Efficient removal of oil, fats and grease from domestic wastewater for water reuse with energy generation as fuel

By

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This thesis is dedicated to my parents for
their love and support

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Ehsan Mustafa Hashmi

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LIST OF ABBREVATIONS

GCMS	Gas chromatography and mass spectrometry.
LHHV	Langmuir Hinshelwood Hougen Watson.
FAEE	Fatty acid ethyl esters.`
LLE	Liquid liquid extraction
WCO	Waste cooking oil
SVO	Straight vegetable oils.
COD	Chemical oxygen demand.
ER	Elley Radial.
BOD	Biological oxygen demand.
FFA	Free fatty acids.
AOCS	American oil chemist society.
HCL	Hydrochloric acid.
KOH	Pottasium hydroxide.

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ABSTRACT

Domestic wastewater effluents contain oils, fats and greases which result in choking of the water distribution systems. These problems arise due to the issues like temperature differences in wastewater flow and flow channel structural differences. By using the end of pipeline cleaner production techniques, these oils and fats can be recovered and reused in the biofuel production. Water recovered after the recovery of oils and fats can also be a good resource for reuse in agricultural lands to meet demands in arid lands. In this way reliance on ground water use for agriculture can be reduced along with continuous energy generation from oil and fats recovered from domestic wastewater discharges. The advantages could be the resource recovery, recycling and reuse of problem causing oils, fats and greases as valuable fuels. The recovery of oil, fats and grease from the domestic wastewater streams as a biofuel, the biodiesel, and the generation of reusable water is investigated in thisstudy.

A batch reactor system was used to study the removal of oil, fats and greases from the domestic wastewater stream (Chakri drain Rawalpindi) using basic anionic resin catalyst Amberlyst A21. The biofuel generation of the recovered oil was achieved with the macro porous acidic resin Amberlyst 15. Oil separation of 33 ± 2.08% was noted by gravity separation from the water stream after providing a retention time of 72 hours to the oily wastewater sample. Esterification reactions were then carried out at temperatures 50, 60, 70 and 75^{o}C with varying oil to alcohol molar ratios of 1:2 to 1:3. Amberlyst 15 acidic resin catalyst percentages in the reaction mixture varied from 2, 4 and 6% by weight of oil mixture respectively. The maximum mono alkyl ester production was noted at a reaction temperature of 70^{o}C with maximum ester yield of 91.38% at a molar ratio of 1:3, catalyst weight percentage of 6 weight % and reaction temperature and time duration of 70^{o}C and 8 hours respectively. After performing the fractional distillation of the reaction products the ester yield was further increased to 95.75%. The COD of recovered water from oil, required to achieve NEQS of 150 mg/L, was observed at the activated carbon dose of 0.8 grams/liter after an adsorption time interval of 45 minutes, only once the oil separation was done. Moreover, parameters like water pH, alkalinity and ammonia after oil recovery and passing through activated carbon were also found meeting the NEQS. With oil recovery and conversion into biodiesel, a profit of 53.811 Million Rupees can be gained in first year and 91.479 million rupees in successive years while discharging water back to the Chakri drain for pollutant dilution and for reuse in horticulture purpose.

Chapter1

Introduction

1.1. Background

Wastewater containing oils, fats and greases result in choking of the water distribution systems. These problems arise due to the issues like temperature differences in flowing wastewater and flow channel structural differences. By using the end of pipeline cleaner production techniques, these oils and fats can be recovered and used for fuel production (Ahmad et al. 2015). Mostly population is not educated enough to dispose of their wastewaters and wastes properly. Release of wastewater in water bodies and on open grounds is causing human health issues on regular basis (Khalid et al. 2018). At the same time, organics can be removed from wastewater and turned into useful bio energy fuels that provide import substitution. As the demand of energy is increasing globally and in Pakistan, so its absence is causing intense economic crisis due to increasing gap between energy demand and energy supply.

Water and fuel reserves are depleting in Pakistan and measures need to be taken to make water and energy supply sustainable. Due to hydroelectricity and nuclear energy limitations, petrochemical sources like coal and natural gas are used to supply energy sources (Lee et al. 2018, Ur Rehman et al. 2019). Increased environmental problems and continuous depletion of the world petroleum sources have developed interest in alternative fuels production (Brandt 2011, Aguilera et al. 2009).

Biodiesel, originated from waste low quality oils like waste cooking oils, non-edible plant oils by esterification with alcohol, is suitable for use in place of petroleum-based diesel in the transportation sector. It is an oxygenated, renewable, biodegradable and environmentally friendly biofuel with similar combustion properties and also less emission profile (Jamal and Boulanger 2010). Biodiesel reduces aromatics and contains almost no sulfur emissions (Lam et al. 2010). Both transesterification and esterification reactions can be performed in presence of a homogenous (Talebian-Kiakalaieh and Amin 2015) and heterogeneous (Jamal et al. 2015) catalyst. Currently, in comparison with petroleum diesel, barrier to the commercialization is related to its high cost. From previous studies, it was reported that 70-85% of the cost for biodiesel production is contributed by the raw material. Waste cooking oils can be utilized in making biodiesel because by using low quality feedstocks such as waste cooking oil (WCO), the cost of biodiesel production can be greatly reduced to make biodiesel competitive in price as compared to petroleum diesel (Leung et al. 2010). Huge amount of waste lipids is produced from the restaurants, fast food shops and food industries every day. For the improvement of environment and for better fuel properties, a few countries provide attention to alternative fuel and create suitable rules and regulations for it. Many low quality feedstock's have greater quantities of free fatty acids (FFAs) (Jamal et al. 2014). These FFAs on reaction with alkali catalysts, result in soap production that restricts the fatty acid ethyl esters (FAEEs) formation. Alkali catalyst can be used for transesterification for the vegetable oils that contains less than 2% FFA. However, in order to avoid catalyst lost to soap, additional acidic catalyst must be added.

The aim of the study is the removal of oil and fats from domestic wastewater before its disposal into the water streams. Further a esterification reaction of recovered oil by the basic resin surface with ethanol in the presence of acidic resin catalyst at different reaction conditions. Also a method for cleaning water for reuse of oil free water is proposed for agricultural and horticulture purpose.

1.2. Problem Statement

Oils, fats and greases result in the choking of water distribution systems. However, oil and fats can be recovered from wastewater for water resources recovery and oil can be reused as energy fuels. This recovered energy fuel can be further utilized in transportation vehicles when mixed with petro-diesel about 5-20%. Thus recovery of the problem creating oil and fats can be made advantageous for reuse like transportation fuel and can substitute fossil fuel diesel import. The recovered water from the system can be reused for horticulture after reducing its COD as it meets the standards of NEQS.

1.3. Objectives of the study

- To determine percentage removal of oil and fats from wastewater
- Production of energy fuel from recovered oil
- Characterization and analysis of esterified oil as biodiesel

1.4. Scope of the research

The purpose of this study is to identify the important variables to efficiently remove oil, fats and greases from wastewater and to suggest a better methodology in scaling up the generation of biodiesel from waste oil by esterification method. Important parameters like concentration of catalyst, reaction time, temperature and alcohol to oil ratio used for greater yield and improved ethyl ester content are studied. The increased energy requirement in the domestic and industrial sector, has created environmental pollution due to the excessive utilization of fossil fuels (Kusdiana and Saka 2004). This makes it necessary to create an alternative fuel of lesser pollution problems compared to fossil fuels. The renewable alternative fuel should be technically feasible and economically competitive. Biodiesel is also biodegradable, non-toxic and has less emission than diesel fuel. The recovered water can be further used for agricultural purposes.

A lab scale experimental work is designed to find out the oil content in chakri drain water. The separated oil mainly FFA will be then esterified in the presence of an acidic catalyst by varying different reaction parameters. The findings of this work further can be used to develop a pilot scale unit at IESE.

1.5. Utilization of Research Work

Wastewaters from domestic and industrial units vary widely in characteristics owing to different types of inputs used and processes involved. The possible implication of this research may be in the following areas.

- Oil and fats recovery as resource and pipe choking will be avoided.
- Treated water can be reused for agricultural purposes.
- Energy fuel generation and fuel system optimization for transportation sector.

In addition, different models may be developed for various industries in Pakistan. Thus, consultancy services can be provided to the firms who are in the business of wastewater treatment plants design.

1.6. Limitations of Research Work

This technique while enjoying almost and order of magnitude advantaged in terms of energy efficiency, has the following limitations.

- Soap formation due to the presence of water if transesterification is performed.
- Variation in quality of biodiesel.
- Not suitable for use at low temperatures.
- May slightly increase NOx emissions depending on the process adopted and type of catalyst used.

Chapter 2

Literature review

2.1. Pakistan water problems

Approach to a safe and pure water supply is an urgent requirement for the people of Pakistan. In Pakistan, per person available water is less and is deteroriating over time. The country is rated as the highly water stressed in the world. It is also expected to be rated as “water scarce” in the coming years. This condition may also have adverse implications for energy production concerning the role of water in thermal and hydroelectric power production (Wang et al. 2010).

High evaporation, increasing seas are promoting towards higher intrusion in saltwater in coastal areas. Also outburst floods in glacier lake are increased due to glacial melt. The major effects of climate change on Pakistan’s water resources are increased rainfall, monsoon changes and the patterns of winter rainfall (Pal Singh and Anbumani 2011). This shortage of water can negatively affect health, domestic water supplies, energy, agricultural sectors and municipal water supplies.

In Pakistan per capita availability of water is annually 1,017 cubic meters and decreasing near to 1,000 cubic meters. The Indus basin aquifer is found the second highly overstressed by the NASA researchers and deteroriating with little to no recharge and this aquifer also lies on the World’s resource institute water stress index.

Experts predict that one out of three people in Pakistan is facing critical water shortage, "threatening their very survival".

2.2. The Sustainable development goals (SDGs)

SDG 6.3 states improvement in water quality by reducing pollution and safe resources by 2030. Surface water runoff from agricultural, urban or industrial sources can greatly affect the quality of ground or surface water which is necessary for human requirements, business operations, and ecosystem requirements (Sánchez et al. 2015). Management of water is a method of decreasing the effects of water quality at catchment level. This may involve management of source prior to discharge, providing financial resources for waste treatment, supporting water sanitation projects or protecting affected aquatic ecosystems, development of waste treatment systems and water reclamation methods, protection of aquatic ecosystems, promoting projects of water sanitation, or increasing financial resources for treatment of waste. Management of water quality also involve rehabilitation of water, like cleanup of rivers and lakes (Pöpken et al. 2000).

