SYNTHESIS AND CHARACTERIZATION OF LITHIUM-MODIFIED MESOPOROUS CATALYST FOR SOLVENT-FREE SELECTIVE OLIGOMERIZATION OF GLYCEROL TO DIGLYCEROL

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2013

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By

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Thesis submitted in fulfillment of the
requirements for the degree of
Doctor of Philosophy

JULY 2013

DEDICATIONS

This thesis is dedicated to my beloved father Rafaqat Ali, mother Rahmat Bibi, wife Sarah Ayoub and my lovely daughters Rameen Ayoub and Farzeen Ayoub

ACKNOWLEDGEMENTS

In the name of ALLAH, the Most Beneficent, The Most Merciful

First of all, I would like to thank to ALLAH the Almighty for the strength, guidance, and blessing until I accomplished my studies. I am grateful to my supervisor, Assoc. Prof. Dr. Ahmad Zuhairi Abdullah. Under his guidance, I was given the freedom to take my research into the areas that interest me the most. Not only he is a valuable information source, but he is also an excellent mentor. Due to my professor, my time at USM has been excellent.

I am thankful to Dean Professor Dr. Azlina Bt. Harun @ Kamaruddin, Dy. Dean Assoc. Prof. Dr. Mohamad Zailani Bin Abu Bakar, Dy. Dean Assoc. Prof. Dr. Mohd Azmier Ahmad, Dy. Dean Assoc. Prof. Dr. Lee Keat Teong, Professor Dr. Bassim H. Hameed and all other persons in the school who encourage me and lead me towards my aim. I greatly appreciate the time and advice of my committee members. Thank you for reading through and editing this document! I am especially grateful to the past and present my research group members. They have been enjoyable to work with and have become life-long friends. I want to acknowledge my colleagues and friends specifically Benoit Faye and Reinhard Eckelt who greatly contributed to my research. I appreciate the laboratory assistance from USM Engineering campus.

I wouldn’t have been able to make it through my PhD without the help of my friends and family. My parents, parents-in-law and all other family members have supported me with their precious prayers throughout my academic career. I finally made my dream come true! I am delighted to express my deepest affection,

appreciation and thanks to my wife, Mrs. Sarah Ayoub, and my beautiful precious daughters, Rameen Ayoub and Farzeen Ayoub, who have always been with me during this period. They encouraged me with their love and understanding during difficult moments and also shared my joy and success all along. The strength of my uncle, K.A.Dost, taught me to fight through even the worst of situations. Special thanks to Dr. Muhammad Faisal Irfan, Dr. Shahid Iqbal, Dr. Muhammad Zubair, Dr. Javed Akhtar, Mr. Ubaid-Ullah, Mr. Khozema bin Ahmad Ali, Dr. Mutaz S.K, Dr. Mushtaq Ahmad and his wife Dr. Sahzia Sultana for their friendship and entertainment during long lab days I would also like to thank all other people whom I could not name here, for being near me in these years. All of them have made immense contribution to my study and life by their support, inspiration, understanding and sacrifices and therefore, I sincerely dedicate this piece of work to these people whom I love and cherish for the rest of my life.

Acknowledgements are also extended to the USM for awarding IPS fellowship during whole period of my research. Lastly, but most importantly, I would like to thank Allah (Subhanaho Wa Tala) and our Holy Prophet Muhammad (Peace be upon him) for always keeping an eye over me and blessing me each day.

Muhammad Ayoub,
April 2013.

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LIST OF SYMBOLS

Symbols	Descriptions	Unit
α	primeray - isomer of glycerol	Dimensionless
β	secondary - isomer of glycerol	Dimensionless
α'	primeray - isomer of other glycerol	Dimensionless
β'	secondary - isomer of other glycerol	Dimensionless
A	Arrhenius factor (pre-exponential factor)	Dimensionless
C_g	Concentration of glycerrol	(mmol/l)
C_{go}	Concentration of initial glycerol	(mmol/l)
C_{DG}	Concentration of diglycerol	(mmol/l)
C_g calc	Simulated data of glycerol concentration	(mmol/l)
C_g exp	Experimental data of glycerol concentration	(mmol/l)
C_{PG}	Concentration of polyglycerols	(mmol/l)
$-dC_g/dt$	Differential of C_g polynomial with respect to time (t)	(mmol/l.h)
dX/dt	Differential of conversion of glycerol with respect to time	(mol/h)
Df	Dilution factor	Dimensionless
Ea	Activation energy	(kJ/mol)
k	Reaction rate constant	(dm^3/mol.h)
m	Order of reaction	Dimensionless
n	Order of reaction	Dimensionless
N_A	Initial numbers of moles	(mol)

P	Pressure	Pa
P_o	Pressure	Pa
R	Gas constant	(J/mol.K)
$-r_A$	Rate of reaction	(mol/dm^3.h)
$-\mathrm{r_g}$	Rate of reaction of diglycerol	(mol/dm^3.h)
T	Reaction temperature	(^{o}C)
t	Reaction time	(h)
t_R	Retention time for GC	(min)
$\mathrm{X_g}$	Conversion of glycerol	Dimensionless
V	Total volume	(dm^3)

LIST OF ABBREVIATIONS

a. u	Arbitrary unit
AMS	Anionic surfactant templated mesoporous silica
ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CCD	Central composite design
CO_2	Carbon dioxide
CCRD	Central composite rotatable design
DF	Degree of freedom
DOE	Design of experiment
EDX	Energy dispersive X-ray spectroscopy
EA	European standard
FID	Flame ionization detector
FTIR	Fourier transforms infrared
GC	Gas chromatography
HMDS	Hexamethyldisilazane
H_2O	Water
HCl	Hydrochloric acid
IEA	International energy association
ISO	International standard organization
IUPAC	International Union of Pure and Applied Chemistry
KOH	Potassium hydoxide
Li	Lithium

LiOH	Lithium hydroxide
MCM	Mobil composition of matter
MK-10	Montmorillonite K-10 clay
MS	Mean square
NaOH	Sodium hydroxide
NO_X	Nitrogen oxides
P123	Pluronic 123
RSM	Response Surface Methodology
SAXS	Small angle X-ray scattering
SBA	Santa-Barbara amorphous
SEM	Scanning electron microscope
SS	Sum of square
TEM	Transmission electron microscope
TEOS	Tetraethylorthosilicate
TCP	Tri-block copolymer
TMCS	Trimethylchlorosilane
TMOS	Tetramethylorthosilicate
TMS	Transition metal oxide mesoporous molecular sieve
XRD	X-ray diffraction
Wt	weight

SINTESIS DAN PENCIRIAN MANGKIN MESOLIANG TERUBAHSUAI DENGAN LITHIUM UNTUK PROSES OLIGOMERISASI TERPILIH GLISEROL KEPADA DIGLISEROL

