Octanol has a large value of higher heating value. In addition, when the amount of Tween 80 increased, it resulted in the larger values of higher heating value of biofuels due to there are so many hydrocarbon molecules in Tween 80 structure to combust in the oxidation reaction. The higher heating value of commercial biofuel (produced from transesterification method) and commercial diesel are approximately 37.24 MJ/kg and 44.80 MJ/kg, respectively [7].

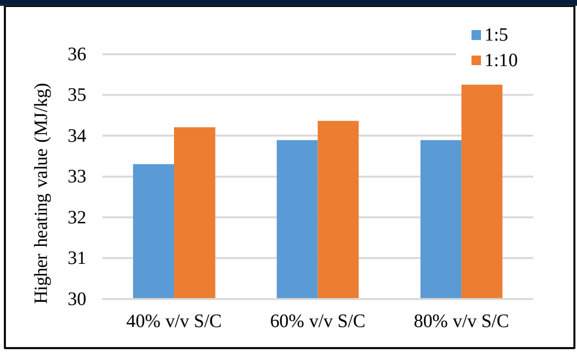
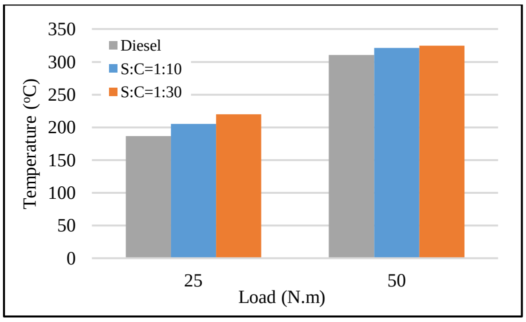


Figure 6. The higher heating value of biofuels for selected systems from Figure 2 (at point no. 1-3) using Tween 80 at different molar concentration of 1-Octanol of 1:5 and 1:10 with varying S/C volume percent

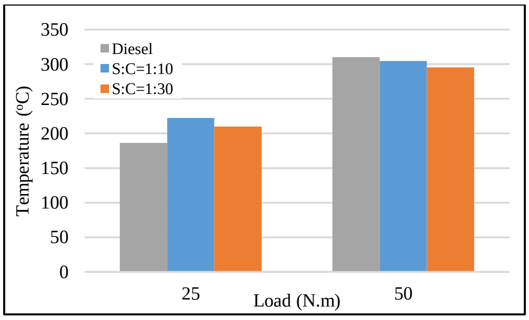
d. Emission test

The experimental results from emission test for exhaust gas temperature, unburn hydrocarbon (HC), carbon dioxide (CO_2), carbon monoxide (CO) and nitrogen oxides (NOx) are shown in Figure 7-11, respectively. The ternary composition at the point number 3 in Figure 1 in Tween 80 and Span 80 with 1-Octanol at molar ratios of 1:10 and 1:30 were used for this analysis with two different load of 25 and 50 N-m. From Figure 7.(a) and (b) the exhaust temperatures resulted from biofuel combustion in a single cylinder diesel engine for both Tween 80 and Span 80 systems were similarly which indicated that the change in molar ratio of S/C were slightly significant. The main reason for exhaust temperature difference could be due to the load apply. Considering the amount of unburn hydrocarbons of biofuels from Tween 80 and Span 80 systems in Figure 8.(a) and (b), the amount of unburn hydrocarbons from the prepared biofuels remained higher than those of commercial diesel, which is a result from incomplete oxidation reaction due to amount of triglyceride in rice bran oil.

In Figure 8.(a), the molar ratio difference resulted in not so different unburn hydrocarbon remain while the significant difference in unburn hydrocarbon amount were observed in biofuels from Span 80 systems at both different load apply. It indicates that the increase in the molar concentration of 1-Octanol in biofuels when using Span 80 as emulsifier, it shall result in incomplete oxidation reaction in the combustion champer in diesel engine. This problem could be solved by further addtion of oxygen compounds (i.e. ethanol) to the mixtures. Considering Figure 9. (a) and (b), it can be observed that the prepared biofuels from both Tween 80 and Span 80 systems have similar results in CO_2 release comparable to commercial diesel. This can be due to the amount of free fatty acid content (as single chain hydrocarbons) while the HC remained much higher because of triglyceride with in good agreement in the further supporting experimental data of higher amount of CO release in the exhaust gases as seen in Figure 10.(a) and (b).