Target 6.3 also aims to enhance ambient water quality for protecting both human health and ecosystem health, by minimizing various ways of pollution into water. The major pollution sources include domestic wastewater, industries (point sources) and commercial establishments. Domestic wastewater can produce pathogens and nutrients in receiving waters if wastewater is discharged in water streams without treatment (Dufreche et al. 2007). Wastewater generated by manufacturing industries can have various types of pollutants, involving substances that can cause serious hazard.

The focus on recycling should be safe reuse for example waste valuables like lipids in wastewater could be turned into new resources while making the water clean for safe reuse. The SDG target 6.3 is on describing the decreasing withdrawal of freshwater and increasing use efficiency. An example could be removal of oil and fats from influent discharge that can be turned with valuable resources.

2.3. Oil separation techniques

Oil and water separation is a field that has direct practical solution for solving the issue of wastewater pollution from domestic and industrial discharges. The effective separation of oil polluted wastewater is important to study. Following techniques can be used for oil separation from wastewater streams.

2.3.1. Gravity oil separation

For gravity separation, the API separator device is used. This device is designed on the basis of Stokes' law that states that the increase in oil droplet velocity depends on its size, density and properties of water. The separator design is based on difference of specific gravity between the water and the oil. The difference in specific gravity between oil and water is much lesser than the difference in specific gravity between the water and suspended solids (Environmental 2019). The basic design should be such that oily layer floats at the top, the solids settle at the bottom as the sediment layer and the wastewater lie in the middle between the oil and sediment layer. In order to apply the API standards correctly, adjustments in design, geometry and separator size must be in accordance or beyond Stokes Law principle. This applies understanding the entrance of water flow and losses due to turbulence flow at exit (Kim et al. 2008). API specification requires that the API separator device ratio of length to width 5:1 and depth-to-width 0.3:0.1 be in these ranges.

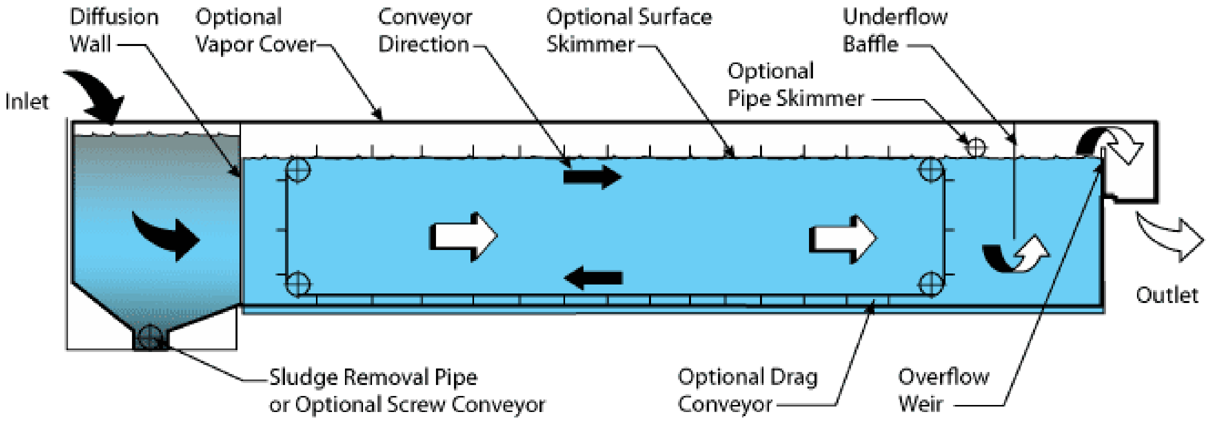


Figure 2.1. API oil water separator (Environmental 2019)

2.3.2. Separatory funnel

In a separatory funnel ,two immiscible phases of solvent with different densities are separated (Chhetri et al. 2008). One phase is aqueous, and the other is an oily layer. In case of an oily wastewater, the light dense phase like lipids (oil) in the water float at the top while the dense liquid phase like the water settles down at the bottom with the passage of time. The dense liquid phase settles down and can be taken out through a valve in the separatory funnel.

Separating funnel has a cone shape with a hemispherical corner end. It consists of a stopper at the top of the funnel and stopcock, at the funnel bottom (Pua et al. 2011). Separatory funnel sizes may vary between 30 millilitres to 3 litres. For industrial environment, these funnel sizes can be greater and for greater volumes , centrifuges are preferred. The slopes on the sides are used to facilitate the layer settlement. The liquid from the funnel is taken out from the stopcock at the bottom of the funnel.

In order to use the separatory funnel, one closes the stopcock valve from the bottom of the funnel and ten insert the mixture to be separated into the funnel. The funnel is then shaked gently by inverting it multiple times.

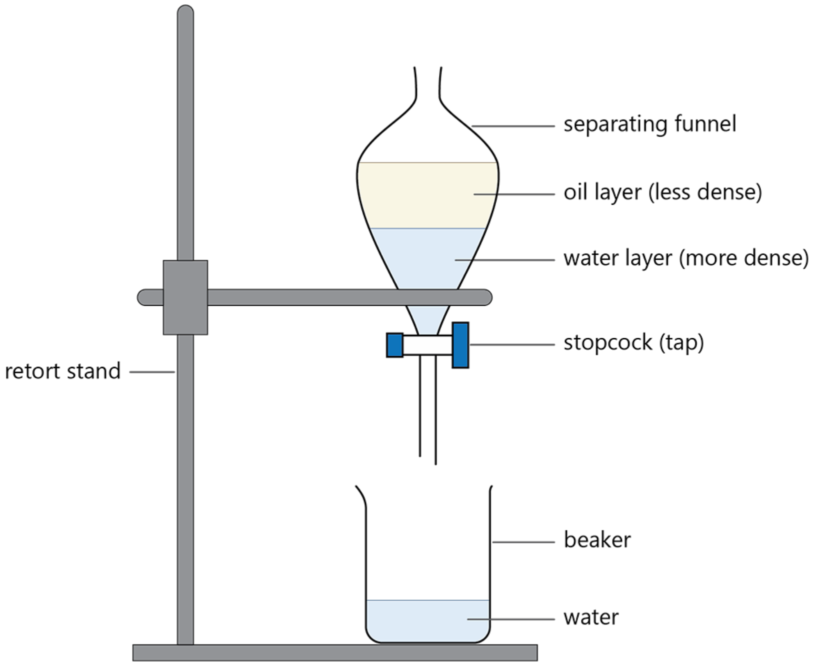


Figure 2.2. Separatory funnel (Science 2019)

2.3.3. Centrifugal separation

Oil and water can be separated using a technique called Centrifugation. It consists of a cylindrical container that revolves inside a big stationary container. Oily layer has less density so it starts accumulating at the axis and is recovered from the center. Centrifugal separators have various applications like they are used in the processing of wastewater, oil spills or lake water cleanup. Diesel and lubricating oils can be filtered using centrifugal separators after removal of waste particles and impurities from them.

Spinning vortex is created on pumping of oily water in a cone shaped apparatus with fixed angle. Liquids with high density are moved outside while displacing the liquids of low density to the center of rotation. As density of oil is less, so it moves outside and removed from the outlet (de Oliveira et al. 2017). Suction orifice in center can be used to remove remaining collected oil.

Figure 2.3. Laboratory centrifuge (Science 2019)

2.3.4. Solvent extraction

In order to separate two chemicals on the basis of their solubilities in immiscible liquids, either polar or non polar, a technique called solvent extraction or partitioning is used. This technique is mainly used for extraction of lipids from microbes, algae and non edible plant oil seeds. In solvent one liquid phase is shifted to another liquid phase (Kwon et al. 2012). Chemical potential involved in the phase change. The solvent containing a large amount of solute is called extract while the solution or feed solution that contains a very small amount of solute is called raffinate. Variety of apparatus can be used in solvent extraction ranging from separatory funnel to counter current distribution known as Mixer settlers (Dufreche et al.2007).

Basically solvent extraction is defined as the substance separation by dissolution of substance in polar or non polar solvent phase. This indicates that a soluble compound can be separated from complex matrix or insoluble compounds. Solvent extraction is also used in the purification of various type of lipids from a mixture of polar or non polar lipids. Solvent extraction major benefit is its strength to selectively separate out similar kinds molecules with solvents of similar properties.

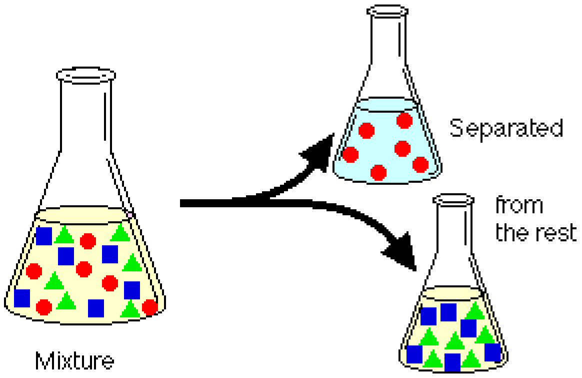


Figure 2.4. Solvent extraction (extraction 1999)

2.3.5. Air flotation

Dissolved air flotation is usually used for dispersed oil removal from water. The processes are identical: gas bubbles are inserted into the mixture of oil and liquid and the oil is captured by the gas bubbles which quickly appear at the surface where the oil is separated. Mixing conditions and the size of bubble are the major differences in the flotation methods. Dissolved gas flotation has bubble size of 50-60 meters in diameter while in induced gas flotation, greater magnitude bubble sizes are used. Good quiescent conditions are required for dissolved flotation and the mobile phase adopts plug flow. In induced flotation, the rotor provides high energy to the mobile phase due to which the contents of the tank are dissolved perfectly. It is difficult to determine the fluid mechanics of the induced air flotation. The turbine arrangement and perforations determined by trial and error method with small scale setups. Gas bubbles and oil droplets interact in the following ways (1) collision of drop and bubble and bubble precipitation on the surface of oil causing the oil absorption of gas bubble (2) Flocculated oil drop structure causing gas bubble entrapment; and (3) Flocculated oil drop structure causing absorption of bubbles on formation. While in dissolved flotation, oil removal is influenced by all these mechanisms interdependently. Following figure 2.5 shows the pictorial view of oil air flotation system.

