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Upgrading Bio-oil over Different Solid Catalysts

by

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(11098)

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

July 2010

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CERTIFICATION OF APPROVAL

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Approved by,

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ABSTRACT

Bio-oil, a liquid product from biomass via fast pyrolysis, by the virtue of its environmentally friendly potential, is regarded as a promising energy source. In spite of that, it has certain limitations that bring on many problems in its handling and utilization. Thus, bio-oils require upgrading to improve their characteristics before they can be used as replacement for fuels. The objective of this project is to upgrade bio-oil over different solid catalysts.

Based on the literature review, it is concluded that esterification is the most preferable upgrading technique due to the properties of bio-oil resulted from the process and its low production cost. To carry out the esterification either a homogenous or heterogeneous catalyst can be used. For this project, heterogeneous catalyst is used whereas the scope is within the usage of solid acid and solid base catalysts, specifically $40SiO_2/TiO_2\text{-}SO_4^{2-}$ and $30K_2CO_3/Al_2O_3\text{-}NaOH$.

The research methodology of this project consists of artificial bio-oil preparation, catalysts preparation, esterification experiment and characterization of bio-oil. The results and discussion analysis along with case study to compare with previous similar project are conducted. At the end, both solid acid and solid base catalysts successfully converted the bio-oil into esters through esterfication experiment. For generating solid acid catalyst, new approach is used: by using silica gel and highly dispersed SiO_2 as the materials. It is also concluded that this project gives a fast reaction rate in achieving the equilibrium conversions and that the characteristics of upgraded bio-oil in this project are improved to standard biodiesel properties.

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ABBREVIATIONS AND NOMENCLATURES

Al	Aluminum
Al_2O_3	Aluminum Oxide
Ba	Barium
Ca	Calcium
CO_2	Carbon Dioxide
EFB	Empty Fruit Bunch
GC-MS	Gas Chromatography – Mass Spectrometry
H_2SO_4	Sulphuric Acid
HT	Hydrotalcites
K_2CO_3	Potassium Carbonate
Mg	Magnesium
NaOH	Sodium Hydroxide
NO_x	Nitrogen Oxide
SiO_2	Silicon Dioxide
SO_2	Sulfur Dioxide
Sr	Strontium
TiO_2	Titanium Dioxide

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

In the future, the earth is expected to run short of its present sources of energy like petroleum, coal and charcoal. Though there may be shortage of energy, the need for energy will never go down and in fact, escalating day by day. The main source of energy today is fossil fuel, the fossilized remains of organic materials. Today's fossil fuels are mainly extracted in the forms of petroleum, coal and natural gas. Present theory regarding fossil fuel formation states that the process in which petroleum and coal are created requires millions of years to complete, and as such, fossil fuels in general can be considered non-renewable. The fact that fossil fuels cannot be replenished means that petroleum and coal are finite, and their supply will dwindle to zero at a future date.

Petroleum makes up 35% of world energy use, mainly in transportation and electricity production. Various interpretation of the peak oil theory that describes the production cycle for an oil field has stated that the maximum oil production had occurred, or will have occurred in the very near future. The largest oil fields in the world have seen this decline, and the United States has seen its oil production peaked in the 1970's. This and the fact that the rate of new discoveries of reserves has been declining seems to support the peak oil theory.

Currently, coal supplies 28% of the world energy, and its usage is expected to grow significantly. The planet's reserve of coal is estimated to be around 800 to 900 Gigaton, and at present rate of coal consumption it can last for 137 years. However, coal usage has been increasing at an annual rate of 2.5%, which means that the current reserve will be depleted around 2065 if this rate of increased coal usage remains unchanged.

Overall, the summary of the world energy usage are shown in Figure 1.1 below.

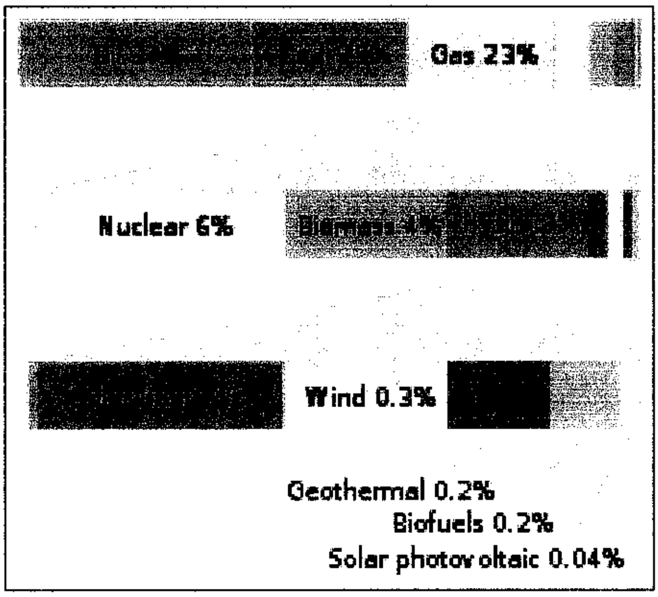

Figure 1.1: World energy usage

Source: MIT Club SWFL (http://alumweb.mit.edu/clubs/sw-florida/energy.html)

1.2 PROBLEM STATEMENT

It is growing clear that the public is becoming more conscious of problems like peak oil and other sources of potential energy crises, and governments around the globe are acting as such. Many suggestions have been made as to how these problems can be fixed or averted. While many sustainable development and energy policy organizations have advocated reforms to energy development from the 1970's, some cater to a specific crisis in energy supply including Energy-Questand, the International Association for Energy Economics. The Oil Depletion Analysis Centre and the Association for the Study of Peak Oil and Gas examine the timing and likely effects of peak oil. It can be concluded that the world is heading towards an unprecedented large and potentially devastating global energy crisis. The answer to this problem lies in alternative energy which comes with its own set of strengths and limitations.

Today one of the best forms of renewable and alternative energy is bio-oil, which is basically a fuel that is produced through pyrolysis process of biomass. However, it has certain limitations as well. The chemical composition of bio-oil is complicated, comprising mainly of water, carboxylic acids, carbohydrates, and lignin-derived substances. The bio-oils are generally acidic, viscous, reactive and thermally unstable. Their compositions and properties differ considerably from those of the petroleum-based fuel oils. These bring on many problems in the handling and utilization of bio-oils. Therefore, bio-oils require considerable upgrading to improve their characteristics such as viscosity, thermal instability, corrosiveness and chemical complexity before they can be used as replacement for fuels and chemical feedstocks.

