

**MIXED ESTERS FROM HIGH FREE FATTY ACIDS WASTE
COOKING OIL USING A HETEROGENEOUS COLUMN
SYSTEM**



By

Jamshed Ali Khan

(NUST201261024MSCEE65112F)

A thesis submitted in partial fulfillment of requirements for the degree of

Master of Science (MS)

In

Environmental Engineering

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School of Civil and Environmental Engineering (SCEE)
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Submitted by

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**This thesis is dedicated to the
departed souls of innocent children**
who became the victims of terrorists attack on
Army Public School on Dec 16, 2014.

ACKNOWLEDGEMENTS

This dissertation would have not been possible without the guidance and the help of several individuals who, in one way or another, contributed in the preparation and of my thesis and completion of my research work.

*I would like to express my sincere gratitude and thanks to my research supervisor **Dr. Yousuf Jamal** for his guidance, suggestions, many good advices and his patience during my whole research work. Also, I can't forget to mention the honorable faculty members, **Dr. Fahim Khokar, Dr. Habib Naisr and Dr. Bryan O Boulanger** of my GEC (Guidance and Examination Committee) who played a pivotal role in completing my research work successfully. The much needed moral and technical support from my fellow colleagues; **Mr. Afeeq Shahid, and Fawad Ahmed**, is deeply acknowledged. My heartiest gratitude covers all the laboratory staff and technicians for their help and support. All the funds for the research work were provided by the Institute of Environmental Sciences and Engineering, SCEE, NUST which is highly appreciated.*

*I would also like to express heartiest thanks to my family members especially my mother and brother **Sharif Ullah** for their constant encouragement and love during my studies.*

JAMSHED ALI KHAN

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LIST OF ABBREVIATIONS

WCO	Waste Cooking Oil
HPAS	Hetero-Polyacids
FTIR	Fourier Transform Infrared Radiation
KBR	Potassium Bromide
BET	Brunauer–Emmett–Teller
BJH	Barrett-Joyner-Halenda
WHSV	Weight Hourly Space Velocity
FFA	Free Fatty Acids
CN	Cetane Number
EPA	Environmental Protection Agency
CARB	California Air Resources Board
FFA	Free Fatty Acids

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ABSTRACT

A heterogeneous catalytic column packed with Amberlyst 15 was used to evaluate the impact of varying column flow rate and fatty acid to ethanol molar ratio on esters production. The reaction temperature was kept constant at 75 °C and the catalyst mass was fixed at 3 g in all experiments. The highest percentage conversion of $95.2 \pm 0.5\%$ was observed at a column flow rate of 0.25 mL/min during esterification of acetic acid when the molar ratio of acetic acid to ethanol was 1:3. Replacing acetic acid with oleic acid into the reaction feed reduced esters yield. Maximum percentage conversion for oleic acid was $43.8 \pm 1.3\%$ at a molar ratio of 1:1. When esterification of fatty acids mixture with their respective molar ratios that resulted in maximum percentage conversion individually (1:3 for acetic acid and 1:1 for oleic acid) was carried out, the esters yield was $71 \pm 1.7\%$. FTIR analysis of the feedstock before and after the esterification reaction in the packed catalytic column showed the presence of acetic acid, oleic acid and their respective esters.

INTRODUCTION

1.1 Background

Energy demand of the world is approximately 3.8×10^{18} GJ and 81% of it is met by the energy coming from fossil fuels which mainly include oil (35%), coal (29%) and natural gas (24%) while energy generated by the nuclear and hydropower sources counts for 5 and 6% respectively (Sorguve *et al.*, 2010; Brennan *et al.*, 2010). Energy demand of the world is expected to be increased to a value of 16,487 Mtoe from 2002 to 2030 with an annual increase of 1.7% (Pandey *et al.*, 2012). Therefore to meet the growing energy demand, stabilize its cost and overcome the serious environmental challenges, developing and investing in renewable energy sources is no more an option; rather it has become our compulsion. Renewable energy is the key for sustainable development as it provides more convincing ways for the energy availability (Demibras *et al.*, 2009).

The rapidly depleting fossil fuel reserves, their soaring prices and the serious harmful effects on our environment are the matters of concern for today's world. Such concerns can be addressed by promoting renewable energy resources which are getting the prime importance to meet the growing energy demands of the world. Biodiesel is one such sustainable alternative renewable energy fuel. Its non-toxicity, biodegradability, and eco-friendly effects are the important advantages (Pirola *et al.*, 2014; Liu *et al.*, 2014; Boey *et al.*, 2013) It can heavily reduce the load on the utility of traditional diesel fuel and can open a new gateway towards a safer and greener world. Biodiesel can be used in transportation vehicles when blended with petro-diesel up to

20% (US Department of Energy 2008), Electricity can also be produced using biodiesel (Tokunaga *et al.*, 2014).

Biodiesel is a fuel chemically composed of mono-alkyl esters of long chain fatty acids, produced (by esterification or trans-esterification processes) from renewable lipid sources like vegetable oils, animal fats, algae lipids and lipids from human wastes. The term “bio” shows the renewable and biodegradable nature of biodiesel. Biodiesel is referred as pure fuel unless it is blended with the petro-diesel. When it is used in blended form with petro-diesel, it is denoted as “BXX” where “XX” denotes the percentage of biodiesel in the blend e.g. B100 means 100% pure biodiesel and B20 shows the 20% presence of biodiesel in the blend. The feedstock lipid for biodiesel mainly consists of fatty acids and triglycerides. In esterification the fatty acid part of lipid is converted into alkyl esters when reacted with alcohol (C_{1-4}) in the presence of some acidic catalyst while trans-esterification is mainly characterized by the reaction between triglyceride and alcohol in the presence of some basic catalyst to produce esters. Reacting triglyceride and alcohol in the presence of acidic catalyst is very time consuming and results in low conversion into esters (Russbuedt *et al.*, 2009).

1.2 Present Study

Research had been carried out on heterogeneous catalysis using batch and column systems separately for the esterification and trans-esterification reactions. Figure 1.1 shows the generalized esterification reaction of fatty acids using ethanol to produce ethyl esters in the catalytic column.

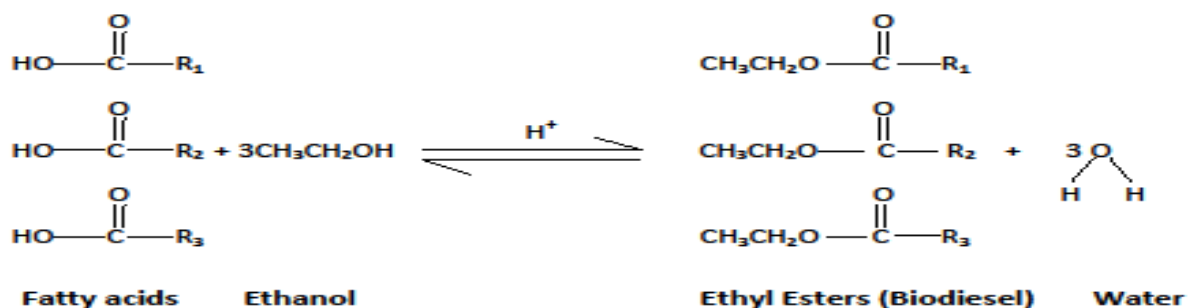


Figure 1.1: Esterification reaction (reaction of fatty acids with ethanol)

In the present research work, a heterogeneous catalytic column system having an acidic resin catalyst was studied for the conversion of alcohol fatty acid oil mixture. In this study a fixed (macroporous resin, Amberlyst 15) catalyst weight was used. The catalyst was selected because of its strong polymeric structure of styrene divinyl benzene. The parameters studied to optimize reaction conversion were flow rate of the mixture through the catalytic column, molar ratio of fatty acids to ethanol and the fatty acids chain length in the reaction mixture.

1.2 Objectives

The objective of this study was to

- check the effect of feedstock flow rate through the column, molar ratio of fatty acids to ethanol and carbon chain length of fatty acids on the esterification process
- find out the best operating conditions for the esterification reaction
- determine the best possible combination of two different chain lengths fatty acids mixture to ethanol molar ratio.