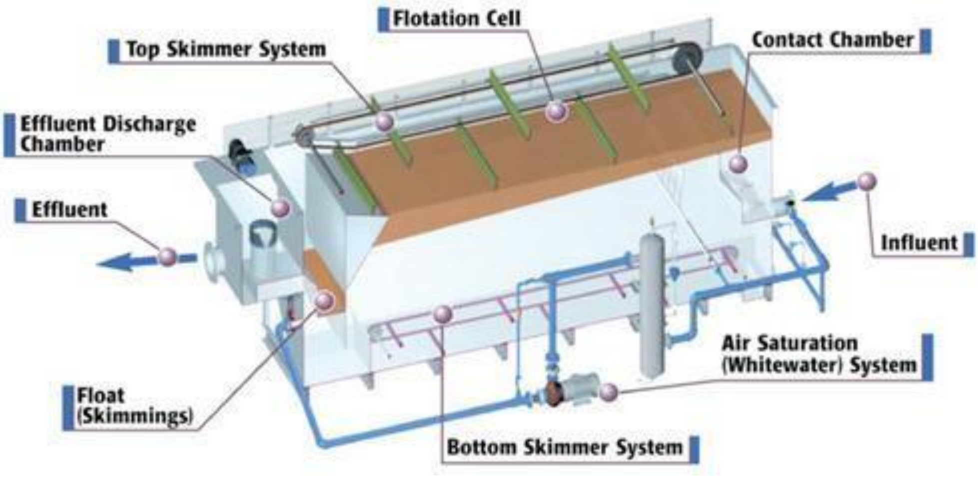


Figure 2.5. Air floatation assembly (Mart 2019)

2.4. Straight Vegetable Oils (SVO)

Above mentioned techniques can also be used to separate out straight oils (triglyceride lipids) from the water streams. Straight vegetable oils are mainly obtained from plants then domestic wastewaters or from the effluent of industries (Pirola et al. 2014). Furthermore, these oils are the best option for biodiesel production due to greater conversion into fatty acid alkyl ester.

2.5. Waste Cooking Oils (WCO)

Waste cooking oils can be collected from different industries such as oil and ghee mills process effluents. They are cheap source of lipids than vegetable or plant lipids and mainly comprise of polar lipids like FFA; s (Maeng and Cha 2018). Hence, the cost of biodiesel production can greatly be reduced by using the waste oils as raw material. The benefits of using these oils are less costs and minimal environmental pollution. Due to unavalibility of grease traps, these oils at houses end up in discharged water. Encinar (2006) concluded that the biodiesel cost can be greatly reduced by using waste oils as raw material. The only limitation in processing these oils into biodiesel is that they require acidic catalyst for the reaction that do produce water of reaction that can hydrolyze the esterified product.

2.6. Solvent

Sprules and Price (2011), proposed that alcohol in range C_1-C_4 can be used for the esterification process. Alcohols like are polar in nature like fatty acids so facilitate their movement towards catalysts. Methanol and ethanol are the shortest carbon chain alcohols and have the highest polarity but smaller boiling point then higher chain alcohols (Lam et al. 2010). Short chain alcohols are peered because they are easy to react with the homogeneous or heterogeneous catalyst used for the processing the lipids of any kind (Jos et al. 2013)

2.7. Catalyst

Catalyst increases the reaction rate by decreasing its energy of activation and does not show in the final product. For lipids esterification and transesterification, following types of catalyst can be used namely: homogeneous, heterogeneous and enzyme catalyst. (Sharma et al. 2014) in their study has shown that quantity of catalyst, has a direct impact on product formation. However, quality and quantity of catalysts also increases the production costs.

2.7.1. Homogeneous Catalyst

When the process has both the catalyst and reactant lipids and alcohol in the liquid phase it is known as homogeneous catalyst system. Some of the examples of homogenous catalysts systems are namely acid catalyst like H_2SO_4 or HCl and basic catalyst used for transesterification are alkali catalyst like NaOH or Sodium methoxide. Basic homogeneous catalyst given higher rates of reaction as compared to heterogeneous catalyst because of their free movement in the reaction but the separation of homogeneous catalyst from the reaction product ester is difficult (Sing et al. 2013). Also basic catalysts are only preferable for triglyceride conversion into mono alkyl esters.

2.7.2. Heterogeneous Catalyst

The process involves two phases: a solid catalyst and the reactants in the gaseous or liquid form. Heterogeneous catalysts are initially expensive but their capacity of regeneration and reuse make them beneficial. Also causes minimal environmental problems, and are easily separated out from liquid and can be regenerated to provide longer activity (Jos et al. 2013).

Heterogeneous catalysts are of different kinds like oxides of alkaline earth metal, anion resins, different alkali metal products supported by alumina, and different kinds of zeolite that can be utilized in different kinds of chemical processes like esterification and transesterification reactions. While in transesterification of catalysts, a lot of anion resins and alkali catalyst are easily deteriorated by that ethanol possess lesser catalyst duration. The oxides of alkaline earth metals are more viable for utilization in transesterification reaction as they disperse slightly in organic solvents (Marchetti and Errazu 2008). Fatty acid lipids are esterified in the presence of acidic catalyst like sulfonic acids and by metallic acid oxides.

2.7.3. Enzyme catalyst

Another way to produce biodiesel is by the utilization of biocatalyst like lipase enzyme. Biocatalyst such as, an enzyme has large molar mass that acts on a molecule of reactant lipid and change it chemically. This lipase action increases reaction rate more as compared to the reaction in absence of a chemical catalyst. However, the performance of chemical catalyst is always found better than the enzyme catalyst (Lam et al. 2010).

2.8. Transesterification process

In transesterification alcohol is reacted with a triglyceride (TGA) lipid molecule in the presence of basic catalyst. Triglycerides is a neutral lipid which has a glycerol molecule attached with three fatty acids. The viscosity of TGA is reduced by transesterification. The process is shown by the general reaction in the following equation. The reaction is reversible reaction and proceed on the addition of catalyst that enhance theconversion.

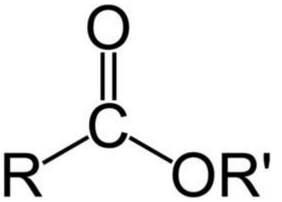
$$\text{Triglycerides+Methanol} \overset{\text{Catalyst}}{\rightleftharpoons} \text{Glycerol+Methyl Ester} \qquad \textbf{(2.1)}$$

Triglycerides transesterification is reported with alcohol (C_1-C_4) and addition of catalyst produce mono alkyl ester di- glycerides and glycerol. The glycerol layer is settled at the bottom of the reaction vessel (de Oliveira et al. 2017). To increase ester formation, additional alcohol is added because the reaction is reversible and can proceed backward. The forward reaction is the first order reaction and the backward reaction is the second order reaction. Alkali or basic catalyst is added in the transesterification reaction proceeds faster.

2.9. Esterification Reaction

When fatty acids content is > 2% in oils reaction with alcohols is performed the presence of an acidic catalyst, then esters are formed and the reaction is called the Esterification reaction. This process is most commonly practiced in chemical industries to form esters (Sharma et al. 2014). Esters are produced by manufacturers daily. If the ester content of the reaction is 95%, it is called biodiesel account for the definition of European standards.

Esters are formed when the carbon is joined to two oxygen atoms but one oxygen atom forms double bond to the carbon atom and the other oxygen atom is joined to another carbon. Here is the general formula for an mono alkyl ester ('R' refers to a carbon chain):



During the reaction, O-H is removed from the carboxylic acid and for this purpose, a large amount of heat and energy is needed which is supplied by the heat and catalyst. After the removal of O-H, the hydrogen will also be removed and the oxygen atom easily join itself to the carbon. As the oxygen was already joined to the carbon, it is joined to carbon from both sides and the ester formation is completed.

2.10. Blending of vegetable oil with petro diesel to use as abiofuel

Vegetable oils cannot be directly used in diesel engines because it can produce lot of problems like choking. Vegetable oils have similar characteristics as esters, however few changes must be applied before using these oils into the engine. A lot of research is going on to make process more viable. Although vegetable oils can successfully run few diesel engines, various problems are created by turbo charged engines (dos Reis et al. 2005). It is reported that pure vegetable oils have similar energy fuel consumption as of diesel fuel. A ratio of 1:10 to 2:10 diesel was found beneficial for short duration utilization.

2.11. Alternate route to Synthesizebiodiesel

Biodiesel can also be produced through different techniques like 1) Thermophilic biphasic system of methanol and oil 2) Micro emulsion process

2.11.1. Thermophilic biphasic system of methanol and oil

In this process different types of vegetable oils can be used like soyabean oil, palm oil, canola oil etc. The reagents and the catalyst (potassium carbonate) are dissolved in alcohol and then the mixture of oil and solvent (heptane’s and methanol) is added. Then the biphasic solution of is turned monophasic by heating the mixture up to 70 to 80°C. The solution is again converted to biphasic after 2 hrs by cooling it down at 60°C and the resultant mixture is separated into a solution containing esters in the heptane phase and glycerol in the alcohol phase. After removal of heptane layer, GCMS is used foresters (biodiesel) analysis. The separated alcohol is returned back to a solution containing potassium carbonate and catalyst is remixed. It is a more economical and greener process as the catalyst and the alcohol is recycled many times without any loss of reactivity.

2.11.2. Micro-emulsion process

In this method the waste cooking oil is first dehydrated using sodium sulphate. The issue of greater viscosity of waste oils is controlled by making a micro emulsion of ethanol, butanol and octanol (Li et al. 2019). Here butanol/octanol acts as a surfactant to maintain hydrophilic-lipophilic balance. Micro droplets are produced that remain in the butanol/octanol phase. The boiling point for combustion of micro emulsion based biofuel is low so they emit less NOx emissions. This type of formulated biofuel has viscosity equal to that of biodiesel and thus can be mixed in the petro diesel fuel.