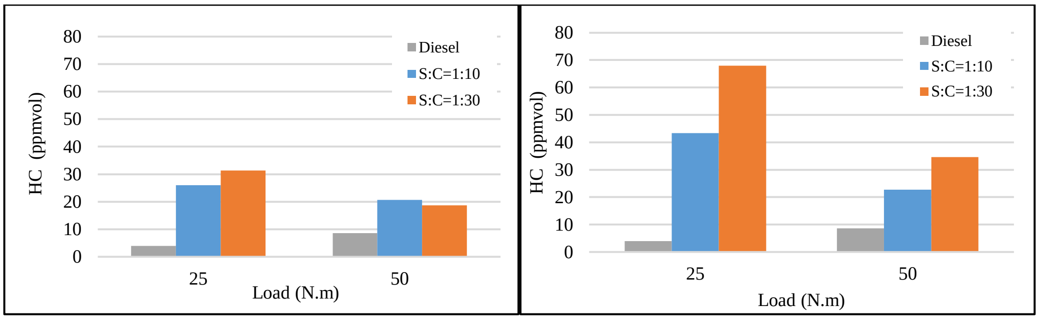


(a)



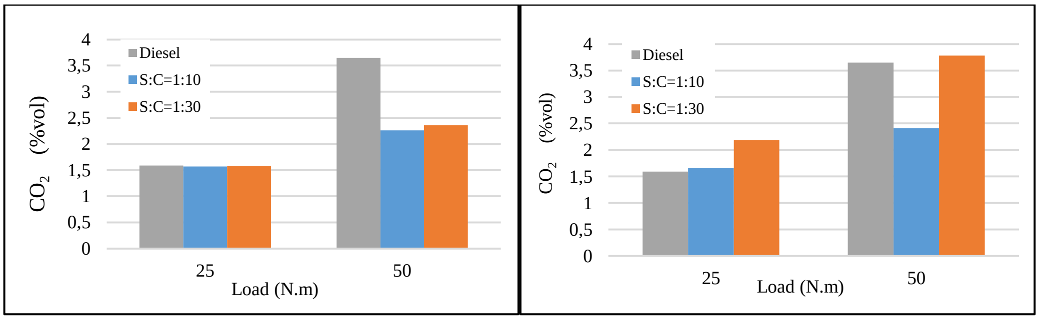
(b)

Figure 7. The exhaust gas temperature of prepared biofuels with different load (a) Tween 80 and (b) Span 80



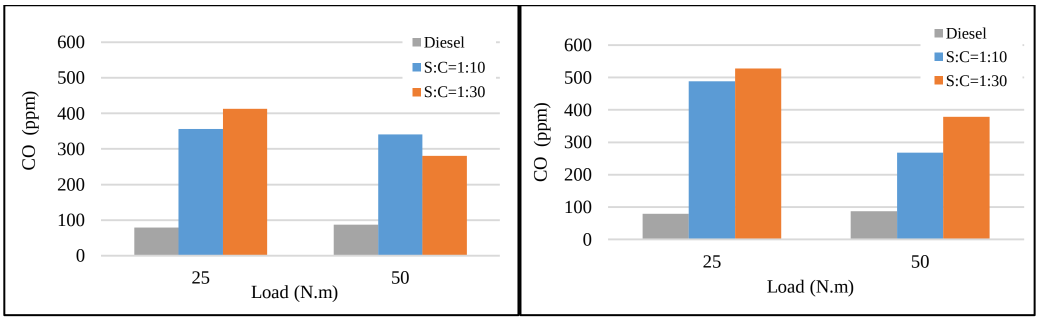
(a) (b)

Figure 8. The amount of unburn hydrocarbon of biofuels with different load apply from (a) Tween 80 and (b) Span 80



(a) (b)

Figure 9. The amount of CO2 release of biofuels with different load apply from (a) Tween 80 and (b) Span 80



(a) (b)

Figure 10. The amount of CO release of biofuels with different load apply from (a) Tween 80 and (b) Span 80

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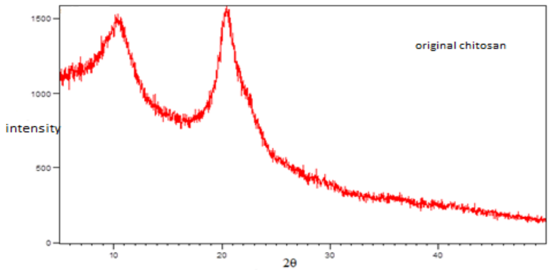

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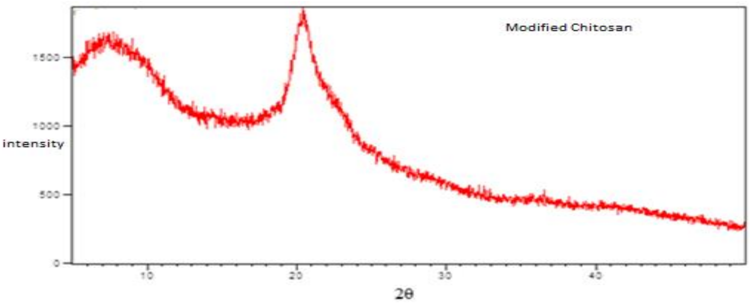