LITERATURE REVIEW

2.1 Biofuels

The energy fuels which are produced potentially from the biomass like plants, animals, microbes and wastes of living organisms are termed as biofuels. Biofuels are the useful energy fuels which can be used for different purposes from space heating , transportation fuel to generating electricity. They can be solid, liquid or gaseous. They are called as renewable sources of energy because their feedstock is obtained from living matter which can be regrown. Biofuels are the potential energy sources that can replace the fossil fuels partially or completely e.g. replacing gasoline and diesel with ethanol and biodiesel respectively. They have some distinct advantages over the petro fuels which depends the specific type of biofuel, nature and supply of feedstock, availability of technology and the process cost. The major target market for the biofuels is the transportation sector.

Biofuels are classified as first, second, third and fourth generation biofuels depending upon their availability of feedstock from which they are produced (OECD/ IEA 2008).

First generation biofuels are produced commercially with the help of conventional technology.

The feedstock includes the human food and animals fodder in the form of seeds, grains and whole plants like sugar cane, wheat, corn, sunflower seeds, rapeseed and soybean oil etc.

Common examples of first generation biofuel are plant oil or animal fat biodiesel and bioethanol.

Second generation biofuels are produced from lignocellulosic sources of feedstock like agricultural wastes, wood and plant stalks and non-edible sources like Jatropha and Miscanthus

plants. Biomass to liquid conversion technology and fermentation for production of cellulosic ethanol are the important features of second generation biofuels.

Biofuels from algae are termed as third generation biofuel (OECD/IEA 2008). The biofuels production technology is the same as for first generation feedstock to produce biodiesel. Some other examples of third generation biofuels include bio-butanol and bio-propanol which are not yet termed as fuel, due to lack of its market and production technology though bio-butanol is more closer in properties to gasoline in comparison to bioethanol.

Fourth generation biofuels are produced from microbial hydrocarbons. Some common examples are biodiesel from microbial lipids, bio-plastics and by bio-hydrogen.

2.2 Biodiesel

Biodiesel are the mono-alkyl esters and considered as substitute of diesel fuel derived from renewable biomass. These mono-alkyl esters can be obtained from a catalyst assisted (an acid, base, or an enzyme) reaction of fatty acids or triglycerides with alcohols in esterification or transesterification mechanism respectively (Mcmath *et al.*, 2010).

Rudolf Diesel, 1900, was the pioneer of using vegetable oil (peanut oil) in internal combustion engine but it couldn't make its place as commercial diesel oil until 1940 due to easy access and availability of fossil diesel. The easy availability of refined fossil fuel has turned down the use of biofuels as energy source for long and fossil fuels were assumed as essential fuel for transportation (Shay *et al.*, 1993).

In 1940, due to limited reserves of petroleum and its derivative, a concern for alternative energy source was emerged (Zanin *et al.*, 2000). Diesel fuel alternative was studied that must be feasible, reliable, more economical, naturally adequate, eco-friendly and promptly accessible (Srivastiva and Prasad, 2000). A large number of these requirements are fulfilled by converting

vegetable oils like triglycerides or by a mixture of free fatty acids (FFA) in triglycerides oil into biodiesel (Cheng *et al.*, 2008). On the other hand fatty acids ethyl or methyl esters were also being suggested as the best energy alternative that were obtained either from trans-esterification of known and available vegetables oils or by esterification of fatty acids with the triglycerides via trans-esterification (Keim *et al.*, 1945).

There are numerous issues connected with vegetable oil being utilized straight forwardly as a part of a diesel motor, i.e. lube oil dilution, higher consistency, injection nozzle failure, inadequate burning, scuffing of the engine liner, high carbon deposits, ring sticking etc.(Murugesan *et al.*, 2009).

Knothe (2005) reported that high consistency of vegetable oil compared to the petroleum fuels will create many problems for engine.

Important feature of biodiesel as a high quality fuel is its cetane number (CN). This number shows the ignition quality of the fuel used. CN basically gauges the fuel's ignition delay which is a time interval between the start of fuel injection and fuel combustion, High CN fuels are characterized by shorter ignition delays thus providing enough time for fuel combustion (Knothe *et al.*, 2005).

Biodiesel can be produced with or without catalyst. Catalyzed method for biodiesel production is currently being employed in large industrial scale setups while non-catalyzed method are designed to process low quality and low cost feedstock by involving some supercritical conditions (Kose *et al.*, 2002).

EPA has registered biodiesel as a fuel and fuel additive. Biodiesel should meet the standards of clean diesel set by the California Air Resources Board (CARB). US Department of

Transportation (DOT) and Department of Energy (DOE) have termed Biodiesel in its pure form (B100) as an alternative fuel.

The high cost of biodiesel production from the plant lipid based feedstock oil as compared to petro-diesel is a barrier in moving towards biodiesel production on industrial scale (Chongkhong *et al.*, 2009). It has also been calculated that up to 60-75% of biodiesel production cost comes from conversion of edible triglyceride based feedstock like vegetable oils (Leung *et al.*, 2010). Biodiesel feedstock in America is being produced from soybean oil whereas rapeseed (canola) oil is the major contributor of biodiesel feedstock in Europe. High cost of biodiesel production is attributed to high clean lipid raw material cost. For example in USA diesel cost was US \$ 0.36/L in 2002 whereas the corresponding cost of biodiesel was US \$ 0.5/L for soybean oil. The utilization of nonedible and less expensive oil as raw material for biodiesel and the use of potential byproducts may results to reduce the production cost of biodiesel (Fukuda, 2001; Ma, 1999). Anh and co-workers (2008) have reported that with the use of low cost feedstock, biodiesel prices can be reduced to almost half. Waste lipids like waste cooking oil (WCO) having high amount of FFA, has an added advantage of having higher fatty acid content than refined oil (Banerjee *et al.*, 2009). Use of WCO is a suitable option for biodiesel production as WCO is readily available. Esterification of waste lipids in WCO can largely reduce the cost of biodiesel production. It will also avoid the misuse of WCO in lubricants and dumping of WCO in water bodies. Another important source for biodiesel production is the non-edible plant oils as the edible oils are primarily utilized as food and using them for biodiesel production make the process expensive and therefore non-feasible.

Biodiesel is produced by two common methods i.e. esterification and trans-esterification. Current research work was focused on biodiesel production via esterification process.

2.3 Esterification

Esterification is a chemical reaction for the biodiesel production involving two reactants i.e. fatty acid and alcohol. These reactants produce an ester as their reaction product in the presence of some acidic catalyst. Caetano C.S and colleagues (2009) examined the esterification of fatty acids with poly vinyl alcohol and polystyrene with sulfonic acid groups as catalyst at 60°C. They observed that catalytic activity of poly vinyl alcohols was most significant when compared with sulfonic acid groups. They studied the Influence of various parameters, such as, molar ratio of palmitic acid to alcohol, catalyst loading and type of alcohol on the esterification reaction. It was determined that with the increase in the molar ratio, equilibrium conversion of palmitic acid was shifted from 30% (1:3) to 90% (1:63) whereas as ethanol was observed to resist the conversion compared to methanol. Also increasing temperature from 60 – 80 °C in the presence of ethanol resulted in increased conversion of palmitic acid. Park et al., (2008) reported about esterification of fatty acids using water-tolerant catalyst Amberlyst 15 and referred it as heterogeneous catalyst. Their findings showed that amberlyst 15 has efficient catalytic activity for free fatty acids oils.

2.4 Biodiesel Standards

For a biodiesel to be used in the engines like petro-diesel, it is important that it meets some quality standards set internationally. Some standards have been developed in this regard but the most commonly used standards include the European standards EN 14214 and US standards ASTM D 6751 (Leung *et al.*, 2010). ASTM standards for B100 (biodiesel) is ASTM D6751-02 which is summarized in table 2.1 below. The various specifications are aimed to ensure the production of quality biodiesel (B100) by manufacturers and its high performance as a fuel in

engines (Gerpen *et al.*, 2004). Further details about the specific methods and the various properties requirements are given in literature (Tyson *et al.*, 2009).