Chapter 3

Materials and Methods

3.1. Materials

Ethanol 99.8% pure was purchased from BDH (Dubai, UAE). Amberlyst 15, AmberlystA21, phenolphthalein and potassium hydroxide (0.1 N) were purchased from Sigma Aldrich (Pakistan distributor). Amberlyst 15 vendor characterization of resin catalyst reports that the catalyst is macro-porous, dry, and spherical with BET surface area of 29.69 m^2/g, with a porosity of 0.36 pore/mL bead, and average pore diameter of 240Ǻ (Khan et al. 2016). While the Amberlyst A21 is a weak base polymer resin. It has vendor reported particle mean size in range 490-690 µm and BET surface area of $35m^2/g$. All chemicals were used as received.

3.2. Methods

For oil separation from water by adsorption and later for esterification, two sets of ion-exchange resin were used. One was the basic quaternary ammonium resin and other was the sulfonic acidic resin. FFA’s were adsorbed from oily water on the basic quaternary ammonium resin that were later washed out with ethanol and esterification reaction was proceeded on the washed out fatty acids and ethanol mixture with the addition of acidic resin in the batch reactor. Esterification reaction was performed by varying oil to ethanol molar ratio 1:2 and 1:3, catalyst weight percentage 2, 4, and 6%, temperature from 50, 60, 70 and 75^{o}C and time duration from 2-8 hrs respectively. Similar temperature ranges for esterification reaction are reported earlier by using methanol as the alcohol (Hayyan et al. 2014). Oil free water from basic column was then analyzed for chemical oxygen demand (COD) method ISO 6060 at pre and post treatment conditions. Titration method and Gas Chromatography Mass Spectrometry (GCMS) were used for the quantification of FFA’s in the mixturefor oil and FAEE’s characterization. Figure 3.1 shows the process layout steps for the adsorption, desorption of the FFA’s and then esterification reaction.

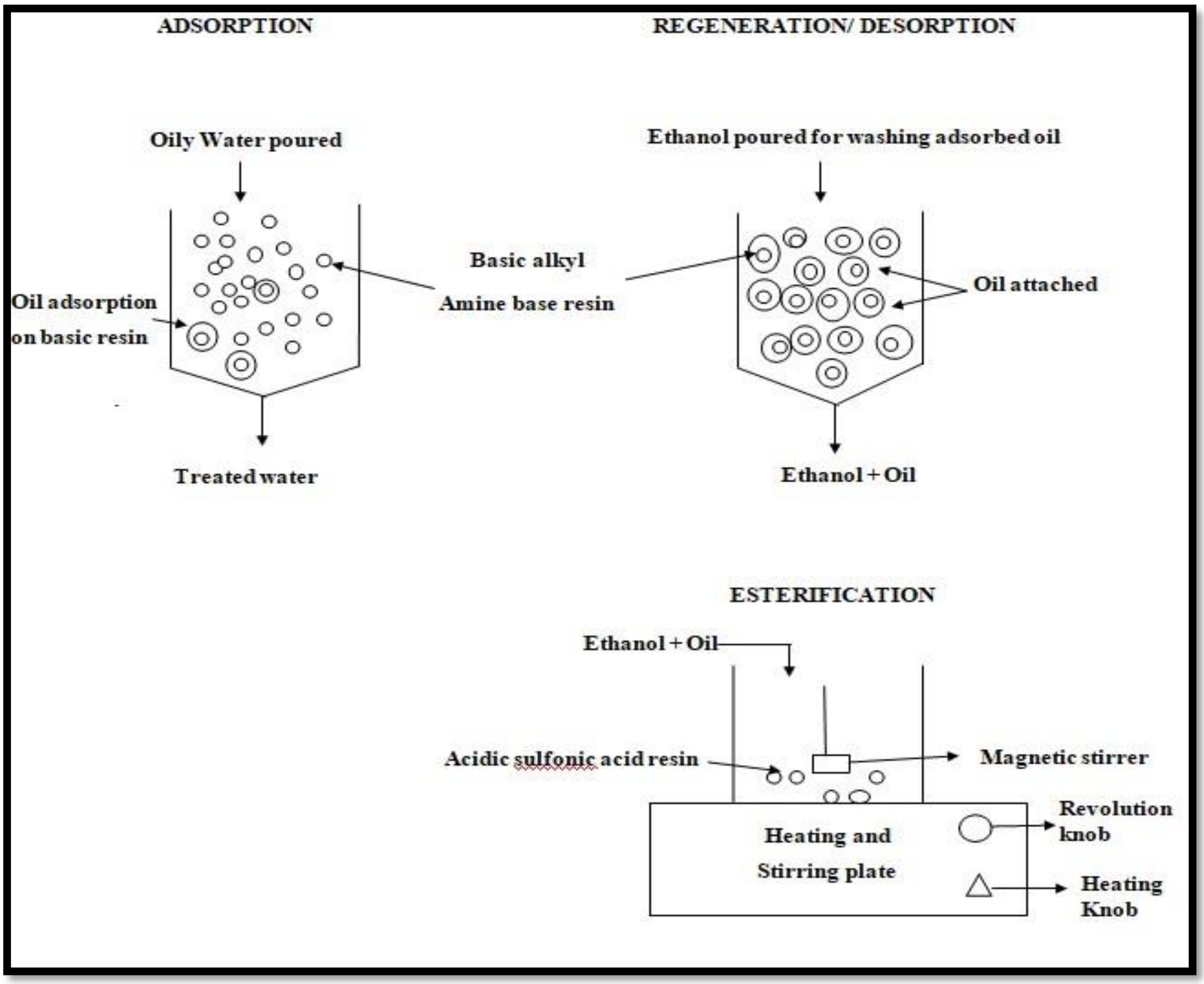


Figure 3.1. Experimental process flow diagram.

The whole process takes place in three steps. First, is the adsorption of free fatty acid on basic quaternary ammonium resin, second is the washing of adsorbed free fatty acids with ethanol and third is the addition of acidic resin in ethanol and oil mixture for esterification of free fatty acids in thereactor.

3.3. Parameters for esterification

For esterification reaction, effect of three parameters were studied namely molar ratio, reaction temperature and catalyst weight percentage with respect to reaction volume of FFA's. For every experiment, one parameter was kept variable and other two parameters were kept constant.

For desorption of FFA's from adsorbed basic catalyst resin surface, ethanol was used to wash the surfaces in 10, 20 and 30 mL. This volume was also used to maintain molar ratio of FFA's and alcohol in ratio 1:2 and 1:3 respectively.

3.4. Sample collection

Oily wastewater was collected from different points of the Chakri drain Rawalpindi Pakistan. It is 22.3 km long drain with variable depth at different locations. Collected samples were placed in 100 mL measuring cylinders and separation of oily layer was noted from 24 hours up to 72 hours. The top layer separated out was then used to find out volume of oil present in every 100 mL of wastewater collected. Nine samples were collected and gravity separations were performed in triplicates. This oily wastewater has also a potential to produce energy fuels and treated water can be reused. Figure 3.2 shows the different collection points of the drain.

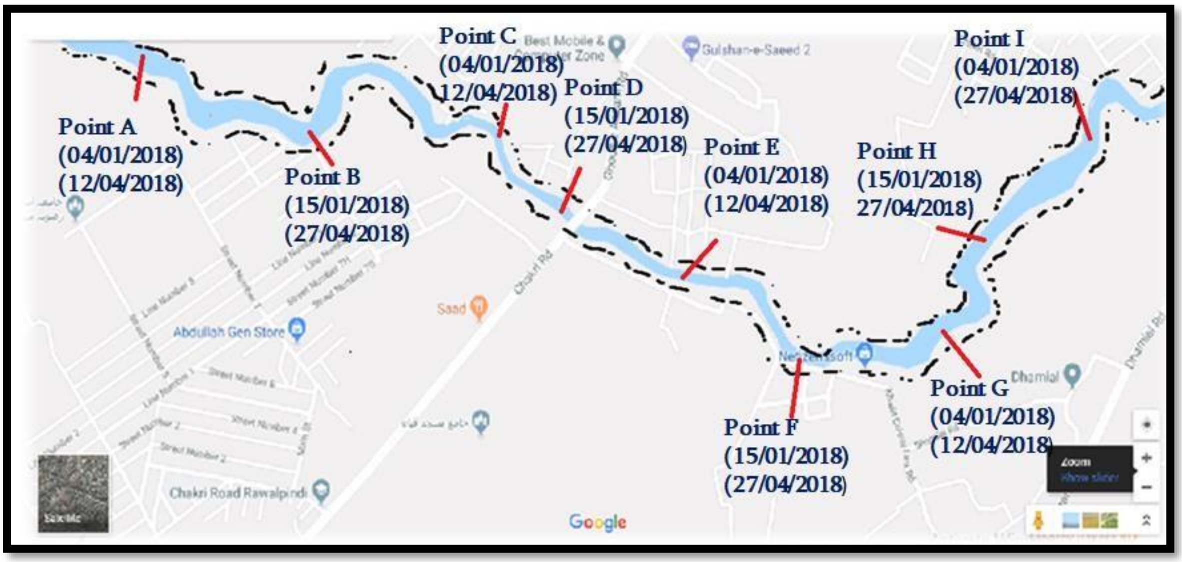


Figure 3.2. Study Area for water sampling.

In order to measure seasonal variation, samples were collected initially in the month of January and later in month of April. GCMS of the collected oil sample was performed to find which compounds were present in the sample and the composition of compounds in the oil fraction.

3.5. Properties of collected oil

Density of collected oil was measured by dividing mass of sample by its volume. Kinematic viscosity of oil was measured by capillary tube technique using American Society for Testing and Materials (ASTM) method ASTM D445. Flash point was measured by using flash point tester method ASTM D93-18 and heating value was calculated by using bomb calorimeter method ASTM D240.

3.6. Molar ratio calculation

Fatty acids were identified with Shimadzu GCMS QP-2010, USA having Sigma Aldrich capillary column product number 24028 dimensions L30 m x I.D x 0.25 mm, d_f 0.25µm. For molar ratio calculation, moles of identified fatty acids were calculated by dividing mass of the acids with the molar mass of the acids. The moles of ethanol were calculated by multiplying the volume of ethanol (10, 20 and 30 mL) with the density of ethanol and dividing the resultant by the molar mass of ethanol. Finally, the total moles of acids were divided by the moles of ethanol and molar ratio was obtained (Attaphong et al.2016).