1.3 OBJECTIVE AND SCOPE

The objective of this project is to upgrade bio-oil through catalytic esterification over different solid catalysts. The scope of this project covers not only the usage of solid acid catalyst but also solid base catalyst. They are $40SiO_2/TiO_2\text{-}SO_4^{2-}$ and $30K_2CO_3/Al_2O_3\text{-}NaOH$ respectively. The results of this bio-oil upgrading over the different catalysts are then compared.

CHAPTER 2

LITERATURE REVIEW

2.1 BIO-OIL

Bio-oil is liquid biofuel created through pyrolysis. Bio-oil has advantages in transport, storage, combustion, retrofitting and flexibility in production and marketing. It is also clean, because it contains negligible contents of sulfur, nitrogen, and ash, and gives much lower emission of SO_2, NO_x, and soot, by combustion, than the conventional fossil fuels.

Virtually any form of biomass can be considered for fast pyrolysis to produce bio-oil. Most work has been performed on wood, because of its consistency and comparability between tests. However, nearly 100 types of biomass have been tested, ranging from agricultural wastes such as straw, olive pits, and nut shells to energy crops such as miscanthus and sorghum (Mohan and colleagues, 2006). Forestry wastes such as bark and thinnings and other solid wastes, including sewage sludge and leather wastes, have also been considered.

Fast pyrolysis is a fairly old technology which dates back to the 1950's. It was developed to liberate a liquid fraction from tar sand or bituminous coal. At that time both the thermal conversion reactors were developed together with proper liquid collection systems. Fast pyrolysis was rediscovered in the 1980's as a technique to obtain liquids from biomass while utilizing the same techniques as were applied for coal liquefaction. Today's fast pyrolysis technology embodies the tested design from the 1950's together with modern materials, control system and energy integration techniques.

Advantages of a biomass liquefaction process is that it allows the conversion of an ill defined granular material like biomass into a well defined liquid energy carrier. Since bio-oil is obtained by a dry distillation process, the liquid is virtually free of ash. It can be stored, pumped and atomized prior to any combustion process. Since the pyrolysis process requires a small heating duty, a part of the fuel gas or char can be combusted to supply the necessary heating duty.

Figure 2.1 below shows the process of biomass fast pyrolysis to produce bio-oil.

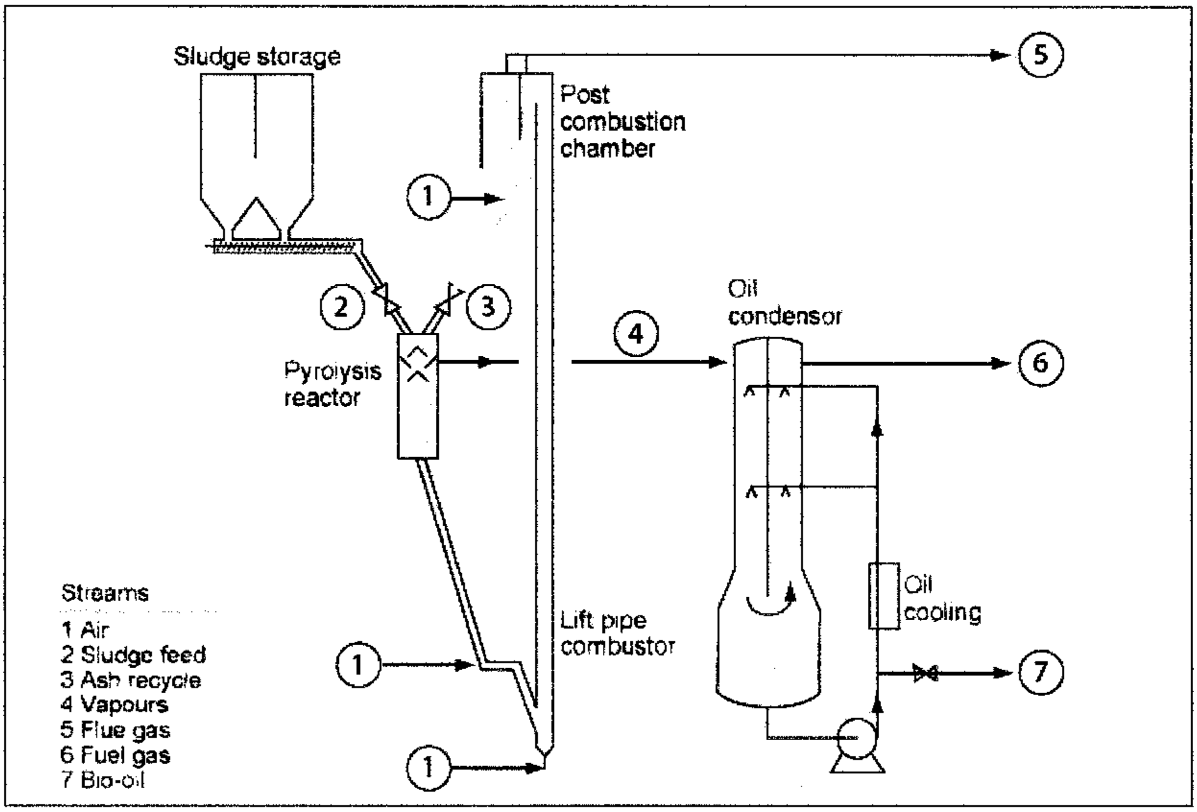

Figure 2.1: Biomass fast pyrolysis process

2.2 RECENT UPGRADING TECHNIQUES

The recent bio-oil upgrading techniques include hydrodeoxygenation, catalytic cracking of pyrolysis vapors, emulsification, steam reforming and esterification.

2.2.1 Hydrodeoxygenation

Hydrodeoxygenation is an alternative for upgrading of bio-oils. Sulfided CoMo and NiMo catalysts are used in upgrading reactions but they have the disadvantage of sulfur stripping causing the deactivation of the catalyst and the contamination of the products (Gutierrez et al, 2008). Furthermore, sulfided catalysts are deactivated due to coke deposition. Therefore, there is a need for more suitable catalysts.

2.2.2 Catalytic cracking

The operating conditions and catalysts used in catalytic cracking to achieve a desired product slate vary, and each feed comes with inherent advantages and disadvantages. Using this upgrading technique, the bio-oils are generally best upgraded by HZSM-5 or ZSM-5, as these zeolitic catalysts promote high yields of liquid products and propylene. Unfortunately, these feeds tend to coke easily, and high Total Acid Number (TAN) and undesirable byproducts such as water and CO_2 are additional challenges.