Table 2.1: Biodiesel standards/specifications (Gerpen *et al.*, 2004)

Property	Units	<u>ASTM D-6751</u>		<u>EN 14214</u>	
		Limits	Test methods	Limits	Test method
Kinematic Viscosity (40 °C)	mm ² /s	1.9-6.0	D445	3.5-5.0	EN ISO 3104
Density (15 °C)	kg/m ³	N/S	N/S	860-900	EN ISO 3675
Ester content	mass %	N/S	N/S	96.5 min	EN 14103
Cetane number	-	47 min	D 613	51 min	EN ISO 5165
Flash point	°C	130 min	D 93	120 min	ISO/CD 3679
Water content	volume %	0.050 max	D 2709	500 max	EN ISO 1293'
Sulphated ash	mass %	0.020 max	D874	0.02 max	ISO 3987
Copper Corrosion	grade	No.3 max.	D130	No.1	EN ISO 2160
Acid number	mg KOH/g	0.80 max	D 664	0.5 max	EN 14104
Free glycerol	mass %	0.02 max	D 6584	0.02 max	EN 14105
Total glycerol	mass %	0.240 max	D 6584	0.25 max	EN 14105
Phosphorous content	mass %	0.001 max	D 4951	10 max	EN 14107
Iodine number	-	N/S	N/S	120 max	EN 14111
Oxidative stability (110 °C)	h	N/S	N/S	6 min	EN 14112
Monoglycerols	mass %	N/S	N/S	0.8 max	EN 14105
Diglycerols	mass %	N/S	N/S	0.2 max	EN 14105
Triglycerols	mass %	N/S	N/S	0.2 max	EN 14105
Methanol	mass %	N/S	N/S	0.2 max	EN 14110
High calorific value	MJ/kg	N/S	N/S	N/S	N/S
Low calorific value	MJ/kg	N/S	N/S	N/S	N/S
Oxygen Content	%	N/S	N/S	N/S	N/S

2.5

Biodiesel Scope in Pakistan

The fossil fuel reserves are depleting at a faster rate and their high cost is convincing the experts around the globe to look for more feasible and sustainable options. Pakistan is a developing country where energy cost and short fall are considered as the most burning issues in the present time. Like all other developing countries, Pakistan is also looking for a clean, cheap, alternative and continuous supply of energy. The developed countries have successfully developed means

and ways to utilize the renewable energy resources, though their economies are still largely dependent on fossil fuels. Currently Pakistan is successfully utilizing the hydropower as an effective means of alternative renewable energy. Some projects of solar and wind energy are also in progress. Another renewable energy source, biomass is quickly gaining the interest of researchers as fuels similar in properties to fossil fuels can be produced from it. The type of biomass feedstock and method of conversion determine the nature of fuels produced.

2.6 Types of Catalysis

For biodiesel production two reaction approaches, homogeneous and heterogeneous catalysis, are mainly adopted. Homogeneous catalysis is characterized by the catalyst and reactants being in the same liquid phase while in heterogeneous catalysis the catalyst is in the solid phase. The homogeneous catalysis, although having some advantages like it is simple process and has short reaction time also has some disadvantages including no recovery of the catalyst, side reactions of the catalyst, treatment and disposal of the contaminated effluent and the equipment corrosion (Huang *et al.*, 2010; Boro *et al.*, 2011). These disadvantages can be neutralized by the use of heterogeneous catalysts. The esterification of free fatty acids is carried out by numerous heterogeneous acidic catalysts (Hayyan *et al.*, 2010; Giri *et al.*, 2005) Some of them include hetero-polyacids (HPAs) (Lam *et al.*, 2010), metal oxides and acid ion exchange resins (Park *et al.*, 2010; Son *et al.*, 2011).

2.7 Alcohols for Biodiesel Production

Alcohols like methanol, ethanol and propanol etc. can be used as a reactant for biodiesel production but the most commonly used alcohols for this purpose are methanol and ethanol. The esters (biodiesel) produced, when methanol is used as a reactant, are called fatty acid methyl esters (FAME) and similarly they are called fatty acid ethyl esters (FAEE) when ethanol is used in the reaction process. Depending upon the country and the ease of availability, both alcohols are used for biodiesel production but overall it's the methanol which takes the lead in consumption for the biodiesel production due to its large scale industrial production (Lam *et al.*, 2010). In Pakistan, indigenously produced sugar industry ethanol is a good and cheap source of this reactant.

2.8 Environmental benefits of biodiesel

Biodiesel is recommended as eco-friendly substitute of petro-diesel because it is oxygenated, renewable and easily biodegradable with low emission profile (Altin *et al.*, 2001).

Biodiesel reduces the emission of carbon dioxide, the major cause behind global warming. It is preferred over common petro-diesels because of its minimum sulfur content, low carbon content and approximately 11% of pure oxygen by weight. These features help in reducing the carbon monoxide emissions, particulate matter and hydrocarbons in the exhaustive gases (Lal *et al.*, 2009) when compared to the conventional diesels derived from petroleum products (Peterson *et al.*, 1983).

Igbum and his colleagues (2014) in their recent study have found a major difference in emission content while comparing biodiesel in different blends with petro-diesel. Based on their findings

and biodiesel demand in Pakistan a hypothetical scenario of emissions is summarized in the following figure 2.1.

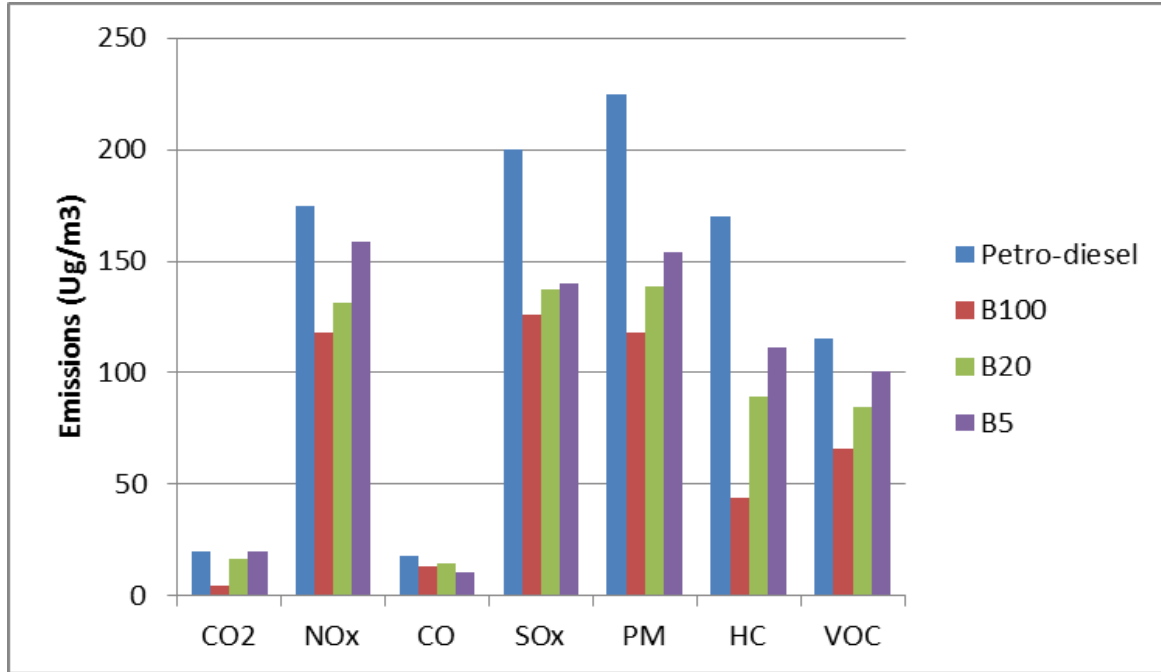


Figure 2.1: Gaseous emissions using biodiesel or its blends in Pakistan

The graph shows the comparison of emissions of different gases with use of petro-diesel, B100, B20 and B5 as fuels. B100 is the biodiesel in its pure form while B20 shows the 20% biodiesel blend with 80% petro-diesel and B5 indicates the blend of 5% biodiesel with 95% petro-diesel. Biodiesel in its pure and blended form have lower gaseous emissions in comparison to petro diesel. Reduction of polluting gases like CO₂, CO, NO_x, SO_x, HCs, VOCs and PM can be clearly seen from the given graph. In case of CO₂ and CO, the emissions show not much difference. It is due to the reason that values of emissions for these two gases are taken after subtracting the amount they are used by biosphere from the total amount produced by different sources. Biodiesel of methyl esters produced from vegetable oil doesn't contain any VOCs which can then produce poisonous fumes. Biodiesel is also free of chlorinated compounds and different

aromatic compounds like toluene, benzene and xylene etc. Chances of producing any corrosive or harmful gases are also nil due to the absence of lead and sulfur in biodiesel.

2.9 Effects of Reaction Parameters on Esterification

Following are some of the important parameters that affect the esterification reaction in a catalytic column.