ABSTRAK

Industri biodiesel menjana kira-kira 10% gliserol mengikut isipadu sebagai satu produk sampingan yang mempengaruhi keseluruhan industri ini. Kajian ini meneliti suatu proses untuk menukarkan gliserol kepada produk yang mempunyai nilai lebih tinggi iaitu digliserol melalui proses pengoligomeran bermangkinkon bes tanpa pelarut. Keberkesanan pelbagai jenis mangkin homogen alkali (LiOH, NaOH, KOH dan Na_2CO_3) dan mangkin heterogen (dengan penyokong yang berbeza iaitu USY, SBA-15 and montmorillonite K-10 clay) telah disiasat untuk meningkatkan hasil dan kememilihan untuk produk yang diingini. Pemangkin pepejal yang disediakan telah dicirikan untuk mengetahui ciri-ciri tekstur dengan menggunakan BET, SEM, EDX, TEM, FTIR, TGA, XRD, SAXS, ICP-AES dan penunjuk Hammet untuk kekuatan bes. LiOH mempamerkan aktiviti yang tinggi berdasarkan penukaran gliserol (99%) tetapi dengan kadar kememilihan yang rendah (18%) terhadap digliserol. Li/USY didapati aktif untuk penukaran gliserol (98%) dan hasil polyglycerol (72%) namun kememilihan digliserol masih agak rendah (29%) pada keadaan tindakbalas yang sama. SBA-15 mengalami keruntuhan struktur yang ketara selepas pembebanan alkali. Namum, kestabilannya dikukuhkan melalui salutan magnesium pada tahap yang sesuai dilakukan sebelum litium dimasukkan. Penukaran glycerol sebanyak 90% dan 59% hasil polyglycerol telah diperhatikan namun kememilihan terhadap digliserol hanyalah sebanyak 14% bagi Li_{10}-Mg_{30}/SBA-15. Mangkin montmorillonite K-10 yang diubahsuai dengan litium (Clay Li/MK-10) telah disediakan dan kecekapannya untuk proses oligomerisasi gliserol kepada digliserol telah disiasat. Penukaran gliserol yang (86%) tinggi dengan kememilihan yang tinggi terhadap diglycerol (68%) telah diperhatikan di bawah keadaan tindak balas yang sama. Kelakuan tindakbalas untuk semua mangkin yang telah disediakan juga disiasat berdasarkan, pembentukan isomer digliserol (isomer αα', ββ' dan αβ) dalam campuran produk akhir telah diselidiki. Di antara semua mangkin yang telah disediakan, Li/MK-10 merupakan mangkin yang paling aktif. Kesan pelbagai keadaan proses termasuk bebanan mangkin, masa dan suhu tindakbalas telah disiasat menggunakan kaedah sambutan permukaan (RSM). Keadaan optimum yang telah ditemui untuk memberikan hasil digliserol 61% ialah pada suhu tindakbalas 240 ^{o}C, 3.35% berat mangkin dan 7 jam masa tindakbalas. Clay Li/MK-10 juga boleh digunakan semula tetapi penurunan aktiviti sebanyak 30.6% dicatatkan selepas penggunaan pertama. Satu model matematik juga telah berjaya dibangunkan. Tenaga pengaktifan yang rendah iaitu sebanyak 1.550 kJ / mol telah berjaya ditentukan bagi tindakbalas oligomerisasi tersebut. Secara ringkas, Clay Li/MK-10 merupakan pemangkin yang berkesan untuk proses oligomerisasi gliserol untuk menghasilkan digliserol. Dari aspek industri, penemuan yang telah dicapai melalui kajian ini dapat menyumbang ke arah menggalakkan industri biodiesel melalui penukaran gliserol mentah kapada diglycerol yang bernilai tinggi.

SYNTHESIS AND CHARACTERIZATION OF LITHIUM-MODIFIED MESOPOROUS CATALYST FOR SOLVENT-FREE SELECTIVE OLIGOMERIZATION OF GLYCEROL TO DIGLYCEROL

ABSTRACT

Biodiesel industry leads to the generation of about 10% glycerol as a co-product, which affects the overall biodiesel economy. This study examines a process for converting glycerol to a higher value product i.e. diglycerol via a solvent free base-catalyzed oligomerization process. The catalytic activity of different homogeneous alkali catalysts (LiOH, NaOH, KOH and Na_2CO_3) and heterogeneous catalysts (with different supports i.e. USY, SBA-15 and montmorillonite K-10 clay) was investigated and with the aim of improving the yield and selectivity to the desired product. The prepared solid catalysts were characterized to study their textural properties and their surface morphology using BET, SEM, EDX, TEM, FTIR, TGA, XRD, SAXS, and ICP-AES while Hammet indicator was used for characterizing their basic strength. LiOH exhibited high catalytic activity as indicated by almost complete glycerol conversion (99 %) but with poor selectivity (18%) towards diglycerol. Clay Li/USY was found to be active for glycerol conversion (98 %) with good polyglycerol yield (72 %) but the diglycerol selectivity was still rather low (29 %) under the same reaction conditions. SBA-15 experienced severe structural collapse after the alkali loading but the stability was improved with suitable amount of magnesium coating prior to lithium loading. 90 % glycerol conversion and 59 % polyglycerol yield were observed but the selectivity to diglycerol was observed at only 14 % for the Li_{10}-Mg_{30}/SBA-15 catalyst. Lithium modified montmorillonite K-10 (Clay Li/MK-10) was then prepared and its activity was investigated. High conversion of glycerol (86 %) and high selectivity to diglycerol (68 %) were observed under the same reaction conditions. The reaction behaviors for all prepared catalysts were also investigated based on the formation of diglycerol isomers (αα', ββ' and αβ isomers) in the final product mixture. Among the catalysts prepared, Clay Li/MK-10 was the most active one. Effect of various process conditions including the catalyst loading, reaction time and temperature were investigated using response surface methodology (RSM). The optimum conditions were found to give 61 % of diglycerol yield at 240 ^{o}C of reaction temperature with 3.35 wt % of catalyst and about 7 h of reaction time. Clay Li/MK-10 could also be reused but it experienced an activity drop of about 30.6 % after the first run. A mathematical model was successfully developed for most active catalyst Clay Li/MK-10. Low activation energy of 1.550 kJ/ mol was observed over this catalyst for the glycerol oligomerization reaction. In short, the Clay Li/MK-10 was an effective catalyst for the glycerol oligomerization process to diglycerol production. Industrially, the findings attained in this study might contribute towards promoting the biodiesel industry through utilization of its glycerol by-product in the form of highly valuable diglycerol.

CHAPTER ONE

INTRODUCTION

1.1 Fuel crisis

Energy demand and its resources are increasing day by day due to the rapid outgrowth of population and urbanization. So, there is a correlation between a country's living standard and energy consumption. Conventional energy resources like coal, petroleum and natural gas are fulfilling the major energy demand but in the verge of getting exhausted. Unexceptional opportunities have been created in last few years to replace petroleum derived materials with bio-based alternatives due to rapid depletion of fossil fuels and their soaring prices. It has been estimated that the fossil oil sources might be depleted by 2050 (Goyal et al., 2008). It means that limitation in fossil fuel resources and existing world oil capacity is a major issue.