2.2.3 Emulsification in diesel

Stable emulsions could be prepared from bio-oil and regular diesel fuel using appropriate surfactants. The stability of the emulsions depends on surfactant concentrations. Bertoli et al. successfully combusted 30% bio-oil oil emulsions produced in a low speed diesel engine (Ikura and colleagues, 2001). The effects on hydrocarbon and carbon emissions were comparable to those from hydrotreated diesel fuel. Although there remain some technical problems related to the utilization, bio-oil emulsification might be a useful tool to assist the market entry of pyrolytic bio-oil.

However, it is found that even apparently stable emulsions formed stratification after a certain induction time. Although the stratified layers can be easily redispersed into the emulsion by gentle shaking, their presence is undesirable in fuel. Thus, it became necessary to establish the ranges of process operating conditions required for producing stable emulsion fuels. It is also found that the fuel properties such as heating value, cetane and corrosivity were unsatisfied.

2.2.4 Steam Reforming

Hydrogen is a clean energy resource and very important in the chemical industry, and the rising focus on reforming the water fraction of bio-oil looks promising. Production hydrogen from reforming bio-oil was investigated extensively, including the reactions in a fixed bed or a fluidized bed and studies of the reforming mechanisms or model compounds. The fixed bed used in the conventional reforming of natural gas is not suitable because of its tendency to decompose thermally and form carbon deposits on the upper layer of the catalyst and in the reactor freeboard. Meanwhile, the development of fluidizable catalyst that has both high activity and mechanical strength at the condition of steam reforming process is needed and being pursued (Czernik et al, 2002).

2.2.5 Catalytic Esterification

In the esterification process, the fat molecules are separated into three individual fatty acid ester chains. This process requires alcohols, in most cases methanol. Esterification catalysts are normally used to accelerate the rate of the esterification reaction. To carry out the esterification either a liquid or solid catalyst can be used. Conventionally used homogeneous catalysts include complexes of transition metals, especially titanium and tin, and strong acids.

The cheapest and well-known catalyst for esterification reactions is concentrated sulphuric acid (Soetaert and Vandamme, 2009). The main disadvantages of this catalyst are the possibility of the formation of side products like dark colored oxidized or other decomposition products. As organic compound, p-toluene sulphonic acid can also be used. However, the high price of the compound has prevented broader application. As heterogeneous catalyst, cationic ion exchange resins can also be used in continuous reaction columns. However, this approach has only been used so far in pilot plants.

The esterification process requires low cost feedstock with high acidic content, and thus it can lower the production cost. In the end, the physical properties of the bio-oil are changed in such a way that they correspond to those of conventional diesel fuels (Zhang et al, 2006). After esterification, the molecules have a viscosity that is similar to that of a normal fossil diesel fuel.

2.2.6 Conclusion and Recommendations

Thus, based on the findings of the bio-oil upgrading techniques mentioned previously, it can be concluded as follow:

- By using hydrodeoxygenation and catalytic cracking as the upgrading method, the yield of upgraded oils is generally low because of the high yields of char, coke and tar. These undesired products, which are deposited on the catalyst and cause its deactivation, make a periodical or continual regeneration necessary.

- Emulsification of bio-oil with diesel provides a short-term approach to the use of bio-oil in diesel engine, but fuel stability and properties were unsatisfied.

- Updgrading of bio-oil through steam reforming still needs development of catalyst that has both high activity and mechanical strength at the condition of steam reforming process.

- Hydrodeoxygenation, catalytic cracking and steam reforming of bio-oils are so complicated techniques that steady, dependable, fully developed reactors are urgently desirable.

- Esterification is the most preferable technique to upgrade bio-oil because the properties of the bio-oils upgraded through this process are similar to those of conventional diesel fuels. It results in lower production cost as well.

- Much more work is needed for the stabilization and upgrading of bio-oils with some modifications to equipment configuration before applying them in generating heat or power.

2.3 COMPARISON OF CATALYSTS FOR THE PROJECT

Based on the conclusion stated in the previous section, the reason why the esterification process is preferable has been justified. Hence, the catalyst required for the esterification process were further analyzed. There are two types of catalyst for this reaction: homogenous and heterogeneous.

Homogeneous base catalysts are an alkaline liquid such as sodium hydroxide, sodium methoxide, potassium hydroxide, or potassium methoxide. Homogeneous acid catalysts are an acidic liquid such as sulphuric acid, hydrochloric acid or sulphonic acid. Whereas, heterogeneous catalysts are acid or base solids that include immobilized enzymes, titanium-silicates, alkaline-earth metal compounds, anion exchange resins or guanadines heterogenized on organic polymers [1]. While the application of heterogeneous catalysts appears promising and growing, the use of homogeneous catalysts such as sodium or potassium hydroxide, sodium or potassium methoxide is still common in industries because the latter are relatively cheap and quite active for this reaction [2-3].

2.3.1 Comparison between Homogenous and Heterogenous Catalyst

It is appropriate to begin the discussion with a comparison of factors between homogenous and heterogenous catalyzied esterification. Such a comparison is given in Table 2.1.

Table 2.1: Comparison of homogenous and heterogeneous catalyzed esterification

Factors	Homogeneous catalyst	Heterogeneous catalyst
1. Reaction rate	Fast and high conversion	Moderate conversion
2. After treatment	Catalyst cannot be recovered, must be neutralized leading to	Can be recovered

	waste chemical production	
3. Processing methodology	Limited use of continuous methodology	Continuous operation is possible
4. Catalyst reuse	Not possible	Possible
5. Cost	High	Low

Thus, based on the table above, it is decided that heterogenous catalyst is more favorable because it has more advantages compared to the homogeneous catalyst.

2.3.2 Heterogeneous Catalyst

A variety of solid catalysts has been examined for the esterification reaction. In the heterogeneously catalyzed esterification reaction, a number of operating parameters such as temperature, extent of catalyst loading, mode of mixing, alcohol/oil molar ratio, presence/absence of impurities in the feedstock and the time of reaction are important. Esterification reaction can also be carried out under supercritical conditions, and this method also may evolve as an alternative to catalytic routes.

Solid Acid Catalyst

Solid acid catalysts can replace strong liquid acids thereby eliminating the corrosion problems associated with their use and consequent environmental hazards posed by them. However, the efforts in exploiting solid acid catalysts for esterification are limited due to pessimistic expectations on the possible reaction rates and side reactions.

Zeolites

Zeolites can be synthesized with extensive variation of acidic and textural properties. They can be synthesized to overcome the diffusional limitations so that optimum biodiesel production can be achieved.

Heteropoly acids

In the search for water tolerant acid catalysts, heteropoly acids appear to be the appropriate choice. Most of these systems have acidity in the range of super acids with the possibility of tailoring the porous architecture as well as solubility in water. Heteropoly acid catalyst was reportedly chosen [4] on the basis of high activity, water tolerance, reusability and environmentally friendly nature of this material for biodiesel production.