- Reaction temperature
- Catalyst mass
- Oil to alcohol molar ration
- Flow rate

2.9.1 Reaction Temperature

Reaction temperature is an important parameter having a direct impact on the biodiesel yield. Increase in reaction temperature reduces the reaction time and increases the reaction rate and yield by reducing the viscosity of the feedstock and increasing the kinetic energy of the reacting molecules. Leung and colleagues 2006 and Eevera and co-researchers 2009 however, came upon a conclusion that the reaction rate and yield doesn't increase beyond a specific value which is the optimum value of temperature. The fact that reaction temperature increases the reaction rate and yield also increase the cost of the process as increasing temperature means increase in input energy. So the value of temperature most suitable for the esterification process should be selected keeping in view the cost of the process and the reaction yield.

Feng and his colleagues (2010) found the increase in free fatty acid conversion from 17.1% to 94.0% when temperature was increased from 25 °C to 65 °C. After further increase in

temperature beyond 65 °C, there was no increase in the conversion and no flow of oil as an effluent was observed as the vaporized methanol (boiling point 64.5 °C) blocked the flow of oil from the outlet.

At 1: 60 molar ratio of oleic acid to methanol, the esterification reaction produced more esters with the increase in temperature up to the optimum temperature of 60 °C (Berrios *et al.*, 2007).

2.9.2 Catalyst mass

The mass of catalyst plays a key role in the esterification reaction as more the mass of catalyst, more are the active sites for reactants to react resulting in faster conversion of fatty acids to esters.

Feng and his co-researchers (2010) increased the mass of catalyst from 24.2 g to 87.5 g to check the effect of increasing catalyst mass on esters formation. With this much increase in catalyst mass, the percentage conversion of fatty acids was noted to increase from 75.1% to 96.2%.

With sulfuric acid employed as a catalyst, the yield of ethyl esters increased substantially with increase in catalyst concentration (Lucena *et al.*, 2011). The increase in catalytic activity was the result of high number of hydrogen ions production which speeded up the reaction.

2.9.3 Oil to Alcohol Molar Ratio

The effect of oil to alcohol molar ratio on fatty acids conversion depends mainly on the type of feedstock (fatty acids).

The free fatty acids in waste cooking oil conversion to esters increased from 89.5% to 94.3% when the oil to methanol molar ratio was increased from 1: 0.35 to 1: 1.25. Further increase in

methanol quantity however didn't increase the conversion which remained almost the same (Feng *et al.*, 2010).

Lucena and co-researchers (2011) investigated the effect of changing molar ratio on fatty acids mixture conversion. Their findings show that increasing ethanol to fatty acids molar ratio decreased the ethyl esters production. The increasing amount of ethanol must have pushed the reaction in forward direction but the water molecules produced as a result of increased alcohol concentration rendered the fatty acids conversion process.

2.9.4 Flow rate

Feedstock flow rate through the column directly affects the esters production. Increasing flow rate decreases the fatty acids conversion to esters and vice versa.

Increase in flow rate from 0.82 mL/min to 2.32 mL/min decreased the esters formation from 94.4% to 81.1% (Feng *et al.*, 2010). Increasing flow rate beyond 1.12 mL/min resulted in a major decrease in biodiesel production. It was inferred from the findings that flow rate is inversely related to reaction time and can impact the reaction conversion and yield.

MATERIAL AND METHODS

3.1 Materials

Following chemicals used during experiments were arranged through company local agents in Pakistan.

- Ethanol (99.8% pure) - BDH (Dubai, UAE)
- Acetic acid (99.8% pure) - Sigma Aldrich (St. Louis, USA)
- Amberlyst 15 - Sigma Aldrich (St. Louis, USA)
- Oleic acid (pure form) - Merck (Darmstadt, Germany).

Physical properties of Amberlyst 15 given in table 3.1 are adopted from (Yu *et al.*, 2004).

Table 3.1: Physical properties of Amberlyst 15

Appearance	Typical particle size distribution retained on US standard screens (%)	Bulk density (kg/m ³)	Moisture (by weight)	Hydrogen ion concentration (meq./g dry)	Surface area (m ² /g)	Porosity (ml pore/ml bead)	Average pore diameter (Å)
Hard, dry, spherical particles	16 mesh 2–5 16–20 mesh 20–30 20–30 mesh 45–55 30–40 mesh 15–25 40–50 mesh 5–10 Through 50 mesh 1.0	608	Less than 1%	4.7	50	0.36	240

3.2 Experimental Set Up

The column system, shown in Figure 3.1, was used throughout all the experiments. The system consisted of two hot plates with magnetic stirrers, a pump, packed catalytic column, two thermometers, heat resistant tubing (4 mm internal diameter), tubing joints, a flow control valve, a diverter, a 2L beaker, flasks and a measuring cylinder.

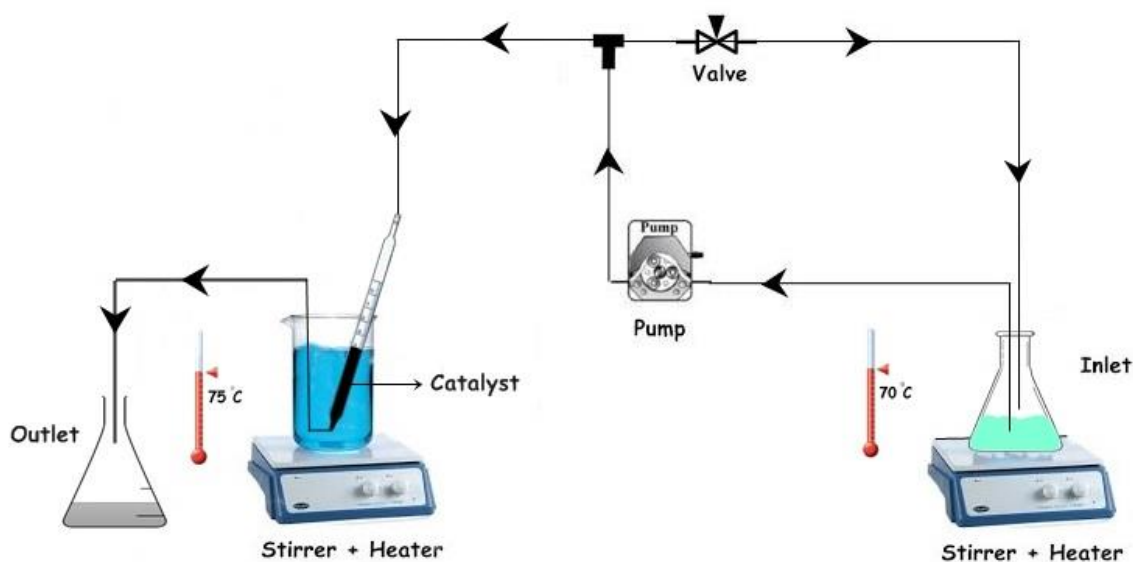


Figure 3.1: Schematic diagram of the experimental set up

3.3 Methodology

Experimental feedstock (consisting of acetic acid and ethanol, oleic acid and ethanol, or mixtures of acetic acid, oleic acid, and ethanol) were mixed in a flask equipped with a magnetic stirrer and pre-heated to 70 °C using a stirring hot plate. Pre-heated feedstock was then pumped through the catalytic column. A 10 mL pipette was used as a column which was partially filled with 3 grams catalyst occupying 4.7 mL volume in the column. Glass wool was plugged on both ends of the catalyst to keep it compact and prevent catalyst particles to get loose and move inside the

column. Pre-heated feedstock was passed directly through the column at the set flow rate without any pre-wetting of the column. The flow rate through the column (which was variable) was set using an in-line flow control valve with a diverter. Excess flow was returned to the pre-heated feedstock flask. The column reaction temperature of 75 °C was maintained by operating the column in a hot water bath heated by the hot plate. Due to continuous water evaporation from the hot water bath, the water level was maintained by adding pre-heated (75 °C) water to hot water bath from time to time. Temperature of the feedstock in the flask; maintained at 70 °C and temperature of the hot water bath; maintained at 75 °C were constantly monitored with the help of thermometers.

FTIR spectra of reactant feedstock (acetic acid, oleic acid and ethanol mixture) sample and the product sample were obtained by using KBr pellet technique in PerkinElmer FTIR spectrometer shown in figure 3.2. A very small amount (3 mg) of the sample was mixed with 300 mg of KBr to make a pellet.