Petroleum is a non-regenerative source of energy and it is also an important resource of the modern society for its roles in areas other than power such as household products, clothing, agriculture, as a basic material for synthetic materials and chemicals. Moreover, the process of obtaining energy from sources other than petroleum can cause atmospheric pollution, and other problem like global warming and acid rain. This has triggered recent interest in alternative source to petroleum-based fuels. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available (Meher et al., 2004). Nowadays, fuel crisis has globally flourished the economy in every region, especially the oil consuming countries due to its rapidly decreasing available global stock. In view of this serious situation, biodiesel which comes from 100% renewable resources provides an alternative fuel option for future.

1.2 World biodiesel production

The most common way to produce biodiesel is by transesterifying triglycerols in vegetable oils or animal fats with an alcohol in the presence of alkali or acid catalysts as shown in **Figure 1.1**. Methanol is the most commonly used alcohol for this process due to its low cost. This process involves the removal of the glycerin from vegetable oil or fat. During this process, methyl esters are separated as the desired product while glycerin is left behind as a by-product. Crude glycerol is normally generated at the rate of one mol for every three mols of methyl esters synthesized. Approximately, it constitutes about 10 wt% of the total product during bio-fuel production.

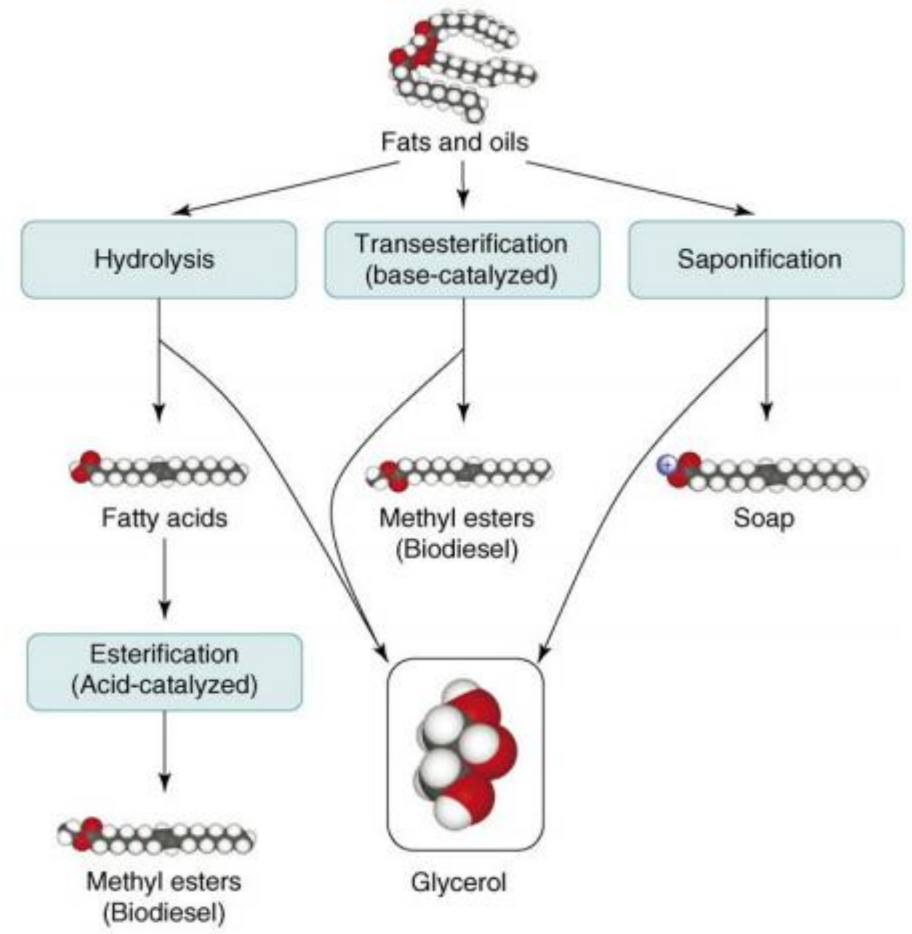

Figure 1.1: Biodiesel production from vegetable oils and animal fats and their relation with glycerol co-product (Yazdani and Gonzalez, 2007).

The United States and Europe are the biggest consumers of fuel in the world. Europe represents 80% of global biodiesel production and consumption but the United States is increasing its production at a rate faster than Europe. According to a report Brazil is expected to surpass the United States and European biodiesel production by the year 2015 (Xiu et al., 2004). In 2008, the global biodiesel production reached more than 11.1 mill tones while it was below 5 mill tons before 2005 (Chai et al., 2007). The annual consumption of biodiesel alone in the United States was 15 billion liters in 2006. It has been growing at a rate of 30-50% per year to achieve an annual target of 30 billion liters at the end of year 2012.

A sharp annual increase as high as 28% of biodiesel production in Europe from the year of 2000 has led to biodiesel production of 5 million metric tons (MTm), The Federal Government of Canada aimed to produce 500 million liters/year of biodiesel by the year 2010 to meet the Kyoto Protocol. In Malaysia, biodiesel production has been targeted to achieve 500,000 tons per year by the year 2010 (Rahmat et al., 2010). At this production capacity of bio-fuel in the world, just in the US, about 3.5 million gallons of crude glycerol is produced every year. **Figure 1.2** shows the increasing trend of production of crude glycerol due to increasing production of biodiesel during the period of 2004 to 2006. Today, with plenty of glycerol stock available in the world market its price and US export have declined. According to a published report (Omni, 2008), the price of pure glycerol varied from \$0.50 to \$1.50/lb and crude glycerol from \$ 0.02/ lb to \$ 0.15 /lb over the past several year. It was also reported that the surplus amount of crude glycerol will increase up to 1.2 metric tons per year at the end of 2010. The price of glycerol in the market will continue to drop in such an over saturated market and currently the main supply of glycerol coming into the market is from the rapidly growing biodiesel industry.