Although it appears attractive, it is necessary that the activity of this class of catalysts is evaluated and compared with the other hydrophobic solid catalysts from the point of important variables and operating parameters such as methanol to oil molar ratio, reaction temperature and the extent of reusability [5].

Functionalized zirconia and silica

The use of sulphated zirconia catalysts and organo sulphonic acids functionalized silica for the esterification was reported previously [6-7]. The idea of utilizing sulphated zirconia catalyst in the esterification arose from the difficulty of recuperating sulphuric acid from the system. The main drawback with these systems was that the sulphate ions leached out from the porous support as a result of hydrolysis. As alternatives to sulphated zirconia, sulphated tin oxide and tungstated zirconia–alumina were also experimented [8-10]. The results demonstrated that the phase composition of zirconia contributed considerably in the reaction. The tetragonal zirconia that was formed from low calcinations temperature produced significantly higher yield than the monoclinic zirconia that was formed from higher calcinations temperature.

Other solid acid catalysts

The other types of solid acid catalysts that were exploited for use in esterification and in the past include tungsten oxides, sulphonated zirconia and organosulphonic functionalized mesoporous silicas. Even though solid acid catalysts have been applied effectively in the esterification, the use of these catalysts to obtain high conversion to biodiesel necessitates much higher reaction temperatures than base catalysts because of their lower activity for esterification. Thermal stability becomes an issue when resin-type catalysts are used at higher temperatures [11] in order to achieve higher reaction rates in an application such as reactive distillation. The other issue is associated with catalyst regeneration.

Solid base catalysts

Basic zeolites

The base strength of the alkali ion exchanged zeolite increases with increasing electropositive nature of the exchanged cation. The occlusion of alkali metal oxide clusters in zeolite cages through the decomposition of impregnated alkali metal salts results in an increase in the basicity of these materials [12]. These exchanges can affect the water tolerant behavior of the basic zeolite system.

Hydrotalcites

Hydrotalcites (HT) are a class of anionic and basic clays known as layered double hydroxides with the formula $Mg_6Al_2(OH)_{16}CO_3.4H_2O$.

Conventionally, HT is synthesized by coprecipitation, wherein metal nitrates and precipitants are added slowly and simultaneously at a fixed pH under stirring, followed by a long ageing time and/or hydrothermal treatment in order to improve the crystallinity. A particular chemical composition and the method of synthesis, i.e., temperature, solution pH, and ageing time of the gels, have a strong influence on the final basicity of the mixed oxides [13-14].

In the methanolysis experiment using Mg–Al HT catalysts prepared by coprecipitaion, the best ester conversions from soybean oil and glyceryl tributyrate were below 80% [15-18]. In another work [19], esterification of rapeseed oil with methanol using Mg–Al HT prepared using Mg/Al molar ratio of 3.0, aged for 12 h and calcined at 773 K converted the methanol ester to about 90.5% yield.

Although relatively lower yield was observed, HT can still provide large opportunity for improvement in the biodiesel production. This is especially true if the specific surface area of the solid pore is improved, its homogeneity is enhanced and the particle size is greatly reduced. A way to achieve these desirable characteristics is by employing a sol–gel method during HT synthesis.

Alkaline earth oxide base catalysts

Alkaline earth oxides are potential base catalysts for use in esterification. The origin of basic sites in alkaline earth oxides has been the subject of review, and it is generally believed that they are generated by the presence of M^{2+}–O^{2-} ion pairs in different coordination environments. The basic strength of the group II oxides and hydroxides increased in the order Mg > Ca > Sr > Ba. Of these, Ca-derived bases are the most promising as they are inexpensive, the least toxic and they exhibit low methanol solubility [20].

2.3.3 Conclusion and Recommendations

The previous explanations describe the various types of heterogeneous solid acids and bases as promising catalysts for efficient biodiesel production via esterification process. In conclusion, from the commercial point of view solid base catalysts are more effective then acid catalysts and enzymes. However, solid acid catalysts have the capacity to replace strong liquid acids, thereby eliminating the corrosion problems and environmental waste pollutants.

In recommendation for the selection of suitable solid acid catalysts, activity should be correlated with the fundamental properties of the catalysts and the validity of these correlations has to be established. Various other technical aspects including the effect of environmental variables like source of the oil, effect of moisture content, molar ratio of alcohol to oil are also important.

For this project, the solid acid and solid base catalysts required in this project are $40SiO_2/TiO_2\text{-}SO_4^{2-}$ and $30K_2CO_3/Al_2O_3\text{-}NaOH$ respectively.

However, it is also recommended that other similar forms of acid and base catalysts are researched in order to foreclose the unavailability of these catalysts. Below is the literature review of related previous experiments using other catalysts.

Esterification of Bio-oil using Acidic Ionic Liquid (HSO_4) Catalyst [21]

A dicationic ionic liquid HSO_4 was synthesized and used as the catalyst for bio-oil upgrading through the esterification reaction with ethanol at room temperature. The reaction system turned into two layers when the reaction was complete. No coke and deactivation on the catalyst was observed. The yield of upgraded oil was about 49%, and its properties were significantly improved. The pH value of the upgraded bio-oil was increased compared to that of crude bio-oil, while the moisture decreased. The chemical composition of the upgraded bio-oil was analyzed with GC-MS. The data indicated that the dicationic ionic liquid was a promising catalyst for esterification to upgrade bio-oil.

Esterification of Bio-oil using Aluminum Silicate in Supercritical Ethanol [22]

The crude bio-oil was upgraded in supercritical ethanol using aluminum silicate as catalyst. The results showed that the supercritical upgrading process performed effectively and the components of the upgraded bio-oil were optimized greatly. Acidic aluminum silicate facilitates esterification in supercritical ethanol to convert most acids contained in crude bio-oil into various kinds of esters. The amount of phenols that exist extensively in crude bio-oil decreased during the supercritical upgrading process. Aldehydes, such as furfural and vanillin, which are typically present in crude bio-oil, were removed during the supercritical upgrading process and not detected in the upgraded bio-oil. The residue of distillated upgraded bio-oil decreased evidently compared to that of distillated crude bio-oil. The density and kinematical viscosity of upgraded bio-oil decreased compared to that of crude bio-oil. The pH value and heating value, on the other hand, increased compared to that of crude bio-oil. The changes of these properties showed that the quality of upgraded bio-oil was improved.