Figure 3.2: PerkinElmer FTIR spectrometer and press m/c

BET surface area and porosity experiment was conducted on amberlyst 15 at a relative pressure (P/P_0) range of 0.00–0.30 using a Micrometrics Gemini VII apparatus shown in figure 3.3. The sample was initially degassed at 100 °C for 5 hours. The BET surface area calculated was 29.68 m^2/g and BJH Adsorption average pore width ($4V/A$) came out to be 20.340 Å.



Fig 3.3: BET surface area analyzer and Micrometrics Gemini VII apparatus

Weight hourly space velocity (WHSV) of the feedstock passing through the packed catalytic column was determined using the concept of mass flow per unit mass of catalyst. WHSV at three different flow rates, given in table 3.2, were calculated by using the following equation 1.

$$\text{WHSV} = \text{mass flow/catalyst mass} = (\text{flow rate} \times \text{density})/\text{catalyst mass} \quad (\text{Eq. 1})$$

Table 3.2: Weight Hourly Space Velocity (WHSV) Through the Packed Catalytic Column

	Flow Rate (ml/min)	Density (g/ml)	WHSV (hr ⁻¹)	Percentage Conversion After 2.5 Hrs.
Acetic acid-ethanol (1:3) feedstock	0.70	0.84	11.76	78.23
	0.50	0.84	8.40	89.25
	0.25	0.84	4.20	95.16
Oleic acid-ethanol (1:1) feedstock	0.25	0.79	3.95	43.81
Mixture of acetic acid-ethanol (1:3) and Oleic acid-ethanol (1:1) feedstock	0.25	0.81	4.05	71.02

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demonstrated that the reaction rate and the conversion of fatty acids to fatty acid esters increase with an increase in catalyst concentration and temperature (Yin *et al.*, 2012; Lucena *et al.*, 2011; Marchetti *et al.*, 2007). This work evaluated the effect of 1) the feedstock flow rate, 2) the molar ratio of fatty acids and ethanol in the feedstock and 3) the feedstock fatty acid chain length on

esterification. The reaction temperature (75 °C) and the mass (3 g) of catalyst in the packed column were kept constant.

The effect of feedstock flow rate was evaluated by monitoring acetic acid esterification with an acetic acid: ethanol ratio of 1:3. Esters formation was analyzed across three different flow rates, including 0.7, 0.5 and 0.25 mL/min. The effect of the fatty acids: ethanol molar ratio was evaluated through conversion of acetic acid and oleic acid individually at a constant flow rate of 0.25 mL/min. The ratio of fatty acid: ethanol for each individual fatty acid was varied from 1:5, 1:3, and 1:1.

The effect of feedstock fatty acid chain length on esterification was evaluated by passing acetic acid-ethanol and oleic acid-ethanol feedstock separately through the column, both with same molar ratio of 1:3 and fixed flow rate of 0.25 mL/min. In the last set of experiments, esterification of fatty acids mixture with their respective molar ratios that resulted in maximum percentage conversion individually (1:3 for acetic acid and 1:1 for oleic acid) was carried out at the same flow rate of 0.25 mL/min.

Multiple runs for each parameter were evaluated to enable meaningful post-hoc analysis statistically. Each experiment was 150 minutes in duration with a total of 7 samples taken at fixed time intervals to evaluate reaction conversion. Sampling occurred at $t = 0, 15, 30, 60, 90, 120,$ and 150 minutes.

3.5 Percentage Free Fatty Acid (FFA) Calculation Method

Esters formation in the heterogeneous catalytic column was calculated by measuring the change in acid value between feedstock going into the column to the reaction product leaving the column (Feng *et al.*, 2011). The percentage of free fatty acids in 2 g samples of the reacted product stream and unreacted feedstock was calculated on the basis of American Oil Chemist Society (AOCS) Method Ca 5a-40 (Food chemicals codex 2003).

Briefly, the 2 grams samples were added to 50 mL of alcohol stored in a previously prepared beaker. 2 mL of phenolphthalein was then added to the beaker and the resulting solution was titrated with 0.1 N solution of sodium hydroxide drop by drop until the solution turned light pink in color. The volume of sodium hydroxide solution used was noted down and the percentage of free fatty acids was calculated as per following equation 2.

$$\% \text{ FFA} = \frac{\text{volume of NaOH solution used (mL)} \times \text{N} \times 28.2}{\text{Weight of sample}} \quad (\text{Eq. 2})$$

Where N is the normality of sodium hydroxide solution.

3.6 Catalyst Regeneration and reuse

Reusability and regeneration of the resin catalyst was checked by performing the esterification reaction in the column. Two sets of columns were used and esterification reaction was first carried out using the fresh resin in the columns. One of the two sets of exhausted resin columns after a reaction time of 150 minutes was regenerated by ethanol. Use of alcohol to regenerate resin surfaces has already been reported (Jamal *et al.*, 2014). The other set of the exhausted resin columns was reused without any washing with alcohol. To understand the impact of flow rate on the regenerated and reused resin two different flow rates were selected. Figure 3.4 shows the percentage conversion of feedstock consisting of acetic acid and ethanol with molar ratio of 1:3. The first three bars shows the first three runs of the feedstock through the catalytic column at

flow rate of 0.7 mL/min and the remaining three bars at flow rate of 0.5 mL/min. It can be inferred from the graph that the regenerated and reused catalyst has no distinct impact on the percentage conversion at each selected flow rates respectively. Based on results we can say resin has long service life and can be used in the column for long reaction times.

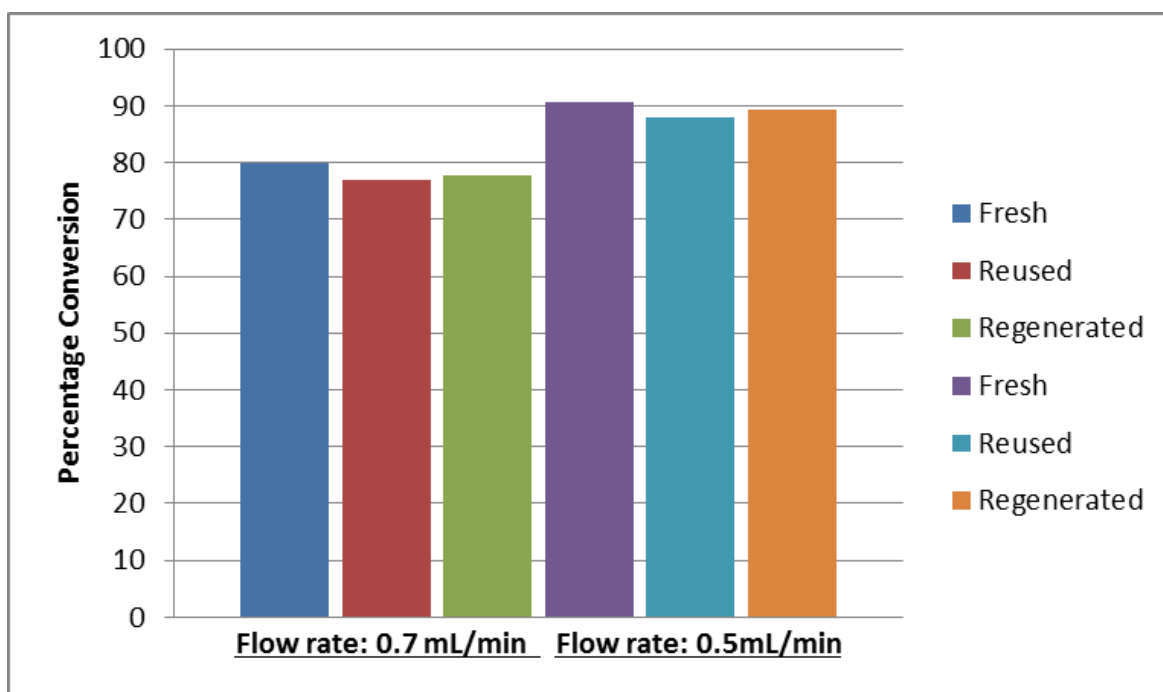


Figure 3.4: Catalyst Regeneration and reuse

RESULTS AND DISCUSSION

All the esterification experiments were carried out at 75 °C (which is below the boiling temperature of ethanol i.e. 78.37 °C) and atmospheric pressure using 3 grams of catalyst in column. Low temperature and pressure was kept to design a less energy intensive esterification heterogeneous column system (Barnwal *et al.*, 2005; Kocsisova *et al.*, 2005). Figure 4.1 shows the effect of flow rate on the acetic acid esterification in the heterogeneous catalytic column at acetic acid to ethanol molar ratio of 1:3. Esterification was demonstrated to increase as the feedstock flow rate through the column decreased. The maximum conversion measured (95.2% ± 0.5%) was observed at the minimum flow rate used (0.25 mL/min) after 150 minutes of running the column system. Conversions above 90% occurred within the first 15 minutes and only marginal increase in yield was realized the longer the column was operated. The slight increase of ester conversion as a function of reaction duration was likely due to complete wetting of the initially dry catalyst with reaction moisture over time.