3.7. Titration

American Oil Chemist Society (AOCS) Ca-5-40 official method was used for the determination of FFAs (Kail et al. 2012). The following formula, (1), was used for the calculations.

$$\mathbf{AOCS-Ca-5a-40=} \quad \frac{\mathbf{b-a\ x\,N \times 28.2}}{\mathbf{Weight\ of\ sample}} \qquad (3.1)$$

b-a= (Difference in volume of KOH, mL)

N = (Normality of KOH solution)

After performing titration, GCMS of the final oil sample was performed to find that which compounds are present in the sample and also the composition of compounds.

3.8. Purification of esterified sample

In order to separate esters from the resultant product mixture and to increase percentage conversion of esters in the esterified mixture, fractional distillation was performed at specified temperature 100°C. Figure 3.3 shows the process layout of fractional distillation.

Different esters have different boiling points and after passing through the fractionating column, low boiling compounds were separated as shown by fraction X in figure 3.3 while high boiling compounds, that remain in the flask, were finally analyzed through GCMS and their properties like density, flash point and heating values were calculated.

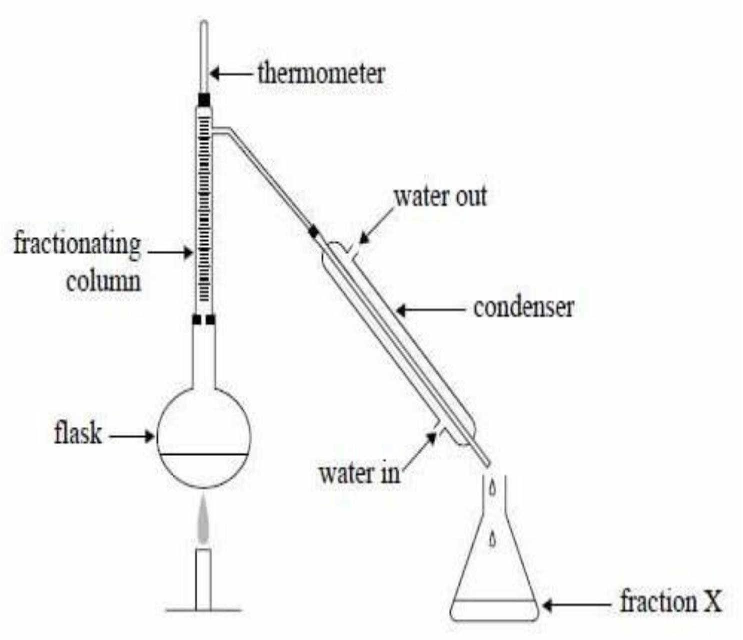


Figure 3.3. Fractional distillation assembly

3.9. Catalyst regeneration

To calculate resin catalysts esterification efficiency in the current process, three scenarios of resin use were studied i.e. new set of resins each, 10 mL ethanol washed basic and acidic resins separately and both used basic and acidic catalysts.

3.10. Reduction in chemical oxygen demand from oil free wastewater for reuse

For treatment of oily wastewater after oil separation, it was passed through different quantities of activated carbon (0.1-1.0 g/L) at a flow rate of 0.36 mL/min. The drop in COD value was noted before and after the filtration by COD method ISO 6060.

3.11. Other wastewater parameters

- **pH**

pH is measured by using pH meter.

- **Alkalinity**

Alkalinity is measured by the formula

Alakalinit y= Normality of acid solution * burette reading * 50 * 1000/ Sample volume

- 0.02N HCLsolution

- Take 100ml of sample in conical flask and add 2 to 3 drops of indicator (Phenolpthalein or methyl orange).
- 50 is the equivalent weight of $CaCO_3$

Ammonia (Using 4500 NH_3B)

Following steps were used to measure ammonia of wastewater

- Distillation of ammonia from the sample into boric acid solution.
- Titration of the ammonia against the standard H_2SO_4 solution.
- After ammonia distillation, residue in kjeldahl flask has cooled down start digestion to determine organic nitrogen.
- Nitrogen would be converted to ammonium sulphate when heated in the presence of sulphuri cacid
- K_2SO_4 and $Cu_2(SO_4)_3$ catalysts increase H_2SO_4boiling point to 370C and organic matter is oxidized toCO_2
- Then ammonia from organic nitrogen is released, it is distilled and determined.
- Before distillation, the pH of the sample is raised to 9.5 to encourage ammonia formation.
- The ammonia which reacts with boric acid can be determined by back titration with a strong acid.

Chapter 4

Results and Discussions

Oil separation results showed that the separation of oil increases with settling time. At 72 hours, a maximum of oil separation was possible from 33 ± 2.08 % is present in the water body. COD of oily wastewater before and after oil separation was found 668.8 ± 1.37 mg/L and 395.0 ± 1.04 mg/L respectively.

4.1. Initial identification of compounds

GCMS of the final oil sample was performed to find that which compounds are present in the sample and also the composition of compounds. The compounds identified are shown in table 4.1.

Table 4.1. Initial compounds identification

Compounds Identified	**Name**	**%**
$C_{12}H_{22}0_{11}$	Isomaltose	3.51
H_20_2	Hydrogen peroxide	5.30
$C_4H_{10}O$	2- methyl-1-propanol	7.98
Na_2HPO_4	Disodium phosphate	3.56
BrF3	Bromine trifluoride	1.67
Unknown	Unknown HC	4.98
H_2S	Hydrogen sulphide	6.81
POCl3	Phosphoryl chloride	1.09
C_4H_9Cl	Coelution of alkane	4.39
$C_{19}H_{38}0_2$	Non adecylic acid	7.32
$C_{18}H_{34}0_2$	Oleic acid	19.20
$C_{18}H_{32}0_2$	Linoleic acid	12.01
$C_{10}H_{20}O_2$	Capric acid	1.47
$C_{18}H_{30}O_2$	Alpha linoleic acid	19.65

These compound include fatty acids, organic compounds and inorganic compounds. The maximum fatty acid percentage achieved is of alpha linoleic acid followed by linoleic acid and oleic acid.

4.2. Characteristics of separated oil

The characteristics of the separated oil density, kinematic viscosity, flash point, lower heating value and higher heating value from oily wastewater are shown in the Table 4.2.

Table 4.2. Separated oil composition

Property	**Experimental values**	**Literature**
Density	947.31 kg/m³	900-940kg/m³ (Chhetri et al. 2008, Katkade et al.2018)
Kinematic viscosity	32.69 mm²/sec	39.74-56.04 mm²/sec (Alias et al. 2018)
Flash point	283°C	198-290°C (Alias et al. 2018)
Lower heating value (LHV)	26 MJ/kg	31.6-39.2 MJ/kg (Mehta and Anand 2009)
Higher heating value (HHV)	28 MJ/kg.	33.9-41.5 MJ/kg (Fassinou 2012)

All values were in the range of reported values of waste oil. Noted heating values (HHV and LHV) of waste cooking oil separated from oily wastewater sample in this work are mainly based on presence of unsaturated fatty acids in the collected oil from the oily wastewater.

4.3. Impact of reaction parameters on the esterification

Esterification of fatty acids washed from the surface of basic catalyst with ethanol in the presences of acidic sulfonic acid resin catalyst showed that with the increase in temperature, fatty acid conversion into esters increased. This is because increase of temperature decreases the viscosity of fatty acid that helps its approach to the catalyst surface resulting in more conversion to esters (Zhang et al. 2014, Khan et al. 2016).