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CHAPTER 3

METHODOLOGY

3.1 MATERIALS AND EQUIPMENTS

Below are the materials and equipments or tools required in this project:

- Materials
  1. Bio-oil

     The bio-oil used in this project is produced / prepared artificially based on EFB (Empty Fruit Bunch) bio-oil chemical compounds. For preparation, the following components are required:
     - Acetic acid
     - Ethyl methyl ketone
     - Phenol
     - Methyl acetate
     - Tetrahydro-furan
     - Methanol
     - 2-Furaldehyde
     - Water
  2. Acetic acid
  3. Catalysts

     The solid acid and solid base catalysts used in this project are $40SiO_2/TiO_2$-SO_4^{2-} and $30K_2CO_3/Al_2O_3$-NaOH respectively. For preparation, the following components are required:
     - SiO_2
     - TiO_2
     - H_2SO_4
     - K_2CO_3
     - Al_2O_3

  - NaOH
4. Ethanol
5. Phenolphthalein

- Equipments and tools
  1. 3-neck flask
  2. Reflux condenser
  3. Magnetic stirrer
  4. Mixer
  5. Oven
  6. Chamber furnace
  7. Burette
  8. Sieve shaker
  9. Viscometer
  10. Calorimeter bomb
  11. pH meter

  The heating and grinding equipments in the list above are shown as per Appendix 1.

3.2 RESEARCH METHODOLOGY

To achieve the objective of this project, the following procedures are carried out:

3.2.1 Artificial bio-oil preparation

Based on GC-MS result, the analysis shows that EFB (Empty Fruit Bunch) based bio-oil is consisted with groups of carboxylic (26.54 wt%), ketone (23.63wt%), phenol (16.98wt%), ester (7.17wt%), furan (6.31wt%), alcohol (5.55wt%), aldehydes

(5.12wt%) and water (8.7wt%). By knowing this composition's percentage and the density of each component, 100ml of artificial bio-oil will be made accordingly.

Table 3.1: Data for artificial bio-oil components

Organic Group	**Chemical**	**Weight%**	**Density (g/cm3)**	**Mass of 1ml**	**Mass fraction**	**Volume**	**Volume ratio**	**Volume used for 100ml mxture**
Carboxylic Acid	Acetic acid	26.54	1.0490	1.0490	2.0428	1.9474	0.2400	23.9959
Ketone	Ethyl Methyl Ketone	23.63	0.8050	0.8050	1.8188	2.2594	0.2784	27.8406
Phenol	Phenol	16.98	1.0700	1.0700	1.3070	1.2214	0.1505	15.0510
Ester	Methyl acetate	7.17	0.9320	0.9320	0.5519	0.5921	0.0730	7.2965
Furan	Tetrahydro-Furan	6.31	0.8892	0.8892	0.4857	0.5462	0.0673	6.7304
Alcohol	Methanol	5.55	0.7918	0.7918	0.4272	0.5395	0.0665	6.6480
Aldehydes	2-Furaldehyde	5.12	1.1600	1.1600	0.3941	0.3397	0.0419	4.1862
Water	Water	8.7	1.0000	1.0000	0.6696	0.6696	0.0825	8.2514
				7.6970		8.1154		100

Where,

$$MassFraction = (wt\%)X(TotalMass)$$

$$Volume = \frac{MassFraction}{Density}$$

$$VolumeRatio = \frac{Volume}{TotalVolume}$$

3.2.2 Catalysts preparation

Since the solid acid $40SiO_2/TiO_2\text{-}SO_4^{2-}$ and solid base $30K_2CO_3/Al_2O_3\text{-}NaOH$ are not purchasable as whole mixture of compounds, the preparation of these catalysts is required. The materials and procedure for this preparation are described as per following section (Zhang et al, 2006).

Solid acid 40SiO_2/TiO_2-SO_4^{2}

- Materials:
  1. TiO_2 powder
  2. H_2SO_4
  3. SiO_2
  4. Ethanol
- Preparation procedure:
  1. SiO_2 is grinded to powder using mixer and sieved.
  2. SiO_2 powder is mixed with TiO_2 powder by 40 wt % in ethanol. The mass balance of SiO_2 and TiO_2 powder are 20 g and 30 g respectively.
  3. The mixture is impregnated in H_2SO_4 (1 M) and stirred for 6 hours.
  4. Drying in the oven at temperature of 120 °C for 4 hours.
  5. Calcination in the chamber furnace at temperature of 400 °C.

Solid base 30K_2CO_3/Al_2O_3-NaOH

- Materials:
  1. K_2CO_3
  2. Al_2O_3
  3. NaOH
- Preparation procedure:
  1. K_2CO_3 and Al_2O_3 powder are grinded by 30 wt % together and sieved. The mass balance of K_2CO_3 and Al_2O_3 powder are 15 g and 35 g respectively.
  2. The mixture is impregnated in NaOH (1 M) solution and stirred for 6 hours.
  3. Drying in the oven at temperature of 120 °C for 4 hours.
  4. Calcination in the chamber furnace at temperature of 500 °C.

3.2.3 Esterification experiment

1 The esterification reaction with Ethanol and bio-oil by a molar ratio of 2.5:1 is carried out in the three-neck flask equipped with a reflux condenser and magnetic stirrer. Following the molar ratio, the mass balance of ethanol and bio-oil for 100 g total mass of solution are 71.43 g and 28.57 g respectively. The calculations are as follow:

$$m_{ethanol} = \frac{2.5}{3.5} \times 100gr = 71.43gr$$

$$m_{bio-oil} = \frac{1}{3.5} \times 100gr = 28.57gr$$

The reaction temperature is maintained at 50 °C. Prior to do this experiment, the model reaction of esterification with Ethanol and acetic acid is carried out first in order to test whether the reaction occurs or not. The set up of the esterification experiment is shown as per Appendix 2.

2 The catalyst is used by 5 wt% of the reaction solution, which is sampled at a 20 min interval and measured quantitatively by NaOH standard solution titration and analysis.

By the titrating the bio-oil with NaOH, the conversion is calculated by applying the equation:

$$Conversion = (1 - V/V_0) \times 100\%$$

Where,

V = volume of the standard NaOH solution consumed in neutralizing 0.5 mL solution sampled in the process

V_0 = volume of the standard NaOH solution consumed at the beginning of the reaction to change the phenolphthalein indicator pink

The conversion is also measured by the internal standard method through Gas Chromatography analysis system, with Isoamyl acetate as the internal standard, and the results of the measurements are kept consistent mutually.

3.2.4 Characterization of Bio-oil

1 The density is measured.
2 The dynamic viscosity is measured with viscometers.
3 The acidity is evaluated by a pH-meter.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 CATALYSTS PREPARATION

Two runs were carried out for each solid acid and solid base catalyst to achieve the desired result. This is to ensure the best particle size and determine the exact drying time. Based on the first run, it was found that the catalyst should have been properly grinded and sieved. Failure to do so had resulted in non homogenous particle size which could affect the performance of the catalyst. In this case, the operating condition of the sieve shaker used in order to achieve the desired particle size is sieve of 355 Mm size with amplitude of 0.8 mm set for 15 minutes. Meanwhile, the drying time of the solid acid and solid base catalyst showed a significant difference. The solid acid catalyst only required 4 hours to dry whereas the solid base catalyst required 12 hours.