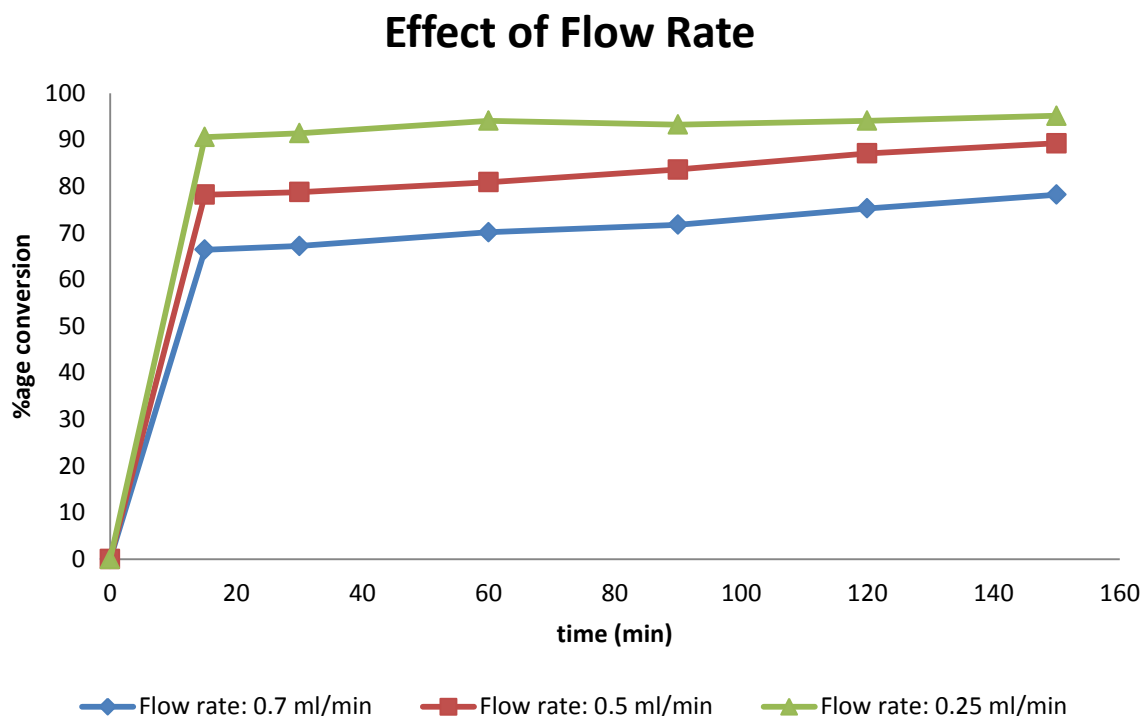


Figure 4.1: Effect of flow rate on acetic acid esterification at molar ratio 1:3, temperature 75 °C and catalyst weight 3 grams

The effect of fatty acid: ethanol molar ratio on esters formation is shown in Figure 4.2. Acetic acid and oleic acid showed different pattern of percentage conversion under varying molar ratios. For acetic acid, the lowest conversion ($75.2 \pm 1.2\%$) occurred at the lowest evaluated molar ratio of 1:1. This means that sufficient amount of ethanol must be present for the reaction to proceed in the forward direction as reducing ethanol quantity below a certain value decreases the esters formation. At molar ratio of 1:5, the percentage conversion noted was $91.9 \pm 0.7\%$ which was almost 3% less than what was observed at a molar ratio of 1:3. This slight drop in the conversion at molar ratio of 1:5 was attributed due to the flooding of catalyst reaction sites with reaction moisture as reported in the literature (Karbaslar *et al.*, 2001). Two sample T-test was performed for pooled variance with H_0 (null hypothesis) of no change to check whether the difference of 3% is significant or not. The P value came out to be 6.8% which indicates that two values are

significantly and statistically distinct at 10%. Oleic acid showed different behavior altogether at different molar ratios. At molar ratio of 1:5, the percentage conversion of oleic acids to esters was the minimum ($15.8 \pm 2.1\%$) of all values. The excess ethanol caused the reaction to result in less esters formation as moisture produced during the esterification reaction adhered to the catalyst surface causes to reduce the catalytic activity. However, high esters formation was noticed when the molar ratio of 1:1 was applied. The percentage conversion noted was $43.8 \pm 1.3\%$ which is in accordance with the earlier findings (Figureiredo *et al.*, 2010).

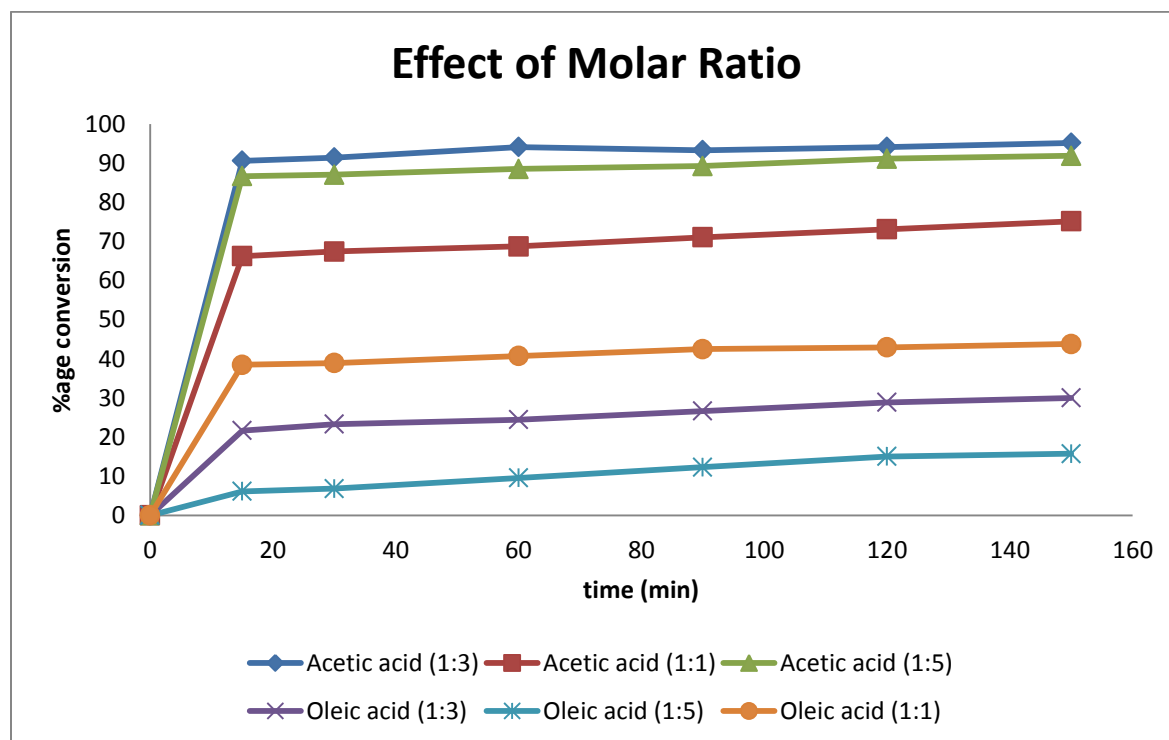


Figure 4.2: Effect of molar ratio on fatty acid esterification at flow rate 0.25 mL/sec, temperature 75 °C and catalyst weight 3 grams

The effect of fatty acid chain-length on percentage conversion is shown in Figure 4.3. When oleic acid: ethanol feedstock with a molar ratio of 1:3 was evaluated, lower esters production was observed. In comparison to $95.2 \pm 0.5\%$ conversion with acetic acid, there was only $30 \pm 2.2\%$ conversion with oleic acid. The difference in behavior of acetic acid and oleic acid during

esterification process with same conditions is due to the difference in chemistry of both the fatty acids molecules. Acetic acid consists of short carbon chain length molecules (C-2) while oleic acid comprise of long carbon chain molecules (C-18). Short chain fatty acids have easy accessibility in the porous structure of amberlyst 15 whereas long chain fatty acids are hindered by their large molecular sizes reducing surface contact area with the porous catalyst for reaction at sulfonic sites.