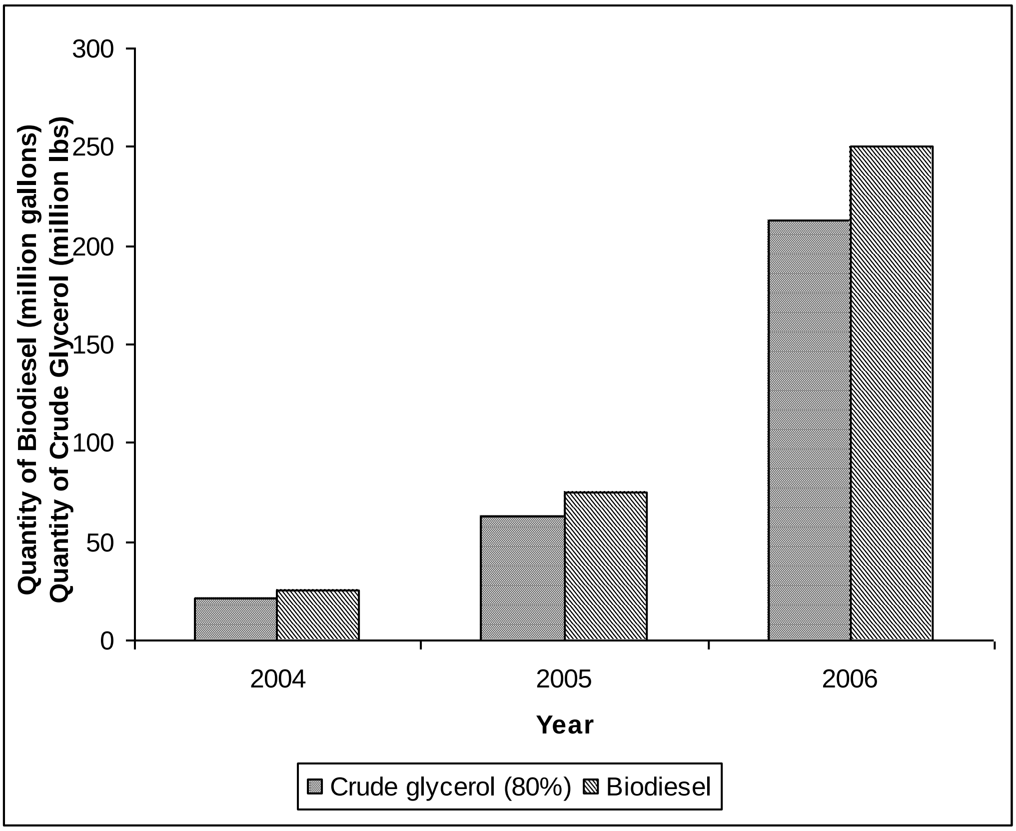

Figure 1.2: Production of biodiesel and crude glycerol during 2004-2006 (Rahmat et al., 2010).

1.3 World glycerol production

The mass production of biodiesel would entail surplus crude glycerol production and this crude glycerol has the highest purity of about 80–88%. Just in the United States, this level of bio-fuel production will yield nearly 1.2 million metric tons of crude glycerol as a primary co-product of the biodiesel production process. **Figure 1.3** shows the clear estimates crude glycerol production resulting from biodiesel production in different countries. This figure is drawn based on the rates of biodiesel production that were published in a report (ABG, 2007). It is clear from this figure that the estimated production of glycerol would reach 5.8 billion pounds in 2020. This is due to the annual demand of biodiesel that is projected at 66.6 billion pounds in 2020.

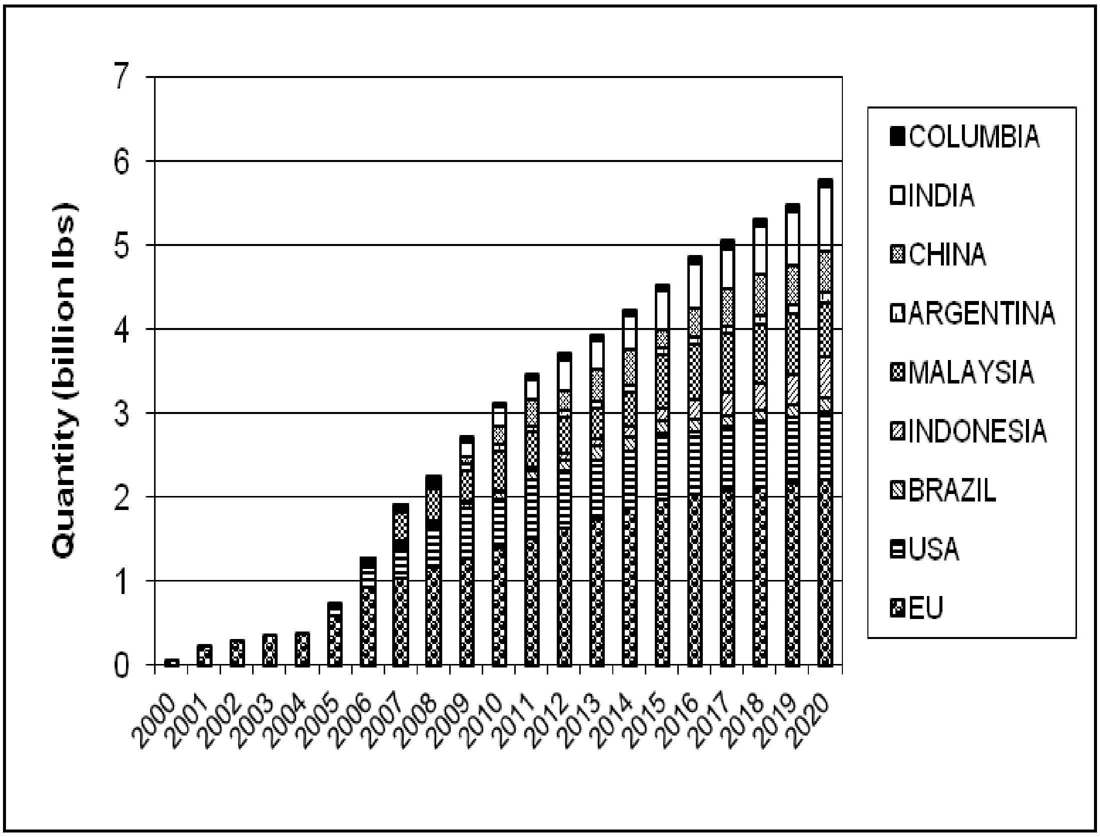

Figure 1.3: Estimated production of crude glycerol in different countries (ABG, 2007).

1.4 World glycerol pricing

Worldwide biodiesel industry expansion is practically limited by high capital costs for its refinery and low value by-products like crude glycerol of purity less than 80 % that needs further purification steps to meet the purity of industrial grade glycerol (99% purity). The conventional application and current market of glycerol could not cope with the excess production. However, purification process is costly and the glycerol market is already saturated. According to a report (Higgins, 2002), the biodiesel production cost ranged from \$ 0.17 to \$ 0.42 per liter over the last decay. However, this price was not constant and continuously decreased over day by day due to purification cost factors. This makes crude glycerol worth very low during production of biodiesel. Thus, the price of crude glycerol that is frequently decline has a direct relation with the biodiesel production cost as shown in **Figure 1.4**.