The preparation of solid acid catalyst is carried out two times using two different materials: silica gel and highly dispersed SiO_2. This is done for comparison to see which catalyst material can give higher conversion. The silica gel and the final products of catalyst preparation are as per Appendix 3.

4.2 ESTERIFICATION EXPERIMENT

As per described in the methodology section, the model reaction of esterification with ethanol and acetic acid was carried out first in order to test whether the reaction occurs or not. It was conducted in different experiments: catalyzed by solid acid, solid base and without catalyst. The results are as per sections below.

4.2.1 Ethanol and acetic acid without catalyst

Table 4.1: Acetic acid conversion without catalyst

Time (min)	V NaOH (mL) during titration	Conversion of acetic acid (%) $(1 - V/V_0) \times 100\%$
0	2.3 (V_0)	0.000
20	2.2	4.348
40	2.1	8.696
60	2.1	8.696
80	2.1	8.696
100	2.1	8.696
120	2.1	8.696

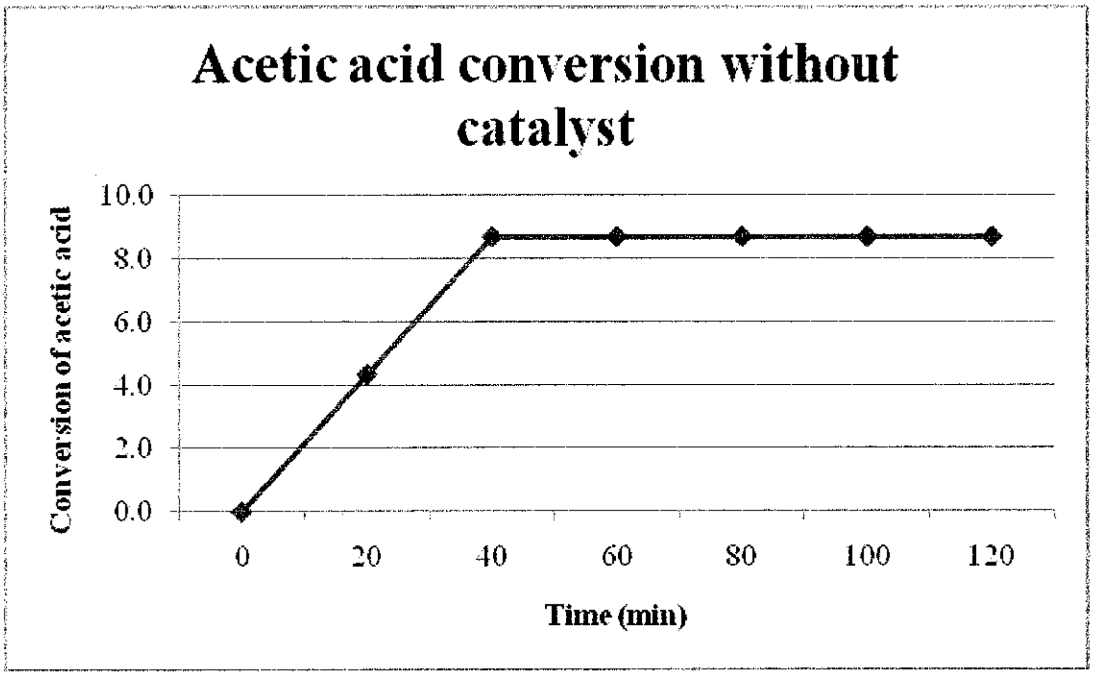

Figure 4.1: Graph for acetic acid conversion without catalyst

4.2.2 Ethanol and acetic acid with solid acid catalyst generated by silica gel

Table 4.2: Acetic acid conversion catalyzed by solid acid from silica gel

Time (min)	V NaOH (mL) during titration	Conversion of acetic acid (%) $(1 - V/V_0) \times 100\%$
0	2.3 (V_0)	0.000
20	1.8	21.739
40	1.6	30.435
60	1.4	39.130
80	1.3	43.478
100	1.3	43.478
120	1.3	43.478

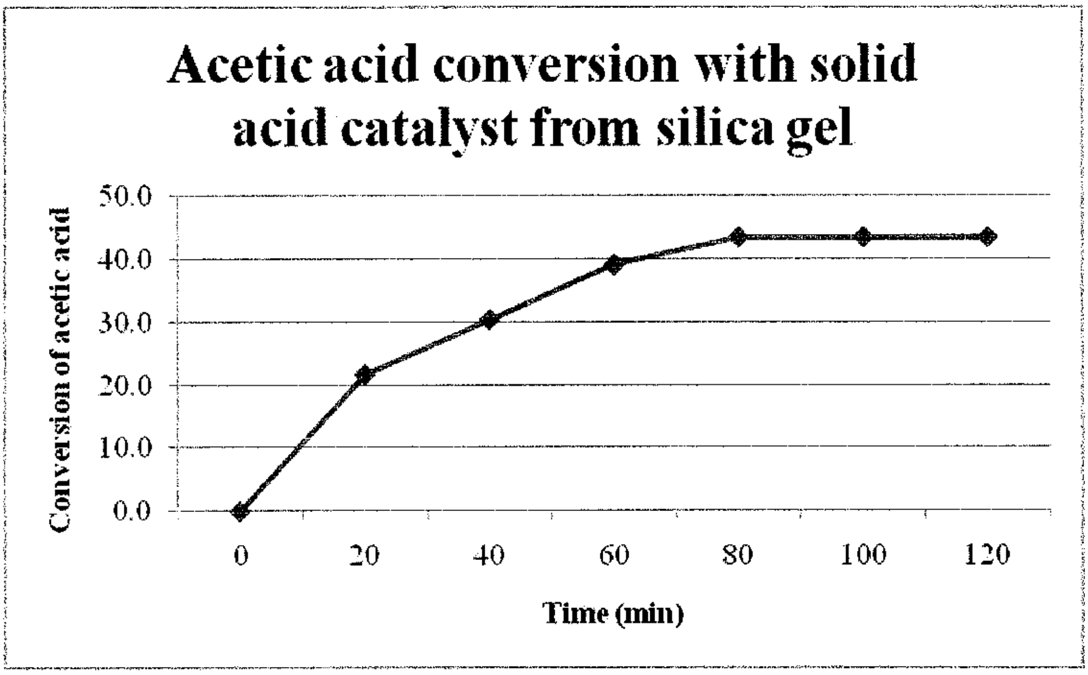

Figure 4.2: Graph for acetic acid conversion with solid acid catalyst generated by silica gel