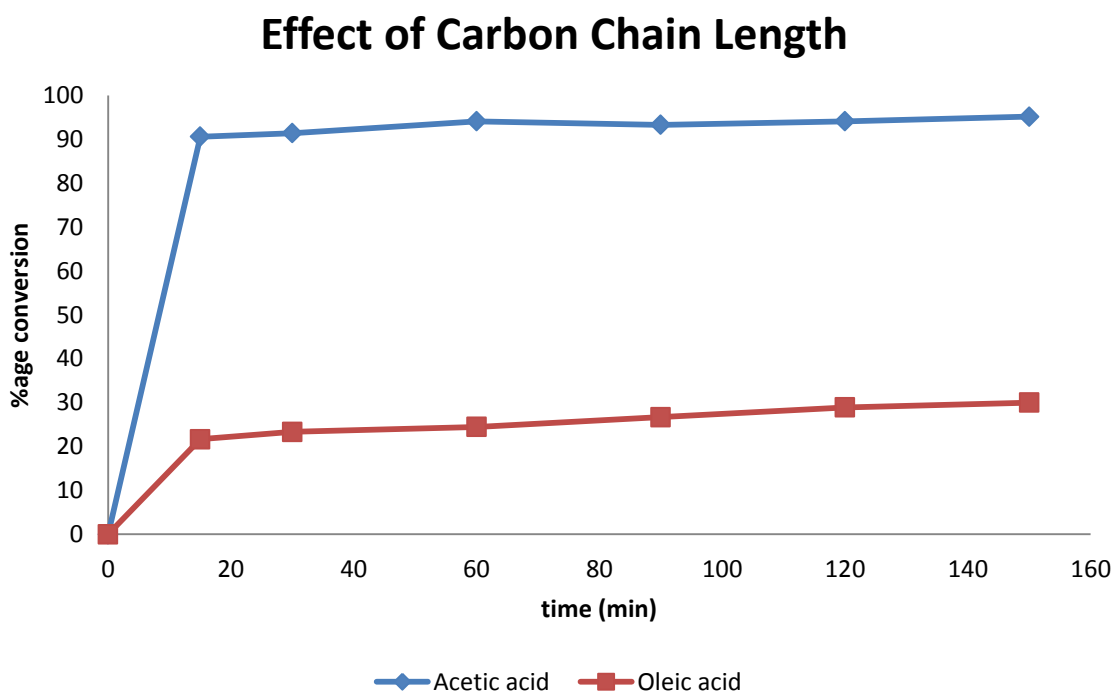


Figure 4.3: Effect of carbon chain length on fatty acid esterification at flow rate 0.25 mL/sec, molar ratio 1:3, temperature 75 °C and catalyst weight 3 grams

The two fatty acids were mixed, each with molar ratio which resulted in maximum percentage conversion (1:3 for acetic acid and 1:1 for oleic acid) and the mixture was passed through the catalytic column. The purpose of mixing was to check the effect of mixing of two different carbon chain length molecules on the esterification reaction. The results in terms of percentage conversion for both fatty acids individually (maximum percentage conversion of each fatty acid)

and as a mixture are compared in Figure 4.4. The mixture of the two fatty acids produced the esters with the percentage conversion up to $71.0 \pm 1.7\%$. The percentage conversion of the mixture was less than that for acetic acid but more than the percentage conversion for oleic acid. What is more obvious from these findings is that it's better to find the best opted values for individual fatty acids in any oil first and then go for esterification of mixed fatty acids oil rather than opting for hit and trial method to find the most suitable value of molar ratio for the oil consisting of number of different fatty acids.

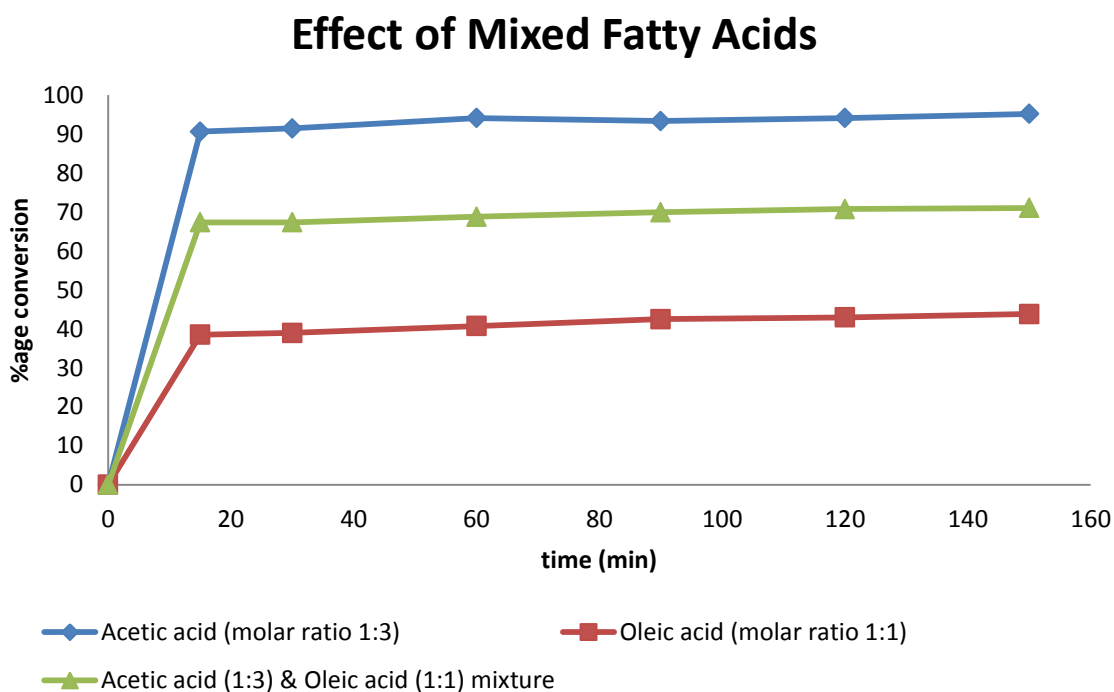


Figure 4.4: Effect of mixed fatty acids on the esterification reaction at flow rate 0.25 mL/sec, temperature 75 °C and catalyst weight 3 grams

At the start of each reaction run, the catalyst was completely dry. When feedstock was pumped into the catalytic column and got in contact with the catalyst, esterification started immediately with fast reaction rate in the very start. All the graphs clearly indicate that almost all the conversions took place in the first 20 minutes and the reaction reached equilibrium very quickly. As time passed and reaction proceeded, water molecules were produced along with esters which started forming water solvation layer around the catalyst surface. This layer blocked the approach of fatty acids from the bulk solution to the interface and finally to the sulfonic acid functional group on the catalyst surface thus reducing the pace of reaction and shifting the reaction to equilibrium state in a short time interval.

Figures 4.5, 4.6 and 4.7 show the results of FTIR of the feedstock (acetic acid, oleic acid and ethanol), esters and their comparison. Percentage transmittance of light was used to show the conversion. Fatty acids give high percentage transmittance in comparison to their respective esters. First main dip is in spectrum range of $2800-3000\text{ cm}^{-1}$ which are due to C-H and =C-H stretching frequencies. Second prominent dip in $1700-1800\text{ cm}^{-1}$ range is due to the presence of carbonyl (C=O) group. The present findings of FTIR results are in concordance with the earlier findings (Basumatary *et al.*, 2012; Al-Arafi *et al.*, 2012).