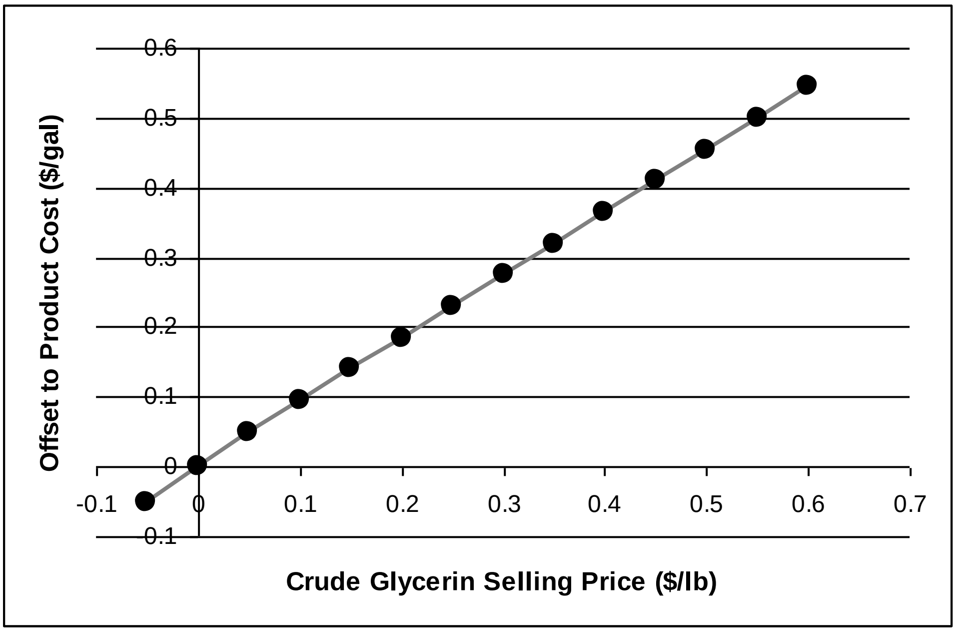

Figure 1.4: Crude glycerol impact on the cost of biodiesel (Tim, 2006).

Today, plenty of glycerol stock is available in the world market and its price is declining day by day. The price of glycerol in the market will continue to drop in such an over saturated market and currently the main supply of glycerol into the market is the rapidly growing biodiesel industry.

Basically, the continual high prices of glycerol makes it worthwhile for users to reformulate with alternative materials such as sorbitol and synthetic glycerol, whereas sustained low prices encouraged its use in other applications. The impact of the additional huge quantity of glycerol on its prices is not clear but it is likely that if new uses for glycerol are not found, the glycerol price may drop to a level that justify its use as a burner fuel, which cost is about 5 cents/lb. This also implies that the overproduction of low grade glycerol would impact the viability and economy of biodiesel production (Kolmetz et al., 2005), market price stability of current crude glycerol as well as environmental concerns due to improper disposal of glycerol (da Silva et al., 2009). The high bio-fuel prices and historically low glycerol prices are two main factors that drive researchers to discover new applications of glycerol and provide an ideal platform for food, chemical and pharmaceutical industries.

1.5 Glycerol applications in industry

Bioavailability of glycerol makes it a green feedstock. It is currently used as a base chemical for the production of plenty of value-added products in chemical industries (Pagliaro et al., 2007). Glycerol is an ideal ingredient in many personal care products, mostly acts in helping to prevent moisture loss while in pharmaceuticals. It provides lubrication and smoothness to many cough syrups and elixirs. For oral care products, glycerol is commonly found in toothpaste, mouthwash and sugar free gum giving a sweet taste without contributing to tooth decay as well as in cosmetics to hold moisture against the skin to prevent dryness (Neumann, 1991).

A wide range of reactions are applicable in these fine chemical industries including dehydration to acrolein, selective oxidation, etherification to fuel-oxygenates, selective hydrogenolysis to yield propanediols, selective transesterification, pyrolysis and gasification, reforming to syngas, polymerisation to oligoglycerols, fermentation to propane-1,3-diol, synthesis of epichlorohydrin, synthesis of fatty esters and conversion of glycerol into glycerol carbonate (Barrault and Jerome, 2008; Jerome et al., 2008; Pagliaro et al., 2007; Zheng et al., 2008). In the current scenario, the biodiesel production is going to skyrocket along with flooding of crude glycerol. Therefore, intense research in science and industry has been made on the selective production of oligomers to valorize this surplus of glycerol.

1.6 Diglycerol as a valuable product of glycerol

The condensation of two glycerol molecules via etherification reaction yields the simplest oligomer, called diglycerol. The product can be linear, branched or cyclic depending on if the condensation takes place between primary or secondary hydroxyls or an intramolecular condensation is involved (Richter et al., 2008). Diglycerol, ($C_6H_{14}O_5$) is a clear, colorless, viscous, practically odorless and sweet in taste liquid. Likewise, the solubility characteristics of this diglycerol are lying between those of the simple alcohols and glycerol. The boiling point of diglycerol is 205 °C under a pressure of 1.3 mbar. It is soluble easily in water and alcohol at room temperature. Generally, diglycerol of concentration 100 g/ L has pH values between 5- 6.

1.6.1 Diglycerol applications

The oligomers of glycerol, i.e. diglycerol and triglycerol have numerous applications in cosmetic, pharmaceutical and additives in nutrition or lubricants. Being biocompatible, diglycerol is incorporated in personal care formulas for its mild humectant properties and its ability to enhance fragrance/flavor impact and longevity. The higher viscosity of diglycerol provides greater a body to personal care formulations and could lead to a reduction in the amount of thickening agent needed. Various Food industries use diglycerol and polyglycerol as emulsifiers in bakery, confectionary, ice-cream, chocolate and margarine products at different percentages as shown in **Figure 1.5** (Charles et al., 2003). Diglycerol is also used in the production of fatty acid ester emulsifiers, and is part of food additives. Often, diglycerol is further processed to useful derivatives.

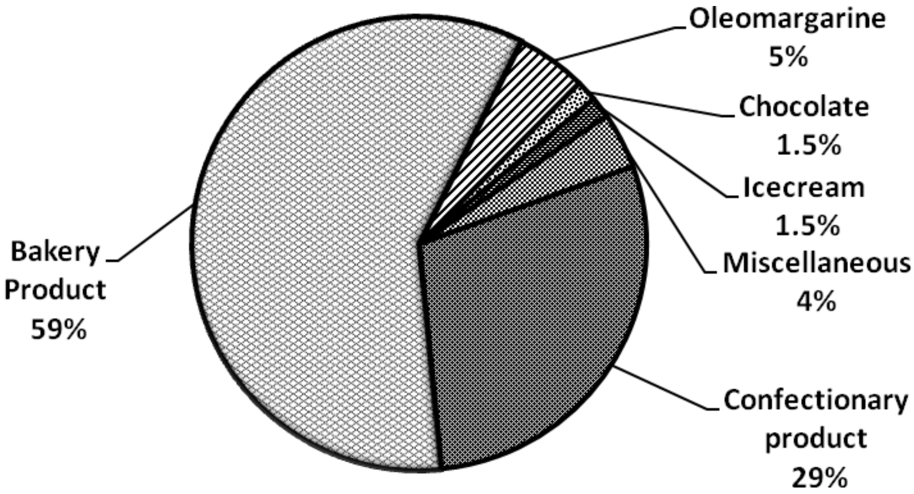

Figure 1.5: Application of diglycerol and other polyglycerol in food industry.
(Charles et al., 2003)