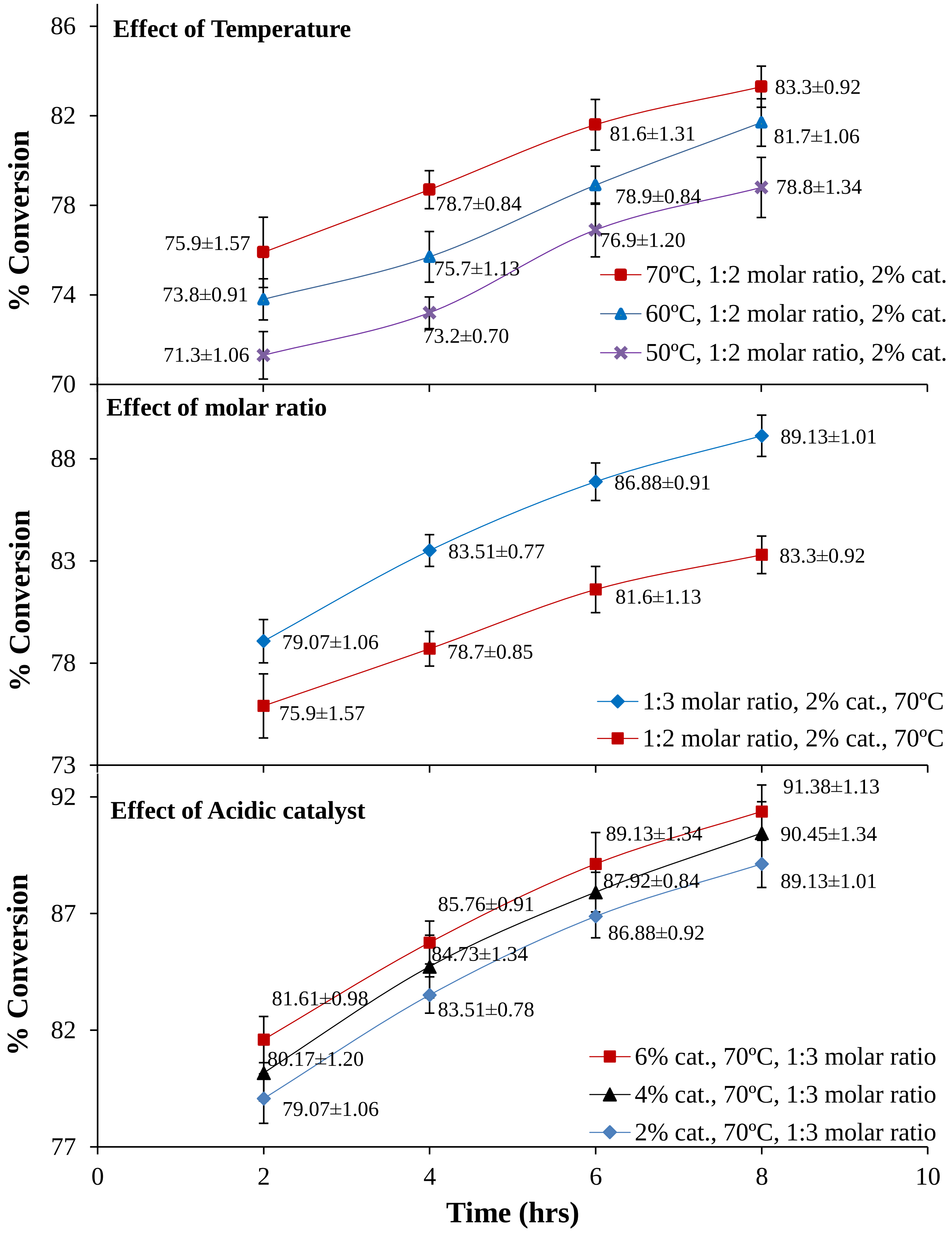


Figure 4.1. Effect of reaction parameters on esterification

At 75°C, the reaction becomes uncontrollable so 70°C temperature for reaction was adopted for further study. This is because the vaporization point of ethanol is 78°C. Molar ratio of alcohol to fatty acid oil also has a positive effect as noted at 70°C (1:2 vs 1:3). This is because of the fact that more alcohol in the reactor increases the conversion of the reactants (Sharma, Wanchoo, and Toor 2014) has shown least conversion when 1:1 molar ratio was selected for esterification. It can also be inferred from the figure 4.1 that the availability of catalyst surface has a positive effect on the esters conversion. This means sufficient amount of catalyst surface must be present in the reaction to proceed, reducing the catalyst concentration decreases the reaction sites for esters formation (Hayyan et al. 2014, Shahid et al. 2017). At 6% acidic resin catalyst, greater than 90% convection of lipids into FAEEs was achieved while keeping the molar ratio 1:3 and reaction temperature 70^{o}C. Adding more acidic resin catalyst not only increases the price of esterification reaction but also the moisture content of the reaction that causes hydrolysis of ethyl esters produced, in the presence of the acidic catalyst (Pua et al. 2011, Libre Texts project 2019). So 6% acidic resin catalyst was adopted for the esterification. Further it is noted that increase in reaction time can increase the overall conversion of fatty acids into esters as the reaction time was increased from two to eight hours more conversion into FAEE's was achieved (Ferdous et al. 2013, Khan et al.2016).

4.4. Identification of compounds in esterified sample

GCMS of the final esterified sample was performed to find that how much fatty acids were converted into esters and their composition. Table 4.3 showing the compounds identified in the esterified sample.

Table 4.3. Identifiation of compounds in esterified sample

Compounds Identified	Name	%
$C_{20}H_{34}O_2$	Ethyl alpha linoleate	20.01
H_2O_2	Hydrogen peroxide	1.21
Na_2HPO_4	Disodium phosphate	0.86
$C_{12}H_{24}O_2$	Ethyl caprate	3.58
$C_{12}H_{22}O_{11}$	Isomaltose	0.59
$C_6H_{12}O_2$	Ethyl butyrate	10.36
$C_{21}H_{42}O_2$	Ethyl non adecanoate	9.13
BrF_3	Bromine trifluoride	1.43
$C_{20}H_{36}O_2$	Ethyl linoleate	14.82
$C_4H_7ClO_2$	Ethyl chloroacetate	6.07
$C_{20}H_{38}O_2$	Ethyl oleate	17.37
$C_{16}H_{32}O_2$	Palmitate	8.06

$POCl_3$	Phosphoryl chloride	1.19
$C_4H_{10}O$	2- methyl -1- propanol	1.16
H_2S	Hydrogen sulphide	4.18

GCMS results showed the presence of esters with maximum presence of ethyl alpha linoleate. At reaction conditions of 6% weight of oil, reaction temperature of 70°C and molar ratio of 1:3 for reaction time of 8 hours, maximum reaction conversion of 91.38% was achieved. However, according to European standard DIN (14214) and American standard ASTM (D6751), 95% conversion into esters is required for a sample to be called biodiesel. Therefore, in order to separate esters from other compounds, fractional distillation was performed at 100°C to separate esters from reaction mixture. Table 4.4 showing the compounds identified in the fractionally distilled esterified sample.

Table 4.4. Identification of compounds in fractionally distilled esterified sample

Compounds identified	**Name**	**%**
$C_{20}H_{34}0_2$	Ethyl alpha linoleate	21.30
H_20_2	Hydrogen peroxide	1.09
Na_2HPO_4	Disodium phosphate	0.80
$C_6H_{12}0_2$	Ethyl butyrate	10.97
$C_{16}H_{32}0_2$	Palmitate	9.13
$POCl_3$	Phosphoryl chloride	1.15
BrF_3	Bromine trifluoride	1.21
$C_{20}H_{36}O_2$	Ethyl linoleate	15.76
$C_4H_7ClO_2$	Ethyl chloro acetate	7.18
$C_{20}H_{38}O_2$	Ethyl oleate	17.94
$C_{21}H_{42}0_2$	Ethyl non adecanoate	9.78
$C_{12}H_{24}0_2$	Ethyl caprate	3.98

Maximum percentage of ethyl alpha linoleate of 21.30 % was observed. After performing fractional distillation, the reaction product resulted in 95.75% ester yield. This conversion is in accordance to the desired standards (95% esters in Biodiesel) as mentioned above. Figure 4.2 shows the type of esters present in the fractionally distilled esterified sample.

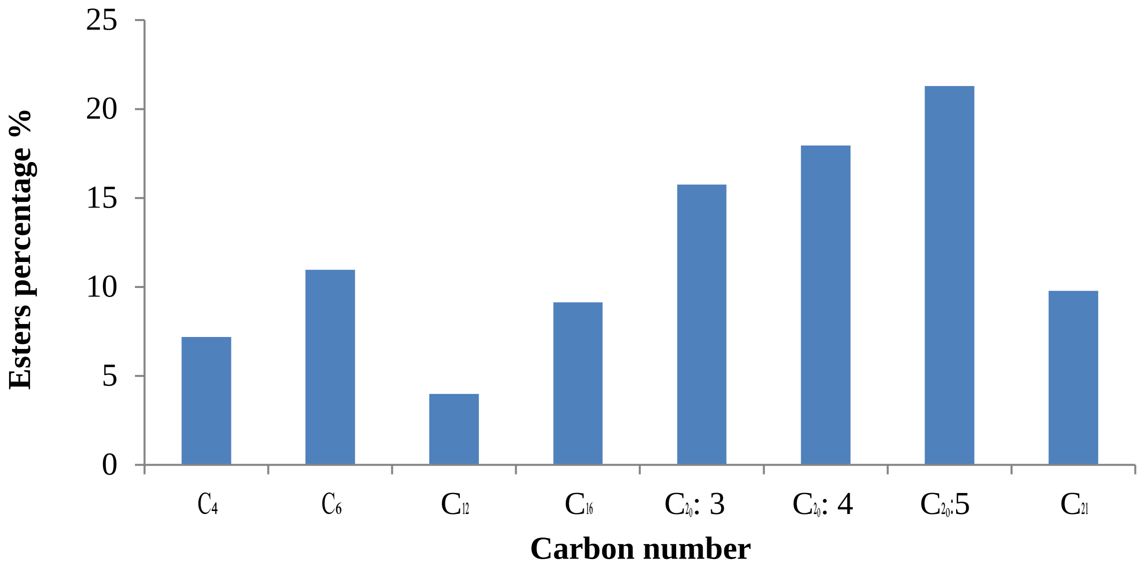


Figure 4.2. Esters type and percentage with carbon number in the esterified sample

The maximum ester percentage obtainedin the reaction mixture was ethyl alpha linoleate. Ethyl alpha linoleate has five double bonds, followed by ethyl linoleate having four double bonds and ethyl oleate forms three double bonds. Presence of long chain unsaturated esters in the fractionally distilled esterified sample shows that oil used for cooking by population in the vicinity of Chakri drain is of low quality (Perumalla Venkata and Subramanyam 2016). Deep frying and use of same oil result in formation of non-volatile oxidized derivatives and cyclic substances leading to the formation of toxic or carcinogenic substances that greatly affects oil properties (Sayyad 2017).

4.5. Biodiesel Analysis

Biodiesel produced from separated oil by heterogeneous esterification showed characteristics meeting all the ASTM standards as shown in table 4.5.

Table 4.5. Biodiesel analysis.

Property	**Experimental values**	**ASTM Standards B100**	**ASTM Method**
Density	886 kg/m³	850-890 kg/m³	ASTM D1298
Kinematic viscosity	4.3mm²/sec	1.9-6.0 mm²/sec	ASTM D445
Flash point	137°C	130 min	ASTM D93
Lower heating value (LHV)	39 MJ/kg	41 MJ/kg	ASTM D240
Higher heating value (HHV)	41 MJ/kg	43 MJ/kg	ASTM D240

Flash point of waste cooking oil (Table 4.2) was higher than the biodiesel produced (Table 4.5) due to the fact that cooking oils are heated at higher temperatures during the cooking process. Similarly, kinematic viscosity depends on free fatty acid type present in the waste cookingoil. According to ASTM D6751, the final value of ethyl esters should be in range 1.9–6.0 mm^2/s. Thus produced biodiesel (Table 2) is of high quality to be used in transportation vehicles (Alias et al. 2018).

4.6. Regeneration of used catalysts

Acidic and basic catalysts regeneration experiments were performed to calculate the esterification efficiency of the system and reusability of both catalysts. Pure (new) catalysts set showed 91.38 ± 1.13% conversion into esters, ethanol washed catalysts showed 85.52 ± 0.86% conversion and used catalysts showed 77.93 ± 1.13% conversion into esters as shown in figure 4.3. Pure catalysts showed best removal of free fatty acids from oily water and maximum esterification conversion by the acidic resin while it was compared to ethanol washed catalyst and used catalysts.