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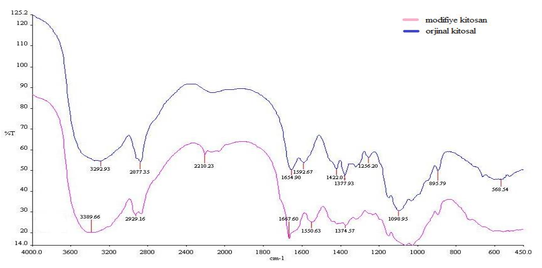

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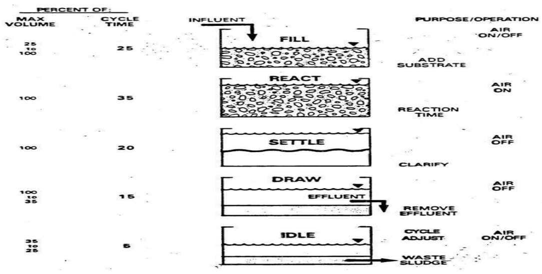

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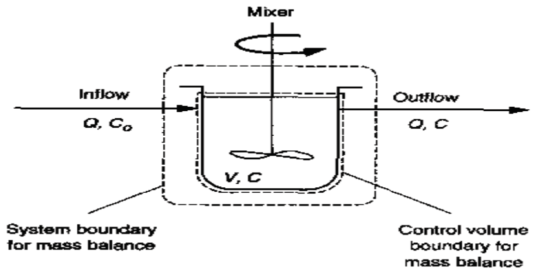

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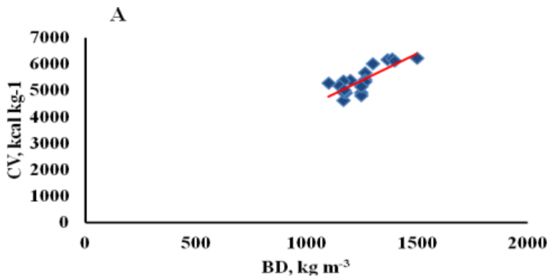

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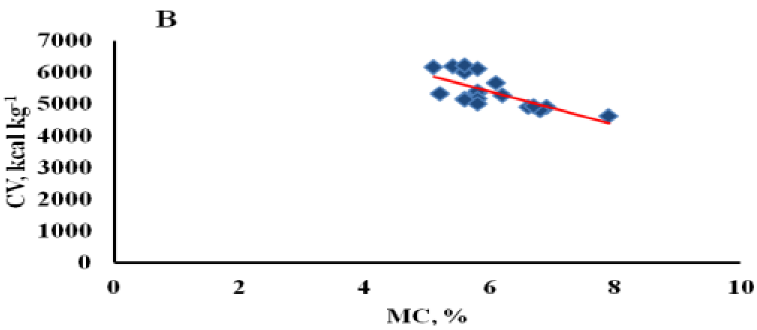

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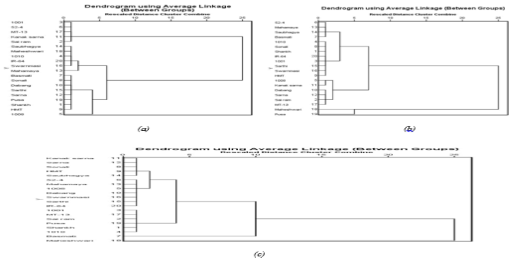

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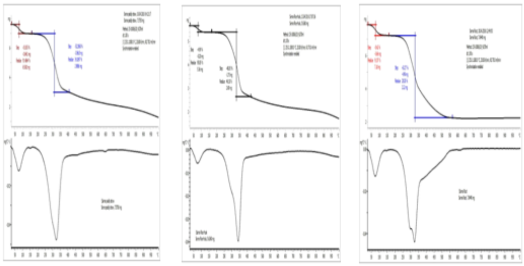

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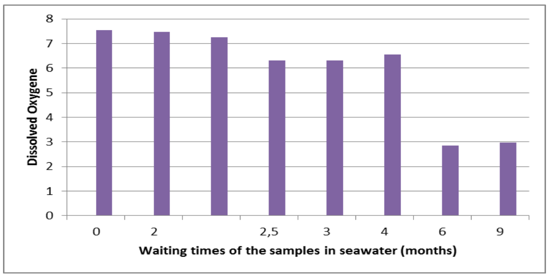

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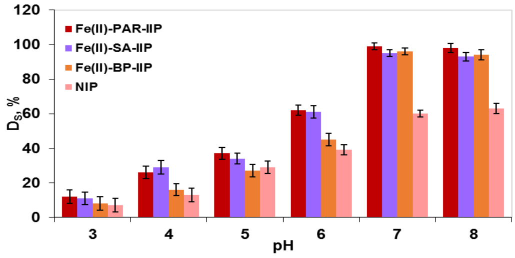

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