1.6.2 Diglycerol formation

On laboratory-scale, pure diglycerol is formed via direct routes such as the alkailation of dichlorohydrine ether, hydroxylation of diallyl ether with permanganate, hydrolysis of glycidyl ether or hydrolysis of diglycidyl ether via acetone and glycerol transformation into 1,2-0-Isopropylidene glycerol and most feasible route is via glycerol oligomerization or polymerization reaction (Martin and Richter, 2011). A purely thermal conversion of glycerol without the addition of a catalyst in inert media is another route for formation of diglycerol but much care is required and product is usually of low quality. On industrial scale, diglycerol is produced via basic hydrolysis of epichlorohydrin (Jakobson, 1986). After diglycerol formation, further separation, purification and water removal steps are required. The raw diglycerol has to be subjected to a fine distillation for this purpose. The oligomerization/ etherification of glycerol using a catalyst in a reaction system is another route for diglycerol formation. This is uniquely preferable route because it saves two steps (separation and fine distillation) for the purification of diglycerol.

1.7 Glycerol oligomerization for diglycerol production

Glycerol oligomerization has been extensively investigated with or without the use of organic solvents for production of diglycerol. In each case, different homogeneous alkali base catalysts such as carbonates and hydroxides or heterogeneous catalysts including zeolite, mesoporous silica and metal oxides have been applied (Clacens et al., 2002; Jerome et al., 2008; Martin and Richter, 2011). The use of solvent could create some problems in the production process leading to a more complex overall process. On the other hand, the need to eliminate the solvents from the homogeneous catalysts is a very challenging task (Clacens et al., 1998). In this respect, solvent free etherification process could promise several advantages but limited information is currently available on this mode of glycerol etherification process for selective diglycerol production.

1.7.1 Homogeneous catalysts

Previously, several researchers have reported the different homogeneous industrial processes of glycerol conversion to polyglycerols. Nevertheless, these reactions are usually not sufficiently fast (in terms of glycerol conversion) or do not selectively produce diglycerol apart from difficulties in filtration, neutralization and product purification (Jerome et al., 2008; Martin and Richter, 2011). The main drawback of homogenous catalysts is that the glycerol conversion is not selective to targeted diglycerol but also produces some unwanted products due to secondary reactions (dehydration, oxidation) that deteriorate the product quality.

1.7.2 Heterogeneous catalysts

Heterogeneous catalysts show some advantages such as ease of their separation from reaction mixture and the potential for reusability. However, in terms of glycerol oligomerization, a few disadvantages of some heterogeneous catalysts have been reported by previous researchers (Martin and Richter, 2011). They are usually high cost materials, difficult to be functionalized, have high solubility in polar media, experience leaching of metal clusters from their surfaces, have low surface area (in some cases), as well as in their thermal stability.

1.7.3 Acid/ base heterogeneous catalysts

In the heterogeneous reaction systems, the oligomerization of glycerol is mostly conducted using basic or acidic catalysts. The acidic catalyzed oligomerization which runs via a cationic intermediate efficiently converts glycerol but mostly in the form of unwanted cyclic oligomer. Under this condition, the catalyst deactivates quickly due to the blockage of the internal surface area and the acidic sites by the formed deposits. Another prominent drawback of this category of catalyst is that they lead to the formation of unnecessary acrolein due to acidic catalyzed dehydration reaction (Katryniok et al., 2010; Vaidya and Rodrigues, 2009). Basic catalyzed oligomerization reaction runs via an anionic, deprotonated glycerol intermediate that reacts with another glycerol molecule forming a dimer with the release of hydroxyl ion (Martin and Richter, 2011). The most promising results of selective glycerol etherification/ oligomerization to diglycerol are usually obtained using basic heterogeneous catalysts.

1.8 Basic solid catalysts for glycerol oligomerization

Generally, the catalysts which have been studied for this reaction are zeolite, mesporous silica mixed metal oxides and metal oxides. The oligromerization of glycerol over zeolite type catalysts has been found to be more active but less selective for diglycerol with short reaction time and also form some higher molecules during reaction attributed to their small microporous structure (Cottin et al., 1998). Mesoporous catalysts like MCM-41 generally show higher selectivity but with rather low glycerol conversion at slightly high reaction temperature. They also suffer from active component leaching and formation of some higher molecules that block mesopores channels causing a reduced activity of the catalyst (Barrault et al., 2004).

Glycerol oligomerization over alkaline earth metal oxides like CaO shows sufficiently high activity and selectivity but severe leaching of active component and at the end of the reaction can occur so that the reaction is not purely heterogeneous in nature (Ruppert et al., 2008). Mixed oxides like MgAl-Na can show significant conversion and selectivity at slightly low temperature but long reaction time is required due to their basic and hydrotalcite texture properties (García-Sancho et al., 2011). These deficiencies in catalysts might be produced due to harsh reaction conditions during solvent free reaction for oligomerization process. Therefore, there is still a gap whole for preparation of a solid catalyst for selective conversion of glycerol to diglycerol in the absence of any solvent. The use of clays can be considered another option for this process so that they keep on receiving considerable attention for their ability to overcome these problems.

1.9 Modified clay as a catalyst for glycerol oligomerization

Clay minerals which have a significant potential in chemical processing technologies, are other options to use as basic heterogeneous catalyst for solvent free oligomerization reaction due to their different and interesting properties. In particular, clay minerals have received considerable attention in different organic syntheses because of their environmental compatibility, low cost, operational simplicity and reusability (Adams and Mccabe, 2006). Clays have been widely studied as catalysts due to a number of attractive features such as high porosity and thermal stability as well as exchangeable acidity (Armor, 1994; Shelef, 1995). They are also very effective catalysts for a wide range of reactions, often presenting highly required selective product. The interlayer cations of clay are exchangeable and that allows modifications of the acidic nature of the material to become a basic one by a simple ion-exchange procedure.

Specifically, montmorillonites clay exchanged with metal ions is an efficient catalyst in many organic transformations including etherification (Ballantine et al., 1984) and polymerization reaction (Backhaus et al., 2001b). Montmorillonite clay is a form of smectite group (2:1 layer clay) which is used to produce new inexpensive materials with properties matching those of zeolites (clays are two-dimensional structure where as zeolites are three dimensional). This type of material is prepared by exchanging charge-compensating cations between the clay layers with large inorganic metal hydroxycations.

They have layer structure with significant basal space between interlayer help to pass big molecules of reactant and highly thermal stable due to silica and aluminum structure. They become basic in nature after loading of lithium and calcined at high temperature. Therefore, clay might increase its basic strength and might not be effected its large surface area after alkali loading. They are non-corrosive, environmentally benign and present fewer regeneration problems due to harsh reaction conditions. They are also much easier to be separated from the liquid products and can be designed to give higher activity and selectivity even under harsh reaction conditions.