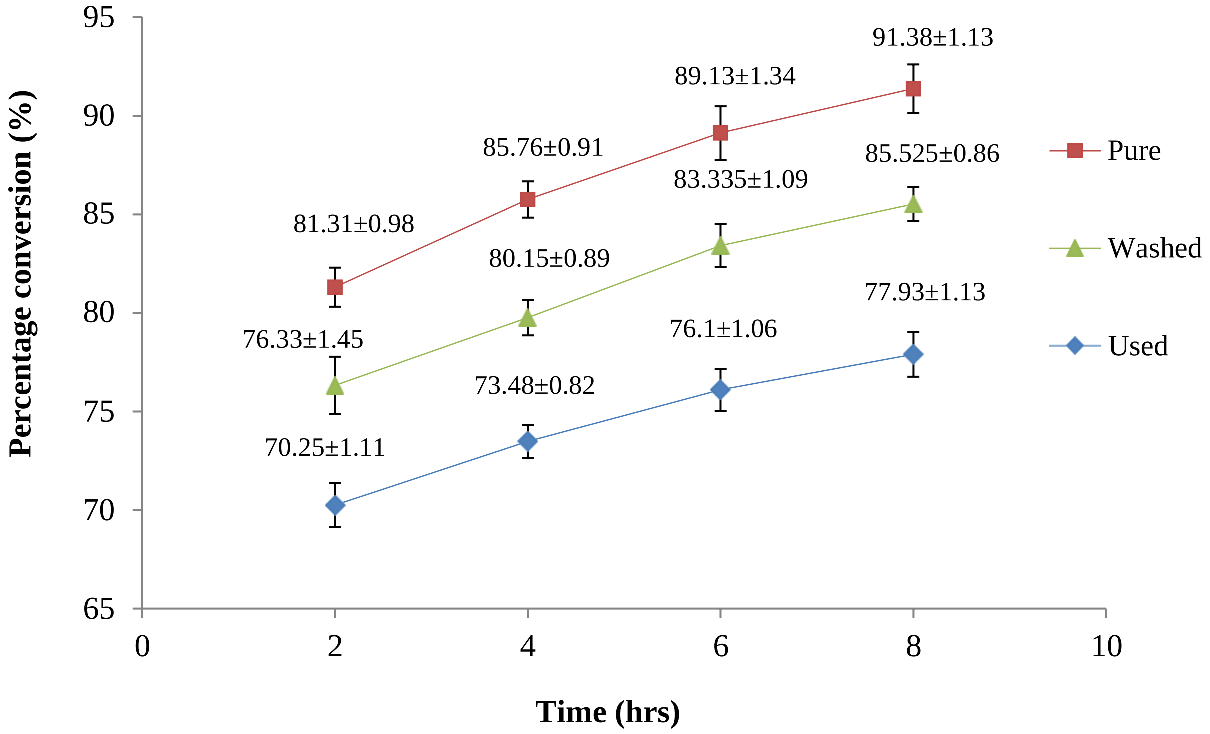


Figure 4.3. Catalysts regeneration efficiency.

This is due to the fact that a catalyst increases the rate of reaction by lowering the activation energy (Chang et al. 2009) and Pure catalyst has highest reaction rate (oxidation reduction reactions) and lowest activation energy as compared to ethanol washed and used catalysts (Li et al. 2019).

4.7. COD of Oil Free Wastewater passing through Activated Carbon

Oil free wastewater of initial COD value 395.2 mg/L, passed at a flow rate of 0.36 ml/min through different quantities of activated carbon 0.1-1.0 g/L, shows a drop in the COD value to the required National Environmental Quality Standards (NEQS) of 150 mg/L at a dose of 0.74 g/L as can be seen from figure 4.4. When the same oil free water was passed at 0.8 and 1.0 g/L dose of activated carbon, COD value reduced to 135.5 mg/L and 106 mg/L respectively.

Reduction in COD value showed that there is a direct relation with the activated carbon dosage. As we increased activated carbon dosage, the removal is increased.This is due to the fact that greater the amount of activated carbon, greater will be the collection of the solute components. The attractive Van- der-Walls forces become more stronger that enhances the adsorption (Cukierman 2013).

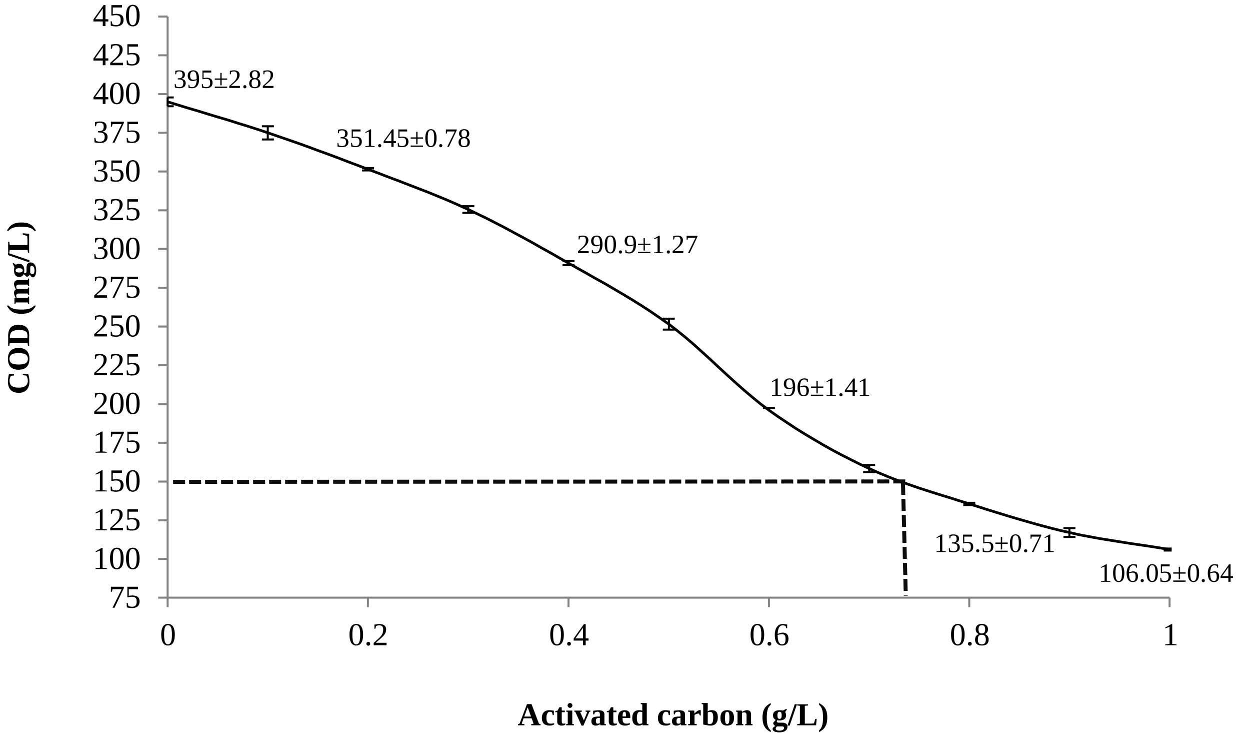


Figure 4.4. Impact of drop in COD vs Activated carbon.

4.8. Impact of oily water adsorption and desorption on the efficiency of activated carbon

When water without oil separation passed through activated carbon column at 0.8 g/L and 1.0g/L dosage it shows no significant reduction in COD values over the time (Figure 4.5). In case of 0.8 g/L, the COD value decreased from initial value of 668.4 to 512.7 mg/L in the time interval of 45 minutes and by increasing time interval from 45 to 90 minutes, the COD value only further reduced to 509.8 mg/l.

Figure 8, also shows that the COD value decreased from 668.4 to 498.6 mg/L on passing the same sample through activated carbon dosage of 1.0g/l in the time interval of 45 minutes and on increasing the time interval to 90 minutes, the COD value only reduced to 497.1 mg/L.

The final COD values, in both the cases, were far away from the NEQS requirement (150 mg/L), indicating that oil removal is necessary to make water reusable for the horticulture purpose (National Environmental Quality Standards (NEQS) 1999, American Society of Civil Engineering 2001).

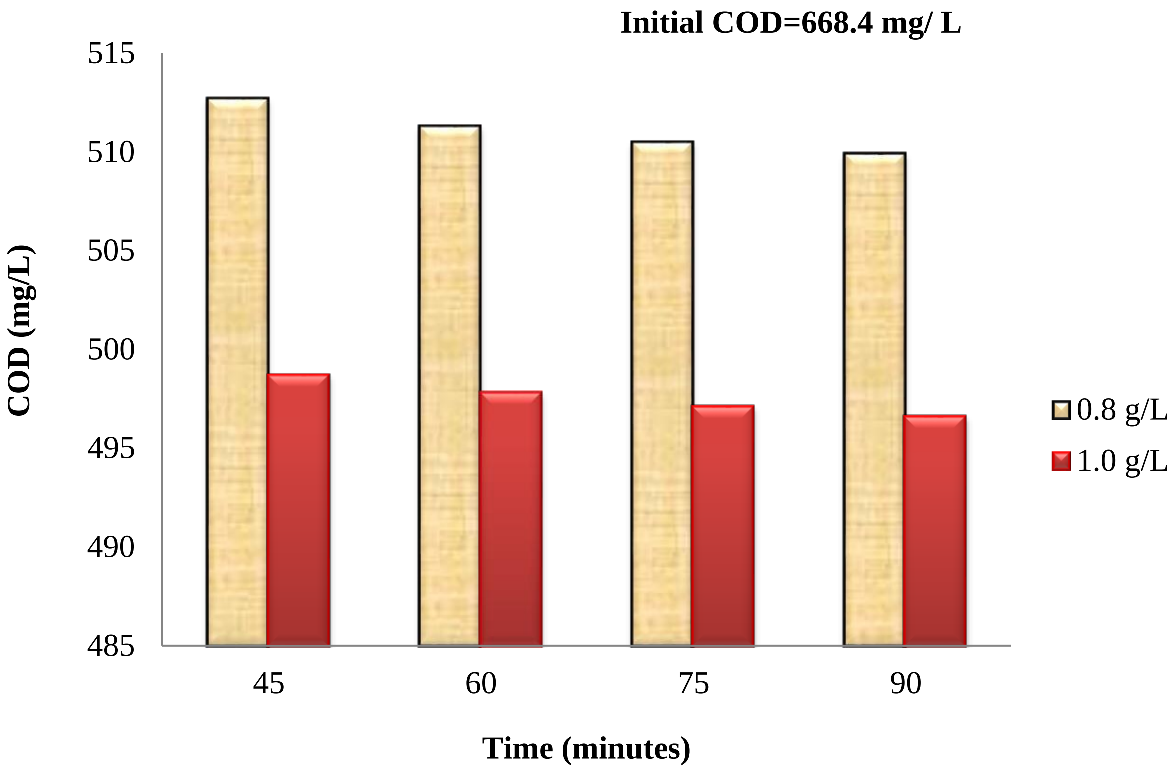


Figure 4.5. Effect of oily wastewater on COD at optimized dosages.