4.2.3 Ethanol and acetic acid with solid acid catalyst generated by highly dispersed SiO_2

Table 4.3: Acetic acid conversion catalyzed by solid acid from highly dispersed SiO_2

Time (min)	**V NaOH (mL) during titration**	**Conversion of acetic acid (%)** $(1 - V/V_0) \times 100\%$
0	2.5 (V_0)	0.000
20	2.0	20.000
40	1.7	32.000
60	1.45	42.000
80	1.25	50.000
100	1.1	56.000
120	1.1	56.000

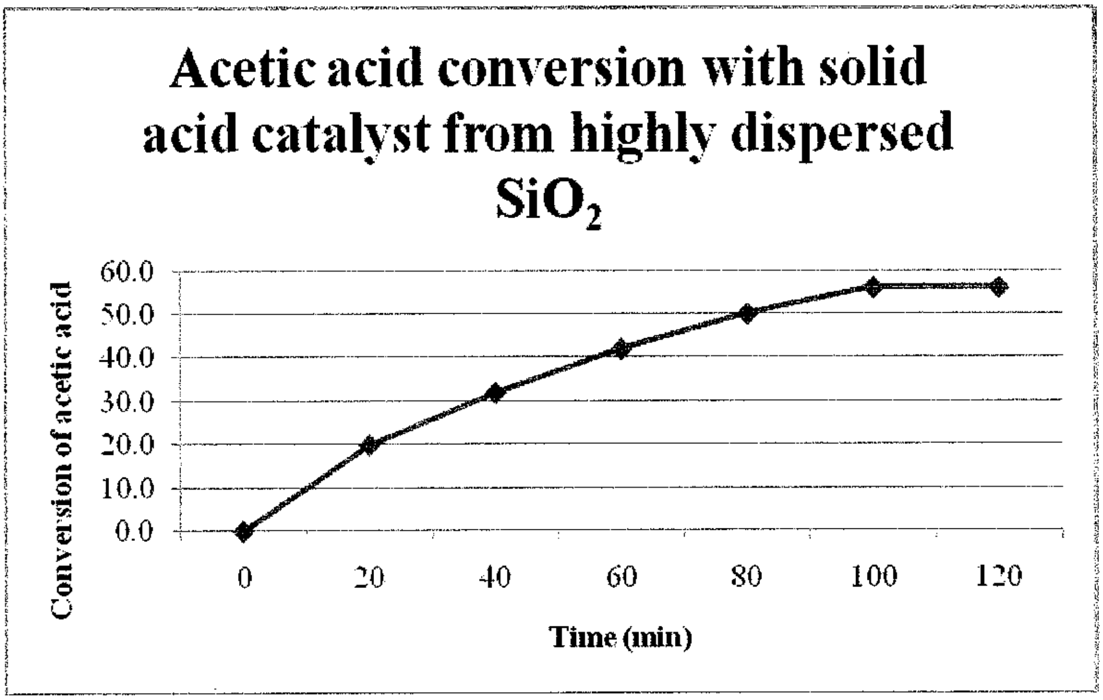

Figure 4.3: Graph for acetic acid conversion with solid acid catalyst generated by highly dispersed SiO_2

4.2.4 Ethanol and acetic acid with solid base catalyst

Table 4.4: Acetic acid conversion catalyzed by solid base

Time (min)	V NaOH (mL) during titration	Conversion of acetic acid (%) $(1 - V/V_0) \times 100\%$
0	2.1 (V_0)	0.000
20	1.9	9.524
40	1.7	19.048
60	1.6	23.810
80	1.5	28.571
100	1.5	28.571
120	1.5	28.571

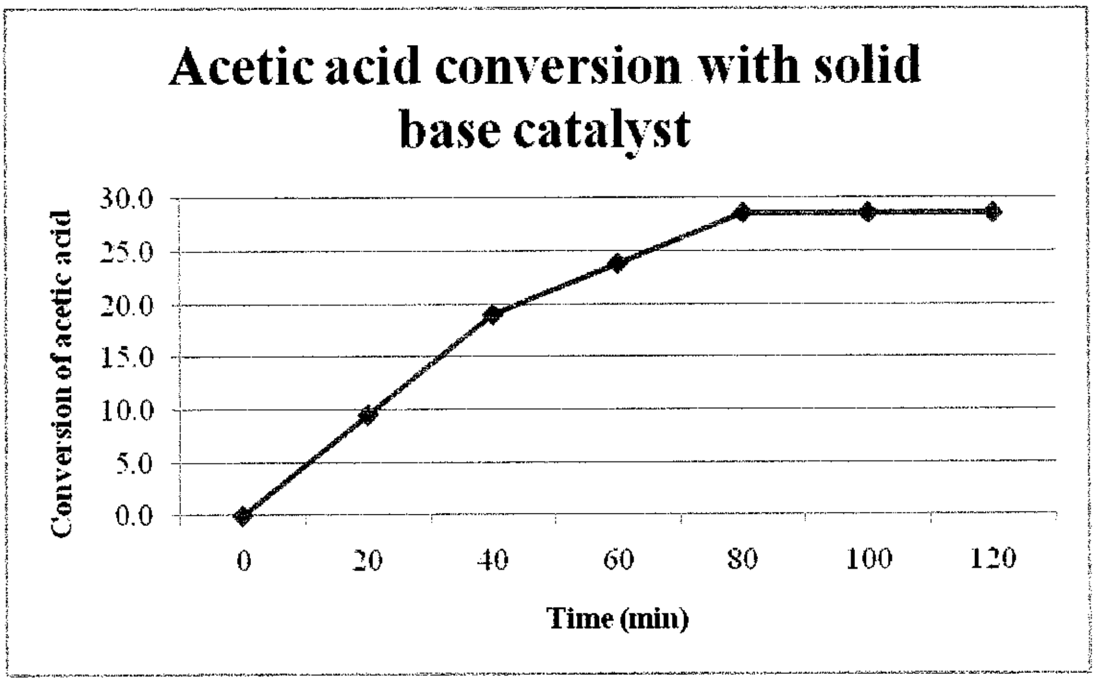

Figure 4.4: Graph for acetic acid conversion with solid base catalyst

Since the reaction occurs in all the model reactions of esterification above, the reaction of esterification with ethanol and bio-oil was carried out next. It was also conducted in different experiments: catalyzed by solid acid, solid base and without catalyst. The results are as per next sections.