It is obvious that the design of a catalyst covers all aspects ranging from the choice of the active phases to the method of forming particles. A heterogeneous catalyst is a composite material, characterized by: (a) the relative amounts of different components (active species, physical and/or chemical promoters, and supports); (b) shape; (c) size; (d) pore volume and distribution; (e) surface area. Suitable promoters are frequently added to achieve adequate performance. They may either modify the catalyst structure, to improve stability, or to enhance the catalytic reactions to give better activity or selectivity. However, the nature of the active species is always the most important factor in heterogeneous catalyst system (Campanati et al., 2003). Solid heterogeneous catalysts are active as much of their surface is exposed to the reacting molecules (Neurock and Santen, 2006). Furthermore, on the basis of previous inventions in heterogeneous catalysis, it can be concluded that increases in the catalyst surface area and pore size; it might significantly improve catalytic activity as well as selectivity towards oligomerization process.

1.10 Problem statement

Currently, many types of heterogeneous catalysts such as alkaline metal/ alkaline earth metal oxides, mixed oxides, various alkaline metal compounds supported on alumina, zeolite or mesoporous material have been reported to catalyze oligomerization reactions. However, zeolites and metal support on zeolite present severe limitations when large reactant molecules (glycerol) are involved, especially in the case of liquid-phase reaction systems for synthesis of fine chemicals. This is due to the fact that mass transfer limitations are very severe for microporous solids. These catalysts have a narrow and uniform micropore size distribution due to their crystallographically defined pore system. In order to overcome the problem, the pursuit of solid base catalyst has been recently focused on mesoporous silica due to very high surface area, uniformity in pore size and high thermal stability which promise great opportunity for application as catalysts and catalytic supports. Most of mesoporous catalysts show high selectivity but very low glycerol conversion with some leaching problem. On the other hand, glycerol oligomerization over alkaline metal or alkaline earth metal oxides or mixed metal oxides show sufficient activity and selectivity but in long reaction time and also involve severe leaching of active component. Therefore, there is still requirement of such solid catalyst which can stabilize itself at these harsh reaction conditions to provide high conversion of glycerol and selective diglycerol over solvent free oligomerization.

It has layer structure with high basal space between interlayer to facilitate the diffusion of large molecules of reactant and product as well as high thermal stability due to presence of silica-alumina structure. It might become more basic in nature after loading with strong alkali (lithium) and calcination it at high temperature. They are non-corrosive, environmentally benign and present fewer regeneration problems under harsh reaction conditions. Therefore, in this study, lithium has been used as active metal component with support montmorillonite clay other than zeolite and SBA-15 support to improve its catalytic performance for solvent free oligomerization process.

Due to the potential advantages and limited research dedicated to on solvent free oligomerization process using mesoporous solid base catalyst, the main goals of this research project are directed towards the synthesis of the high surface area of mesoporous catalyst and the identification of the final metals which meet specific needs for effectively catalyzing the oligomerization process of glycerol to diglycerol. Moreover, the process optimization is also required for economization and industrial application. Due to the harsh reaction conditions, catalyst stability and regeneration will be addressed besides other topics such as reaction kinetics and process modeling. The main points of our study that have impact towards society are;

i) The development of basic layered catalyst could be tuned to meet the specific needs of any catalytic reaction to ensure higher activity, selectivity and yields towards desired product.

ii) The development of low temperature solvent free reaction system in chemical processing which can enhance both the chemical reactions and physical appearance of end product. It may offer the potential for shorter reaction cycles, cheaper reagents, and less extreme physical conditions, leading to less expensive and perhaps smaller chemical producing plants.

iii) This present study may serve as a basis for the analysis of metal loaded layered catalyst (heterogeneously) and reactions of loaded metals with liquids phase glycerol.

iv) The development of effective heterogeneous catalyst instead of homogeneous may overcome the industrial problems such as in recovering the catalyst after the reaction.

v) The knowledge about reaction mechanism and its kinetics study may helpful for future studies on oligeromerization reaction behavior with basic layered catalyst and its modification forms.

1.11 Objectives

1) To identify the most suitable and stable catalyst among all lithium modified with different type of supports (micropore, mesopore, and layered clay) for solvent free selective oligomerization reaction.

2) To characterize these modified and unmodified form of catalysts in order to establish the understanding on the correlations between the characteristics of modified catalyst with the performance in the oligomerization process**.**

3) To optimize the established solvent free glycerol oligomerization reaction with the most suitable active catalyst by varying reaction parameters.

4) To perform kinetic study for the optimized glycerol oligomerization reaction in the presence of most suitable catalyst by finding activation energy and rate of reaction of the process.

5) To demonstrate the reusability of the most suitable catalyst for the optimized oligomerization process.

1.12 Scope of study

The aim of this study is to prepare a solid base catalyst for high conversion of glycerol to diglycerol via oligomerization reaction at optimized reaction conditions. For active component of this catalyst, different alkali (LiOH, KOH, NaOH) are used in the form of homogenous catalyst for prescribed reaction. After finding best alkali LiOH as an active component for oligomerization reaction, lithium in the form of salt (10 wt % Li over support) has been impregnated over three different supports for glycerol oligomerization under same reaction conditions. In this study, three different types of support have been chosen including microporous Y Zeolite, mesoporous SBA-15 and layered material montmorillonite K-10 clay. The lithium salt $LiNO_3$ has been loaded over all supports under same conditions by special impregnation method described in methodology section. These lithium modified and parent supports have been subjected to comprehensive characterization for changes in the characteristics of their structures using available techniques such as; surface analyzer with Brunauer-Emmett-Teller (BET) surface area measurement, X-ray diffraction (XRD), small angle X-ray scanning (SAXS), inductive couple plasma (ICP-AES) analysis, Hemmett indicator method for basic strength, energy-dispersive X-ray spectroscopy (EDX), transmission electron microscope (TEM), and scanning electron microscope (SEM). The investigations on the suitable lithium modified catalyst and its activity for solvent free glycerol oligomerization to diglycerol have also been performed. A simple and economical three-neck glass reactor with Dean Stark and PID temperature controller system has been established for the oligomerization reaction that provide good quality and reproducibility on the results. Lithium over montmorillonite K-10 catalyst (Clay Li/MK-10) has been found to be the best catalyst for prescribed reaction. Then reaction parameters were optimized with the help of Design of Experiments (DOE) to get better results at optimum reaction conditions that might be feasible for industrial applications. The product sample has been analyzed by means of gas chromatograph (GC), equipped with a capillary column DB-HT5 and a flame ionization detector (FID). Besides that, a kinetic study for the reaction has been studied by preparing a kinetic model and its validation for best active catalyst using Arrhenius equation with the help of obtaining the activation energy (E_a), reaction rate ($-r_g$) and order of reaction (n). Finally, the best catalyst has been studied for its reusability for up to three runs. It has also been tested for leaching of active component i.e. lithium from the clay support to liquid phase and drawn a relation of this leaching with activity of best catalyst for oligomerization reaction.