4.8.1. Other wastewater parameters

Different wastewater parameters like pH, alkalinity also found meeting the NEQS limits on passing through optimized activated carbon dosage of 0.8g/l as shown in table 4.6. The NEQS standard limit of ammonia achieved at activated carbon dosage of 1.2 g/l while the other parameters were reduced to NEQS limits at 0.8 g/l dosage of activated carbon as shown in the following table.

From the results it can be concluded that after oil removal from wastewater and after passing the wastewater through activated carbon column dosage of 0.8 g/l -1.2 g/l, the wastewater can be further made available for reuse in horticultural and agricultural purpose. For ammonia, high dosage of activated carbon column is required while other parameters were reduced to their NEQS limits at activated carbon dosage of 0.8g/l.

Table 4.6. Wastewater parameters.

Parameters	**With oil**	**Without oil**	**After passing through Activated carbon 0.8 g/l**			**NEQS**
COD (mg/l)	638.4	395.2	135.5			< 150
pH	8.4	7.9	7.2			6-8
Alkalinity (mg/l)	1803 ± 1.86	1227 ± 1.48	908 ± 1.51			< 1000
Ammonia (mg/l)	72 ± 1.97	51 ± 1.30	0.8 g/l	1.0 g/l	1.2 g/l	< 40
			44.27±1.82	42.06±1.51	39.94±1.67	

4.9. Economics of operation

Calculations showed that conversion of recovered FFA’s into biodiesel is economically feasible with energy balance for the heating of oil and energy required for fractional distillation. 300 gallons of oil can be separated per 1000 gallons of oily water of chakri drain Rawalpindi Pakistan and 286.56 gallons of biodiesel can be produced at 95% esters conversion. Pakistani Rupees 53.811 million can be earned from oil separation and its conversion into pure biodiesel with 95% ester content. Further water can be made available for agricultural reuse with COD value less than 150mg/L.

The amount of oil recovered from 1000 gallons of domestic wastewater = 300 gallons or 1135.62 litres and the amount of biodiesel produced out of 300 gallons in this research =286.56 gallons or 1084.74 litres.

STEPS

- **The energy required to heat oil (Qoil) is calculated by using the following formula** (Equation1)

$Q_{oil} = mCp\Delta T$……………………………………………**Equation 1**

Where Q= Energy of oil, m= mass of oil,

Cp= Specific heat of Alpha linoleic acid and

ΔT= Change in temperature

Here

Density of Alpha linoleic acid = 0.947 kg/l

Specific heat of Alpha linoleic acid= 1.6 KJ/Kg-K

Mass of oil is calculated by the following formula

m = Volume * Density

Volume of oil obtained = 1135 litres

So

M = volume X density

M = 1135.62 x 0.947= 1075.43 kg

Now with rise in temperature from 25-70 ^{o}C,

Change in temperature

ΔT= 70-25= 45^{o}C= 318.15 K

Then by using equation 1, Q_{oil} is calculated

Q_{oil} = 1075.43*1.6*318.15

Q_{oil} = 547436.887 KJ or 547.43 MJ.

- **The energy supplied by biodiesel is calculated by the following formula** (Equation2)

Q_{bio} = m* HHV…………………………………**Equation 2**

Where m= mass of biodiesel produced

and HHV= Higher heating value of

biodiesel

Higher heating value (HHV) = 41MJ/Kg

Again mass of oil is calculated by the following formula

m = Volume* Density

Volume of biodiesel produced= 1084.74 litres.

Density of produced biodiesel = 886 kg/l

So energy supplied by biodiesel (Q_{bio}) is calculated by using Equation 2

Q_{bio}= 41 x 0.886 x 1084.74= 39404.26 MJ

Remaining energy of biodiesel is calculated by subtracting the energy of biodiesel from the energy of oil

Energy of biodiesel left

= $Q_{bio} - Q_{oil}$

= 39404.26 - 547.43 = 38856.83 MJ

Equal volume of biodiesel would be

1084.74 L = 39404.26 MJ

1069.67 L Biodiesel = 38856.83 MJ

- **The energy required for fractional distillation (Q_{fd}) of 91% ester product is calculated by using equation1**

$$Q_{fd} = mCp\Delta T$$

Mass of biodiesel is calculated by the following formula = m = volume * density

Volume of 91% biodiesel= 1135.62 litres

Density of biodiesel produced= 0.886 kg/l

So by applying formula, mass is calculated

m = 1135.62 * 0.886 = 1006.15 kg.

Also

Specific heat of ethyl alpha linoleate = 1.53 KJ/Kg-K

Now with rise in temperature from70-100ºC, the change in temperature

$\Delta T = 100-70 = 30\ ^{o}C = 303.15\ K$

Then by using quation 1, we get

$Q_{fd} = mCp\Delta T$

$Q_{fd} = 1006.15 * 1.53 * 303.15 = 466671.98\ KJ = 466.67\ MJ$

- **The energy supplied by biodiesel produced after fractional distillation is calculated by using equation2**

$\mathbf{Q_{bf} = m * HHV}$

Here

Higher heating value (HHV) = 41MJ/Kg

Again mass of oil is calculated by the following formula

m = volume * density

Volume of biodiesel produced = 1069.67 litres.

Density of produced biodiesel = 0. 886 kg/l

So energy supplied by biodiesel is calculated by using Equation 2

$Q_{bfd} = 41 * 0.886 * 1069.67$

$= 38856.83\ MJ$

Remaining energy of biodiesel is calculated by subtracting the energy of biodiesel from the energy of oil

Energy of biodiesel left = $Q_{bf} - Q_{fd}$

$= 38856.83 – 466.67$

$= 38390.15\ MJ$

Then

Equal volume of biodiesel would be

1069.67 litres = 38856.83MJ

1056.82 litres = 38390.15MJ

- **The profit in producing biodiesel is calculated**

Here the biodiesel price per lire in Pakistan= 93 Rs/litre.

So the price of produced biodiesel is

1056.82 x 93 = 98284.26 Rs =0.098 million (Biodiesel Price= 93 Rs/litre)

Profit in a day would be equal to three shifts the price of biodiesel.

Profit in a day = 98284.26 * 3

= 294852.78 Rs / day = 0.294 million / day.

Profit in a month is calculated by multiplying the profit in a day by 30 days

Profit in a month = 294852.78 * 30

= 8845583.4 Rs/month - 8.845 million/ month (Profit in a month)

Profit in a year is calculated by multiplying the profit in a day by 365 days

Profit in a year = 294852.78 *365

= 107621264.7 Rs / year. = 107.621 million/year (Profit in a year)

Chemicals (basic and acidic resin catalyst plus ethanol) cost required to process lipids from Chakri drain is equal to 15 percent of the biodiesel produced price = Rs. 16.143 million / year (EL-Gharbawy 2017 .

Equipment plus installation cost is equal to 35 percent of the total biodiesel produced price = Rs. 37.667 million (EL-Gharbawy 2017) .

The first year annual profit from chakri drain is calculated by subtracting the chemicals and equipment plus installation cost from the produced biodiesel profit

= Rs. 107.621 million – Rs. 16.143 million – Rs. 37.667 million = Rs. 53.811

million. First year biodiesel production profit= Rs. 53.811=Rs. 53.8 million.

Second year biodiesel production profit without considering equipment plus installation cost = Rs. 91.478 = Rs. 91.5 million. According to the literature, chemicals cost is equal to 10 percent of the total cost

With oil recovery and conversion into biodiesel, a profit of 53.811 million rupees per annum can be gained while discharging water back to the Chakri drain for pollutant dilution. Further water can be made available for agricultural reuse with COD value less than 150 mg/L.

Chapter 5

Conclusions and Recommendations

5.1. Conclusion

Waste oil from domestic wastewater streams can be esterified into esters with the use of acidic and basic catalysts. For esterification different parameters like reaction temperature, molar ratio, acidic catalyst percentage in the reaction and reaction time were studied. It is concluded that esterification reaction increases with the reaction temperature, ethanol molar ratio, catalyst surface availability and reaction time. Maximum conversion was achieved at 70^{o}C , with molar ratio of 1:3, using 6% acidic catalyst and reaction time of 8 hrs. Beyond this temperature, the reaction becomes uncontrollable. It is also noted that the esterified sample at optimized conditions after 8 hours contained 91.38 % esters and 8.62 % organic and inorganic compounds. Since as per definition of American and European standards to be called as biodiesel; the ester content in the reaction mixture should be 95% esters.

The percent content of esters in the reaction mixture was increased with fractional distillation, by separating organics from esters. After performing fractional distillation, GCMS of the esterified sample showed 95.75% ester content presence. In this way, biodiesel formation as per definition of ASTM and European standards were achieved.

300 gallons of oil can be recovered for every 1000 gallon of oily wastewater treated from Chakri drain resulting in 286.56 gallons of biodiesel production. Further, it is noted that after oil removal from oily wastewater, its COD value can be brought within NEQS limit after 45-minutes of adsorption on activated carbon column (0.8 g/l). With oil recovery and conversion into biodiesel, a profit of 53.811 million rupees can be gained in first year and 91.479 million rupees in successive years while discharging water back to the Chakri drain for pollutant dilution and for reuse in horticulture purpose.

5.2. Recommendations

5.2.1. General

Ester formation through batch reactor technology has now reached to its full application potential but still a better understanding of the reaction mechanism is needed to avoid soap formation. Various catalyst systems (homogeneous or heterogeneous) could be studied to minimize the economic cost and increase the biodiesel yield. Further oil separation techniques with oil separating equipments should be studied to reduce retention time of oily wastewater.

5.2.2. Future Studies

In the coming years, we will see more development in technologies from catalytic, biological to thermal conversion of lipids into mono alkyl esters with many applications just beyond the water reuse. Economic optimization requires the minimal catalyst usage and low investment cost related to lipids source materials. Development of heterogeneous catalysts with in-situ and ex-situ conversion could be the area of future development at IESE. Along with this various algae based remediation projects could be the area for biofuels production in supplement to the main research.

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