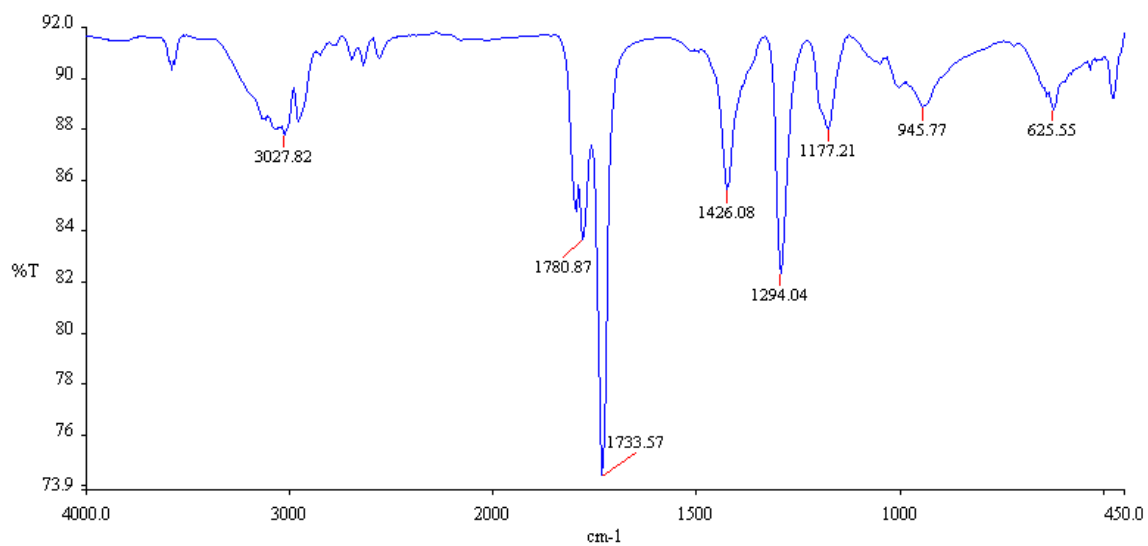


Figure 4.5: FTIR spectra of feedstock

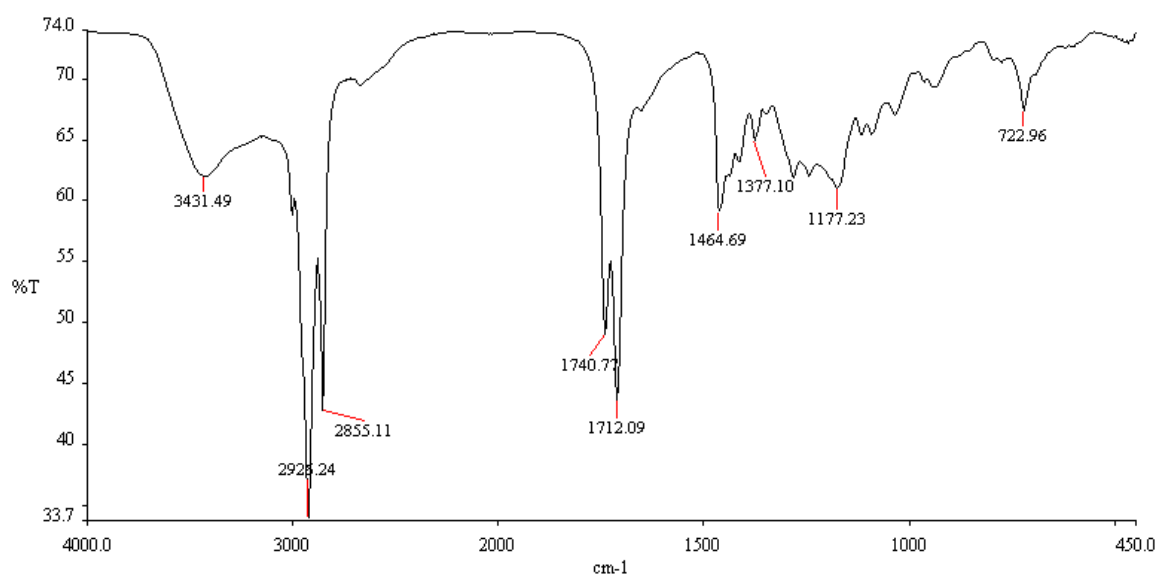
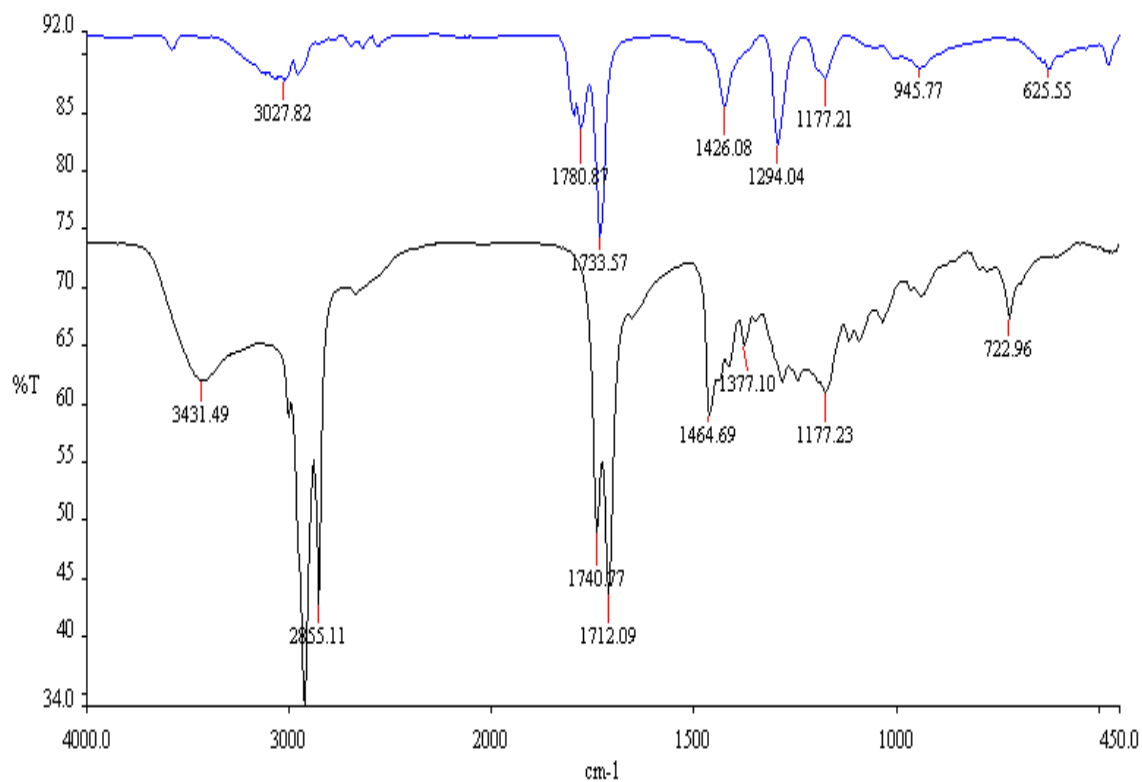


Figure 4.6: FTIR spectra of esters



fatty ACID.sp
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Figure 4.7: FTIR spectra showing comparison of feedstock and esters

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Heterogeneous esterification of single fatty acid and mixed fatty acids - ethanol feedstock was performed in a continuous packed catalytic column. Mixed esters can be produced by using heterogeneous acidic catalytic column when feed is rich in fatty acids. Flow rate has a direct impact on conversion as more contact time helps to convert more lipids. Esterification can take place at below boiling temperature of alcohol and atmospheric pressure. Percentage conversion of fatty acids is different at different molar ratios depending on carbon chain length of fatty acids. Small chain length fatty acids (like acetic acid against oleic acid) give high percentage conversion. Keeping the temperature fixed at 75 °C and the catalyst weight at 3 grams, the best operating conditions for the acetic acid esterification was found out to be molar ratio of 1:3 and flow rate of 0.25 mL/min. The oleic acid at the same flow rate of 0.25 mL/min gave the best results when molar ratio of 1:1 was applied. FTIR analysis can be used to find the composition of the feedstock going into the column and the reaction product leaving the column. Sulfonic acid resins on divinyl benzene structure can actively convert lipids into esters.

5.2 Recommendations

- Indigenous macro-porous and gellular catalysts should be studied to report reaction yield and percentage conversion.
- Effect of moisture in the feedstock can be studied.
- Impact of various carbon chain length fatty acids on esterification reaction can be studied.

- Group Research at IESE Level
 - Producing short chain fatty acids from genetically modified micro-organisms .
 - Reaction mechanism for short chain FFA studied.
 - Reduction of SO_x, NO_x emissions from diesel blends.

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