1.13 Thesis organization

This thesis consists of five chapters. Each chapter explains the important information of this research.

Chapter One: gives an introduction to the world's energy crisis, biodiesel demand, glycerol production worldwide, glycerol and its product diglycerol applications. Different catalyst types and their importance for glycerol conversion to diglycerol are also covered. This chapter also presents the problem statement, objectives of the present studies, research scopes and finally the thesis organization.

Chapter Two: focuses the literature review of the three main parts in this study i.e. selective conversion of glycerol to diglycerol, solid base catalyst in oligomerization process and kinetic studies of etherification reaction. This chapter highlights the previous work done on glycerol conversion into diglycerol via different methods and using different types of catalyst. It also provides a brief overview over oligomerization reaction and its products in the form of diglycerol isomers.

Chapter Three: provides details about the experimental methodology and analysis, the materials and chemical reagents used in the present research work, the experimental setup for oligomerization process, experimental method for support and catalyst preparation and modification along with the characterization studies. Details product analysis, optimization studies, performance of catalyst, reusability of the catalyst, and kinetic study are also presented.

Chapter Four: covers all the results and explanation of the findings in the study. This chapter has been organized into seven main sections based on the chronology of the work to provide an ideal flow of information and subsequently an easier understanding of the study. Overall results obtained from this study are discussed and presented in this chapter in the following sequence ; 1) Homogeneous alkali catalyst for glycerol oligomerization to diglycerol, 2) Modified microporous zeolite catalyst for glycerol oligomerization 3) Stabilized modified mesoporous SBA-15 catalyst for glycerol oligomerization, 4) Modified mesoporous clay catalyst for glycerol oligomerization, 5) Optimization of operating parameters via DOE method, 6) Kinetic study and 7) Reusability study of the catalyst. A logical discussion was made on the prepared catalyst and their characteristics to chose the best catalyst among different types of support (micropore, mesopore, layered clay) for prescribed reaction under given conditions. Subsequently, discuss the optimization of the reaction conditions with the help of DOE and then study the kinetics of the optimized solvent-free glycerol oligomerization reaction in the presence of best catalyst. In the last section of this chapter, the reusability and leaching results for best catalyst were studied and the summary of this section has been given at the end of this chapter.

Chapter Five: gives the conclusions to the findings made in the present study. It also provides some recommendations for future studies based on the results of the present study.

CHAPTER TWO

LITERATURE REVIEW

2.1 Background

The forecasted decline in the production of petroleum fuels and the growing concern about atmospheric greenhouse gas concentrations have necessitated the search for clean, renewable (sustainable), efficient and non expensive alternative fuel. Biodiesel is becoming a key fuel in motor engines if blended in certain portions with petrodiesel (Hasheminejad et al., 2011). It can be readily produced via the transesterification of vegetable oils (edible, non edible or reused) with low alcohols (methanol or ethanol). Indeed, the inevitable formation of glycerol that accompanies the biodiesel production process is affecting the process economy (Olutoye and Hameed, 2011; Yuan et al., 2010). Moreover, the growth of the biodiesel industry will result in overproduction of glycerol and create a surplus of this impure product as its production is equivalent to 10 % of the total biodiesel produced (Cardona et al., 2007; Khayoon and Hameed, 2011).

Glycerol is an abundant carbon-neutral renewable resource for the production of biomaterials as well as source for a variety of chemical intermediates (Garcia, 2011; Rahmat et al., 2010). The physical and chemical properties of glycerol are shown in Appendix A. Unfortunately; biodiesel-derived glycerol is not biocompatible due to its contamination with toxic alcohol (methanol or ethanol). Therefore, global research is focused on the effective conversion of glycerol to valuable chemicals to ameliorate the economy of the whole biodiesel production process. Recently, many studies have been dedicated to the transformation of this renewable polyol by various catalytic processes (Melero et al., 2012; Rahmat et al., 2010). This encompasses oxidation process to obtain dihydroxyacetone, glyceraldehyde, glyceric acid, glycolic acid and hydroxypyruvic acid (Augugliaro et al., 2010; Liebminger et al., 2009). It also includes the fermentation process towards 1,3-propanediol production (Tokumoto and Tanaka, 2011), acetylation process with acetic acid to obtain polyglycerol esters (Balaraju et al., 2010; Dosuna-Rodriguez et al., 2011; Goncalves et al., 2008; Khayoon and Hameed, 2011)and acetalisation process with ketones to obtain oxygenated acetals and ketals (da Silva and Mota, 2011; Silva et al., 2010; Umbarkara et al., 2009; Vicente et al., 2010).

Glycerol is also an efficient platform for the synthesis of oxygenated components such as diglycerol, polyglycerols and ployglycerol ethers by means of etherificationor oligomerization process (Arzamendi et al., 2008; Melero et al., 2010; Melero et al., 2012; Yuan et al., 2011). Diglycerol is produced from catalytic etherification or oligomerization of glycerol with or without use of any solvents. The use of solvent could create some problems in the production process leading to a more complex overall process. In this respect, solvent free etherification process could promise several advantages but limited information is currently available on this mode of glycerol etherification process for diglycerol. Venturing into the possibility of such process is a worthwhile research effort.

This literature review contains information about the preparation methods of diglycerol, glycerol oligomerizaion reaction, and different types of catalyst used for this reaction, behaviors of used catalysts, activity, reusability performance and other knowledge gaps in previous studies. Properties of innovative clay as a catalyst for this reaction, optimization, and kinetic study for glycerol oligomerization reaction are also revived. Finally, conclusive statements about this research work are also given at the end of each section.

2.2 Existing diglycerol synthesis methods

2.2.1 Small scale method

On small-scale, pure diglycerol is produced via direct synthesis routes which are already described by different previous researchers (Behrens and Mieth, 1984; Jakobson, 1986; Wittcoff et al., 1949). Favorably, diallyl ether is used as a primary reactant. Diallyl ether is accessible by reaction between allyl chloride and allyl alcohol in inert solvents under HCl release. Direct hydroxylation of this product can be performed with peroxyformic acid, CH_2O_3, or permanganate, at 40 °C under safety precautions for 4.5 h. However, several additional steps are needed for neutralization, filtration, dry and fractional distillation are necessary for isolation of the diglycerol and triglycerol. Isolation of diglycerol prepared by this method can be done using neutralization with e.g. barium hydroxide solution, centrifugation to separate the solid, digestion of the product in absolute ethanol and fractional distillation under reduced pressure.

2.2.2 Glycerol derivatization method

Further routes for manufacturing diglycerol and triglycerol proceed via glycerol derivatization methods (Steinberger, 1989; Kanzler, 2008), using e.g. isopropylidene rests as protecting groups. All described possibilities so far have the disadvantages of either the starting substances are difficult to get or the synthesis requires several intermediate steps, and the conversion produces great amounts of salts as by-products.