4.2.5 Ethanol and bio-oil without catalyst

Table 4.5: Bio-oil conversion without catalyst

Time (min)	V NaOH (mL) during titration	Conversion of bio-oil (%) $(1 - V/V_0) \times 100\%$
0	0.6 (V_0)	0
20	0.55	8.333333
40	0.55	8.333333
60	0.55	8.333333
80	0.55	8.333333
100	0.55	8.333333
120	0.55	8.333333

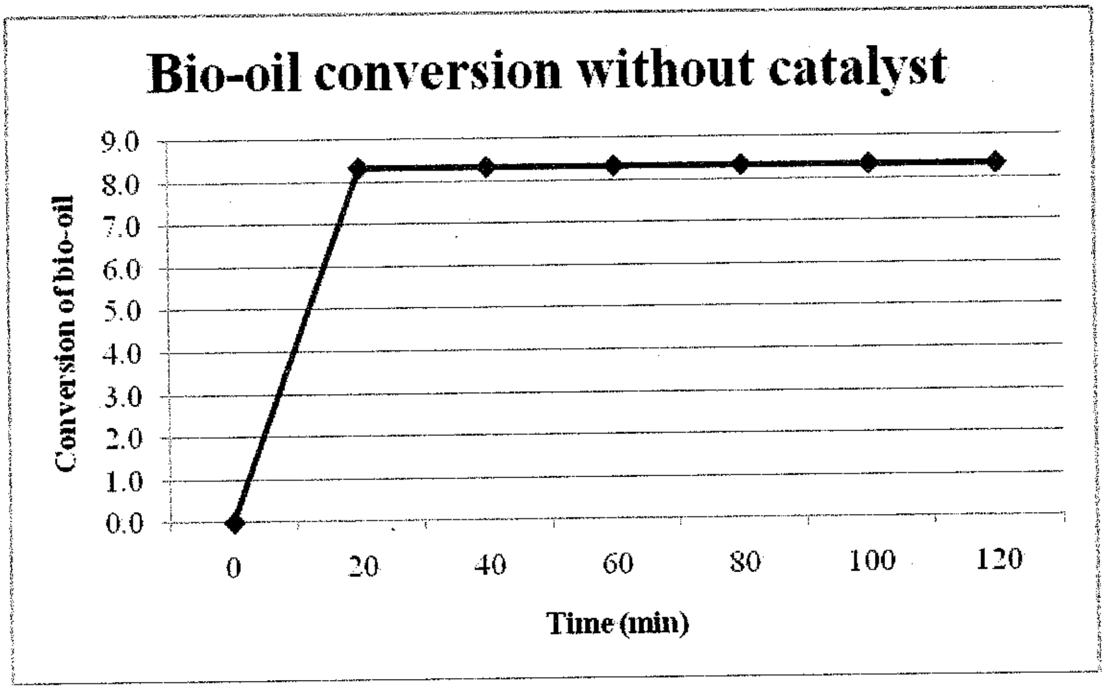

Figure 4.5: Graph for bio-oil conversion without catalyst

4.2.6 Ethanol and bio-oil with solid acid catalyst generated by silica gel

Table 4.6: Bio-oil conversion catalyzed by solid acid from silica gel

Time (min)	**V NaOH (mL) during titration**	**Conversion of bio-oil (%)** $(1 - V/V_0) \times 100\%$
0	0.7 (V_0)	0
20	0.5	28.57143
40	0.4	42.85714
60	0.4	42.85714
80	0.4	42.85714
100	0.4	42.85714
120	0.4	42.85714

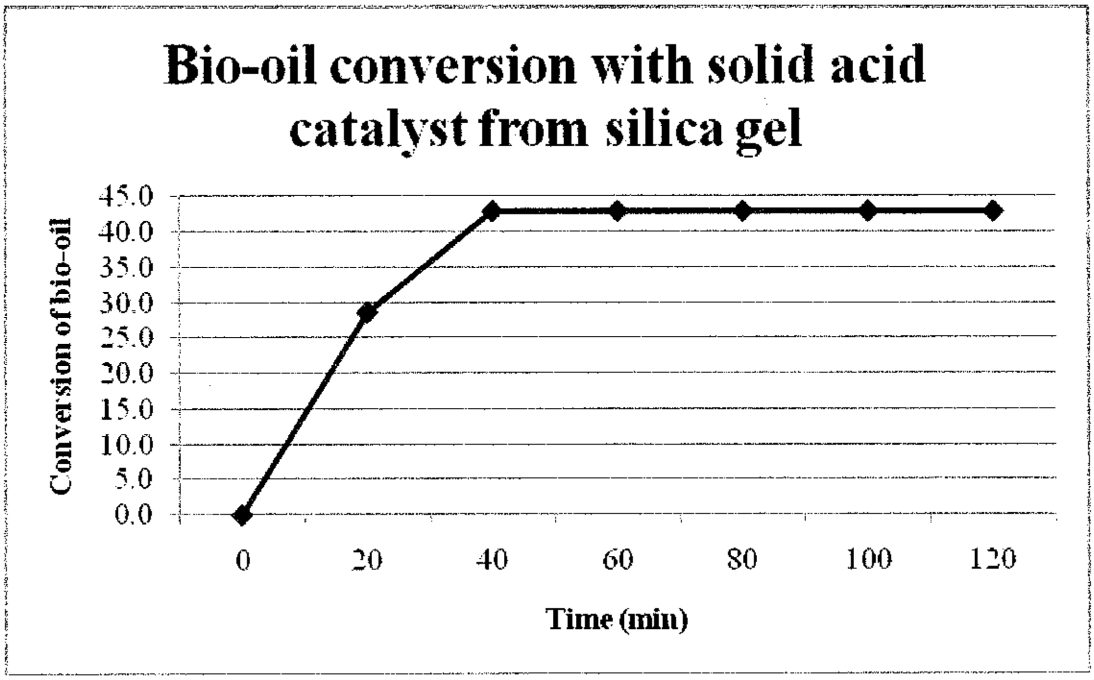

Figure 4.6: Graph for bio-oil conversion with solid acid catalyst from silica gel

4.2.7 Ethanol and bio-oil with solid acid catalyst generated by highly dispersed SiO_2

Table 4.7: Bio-oil conversion catalyzed by solid acid from highly dispersed SiO_2

Time (min)	V NaOH (mL) during titration	Conversion of bio-oil (%) $(1 - V/V_0) \times 100\%$
0	0.7 (V_0)	0
20	0.45	35.71429
40	0.35	50.00000
60	0.3	57.14286
80	0.3	57.14286
100	0.3	57.14286
120	0.3	57.14286

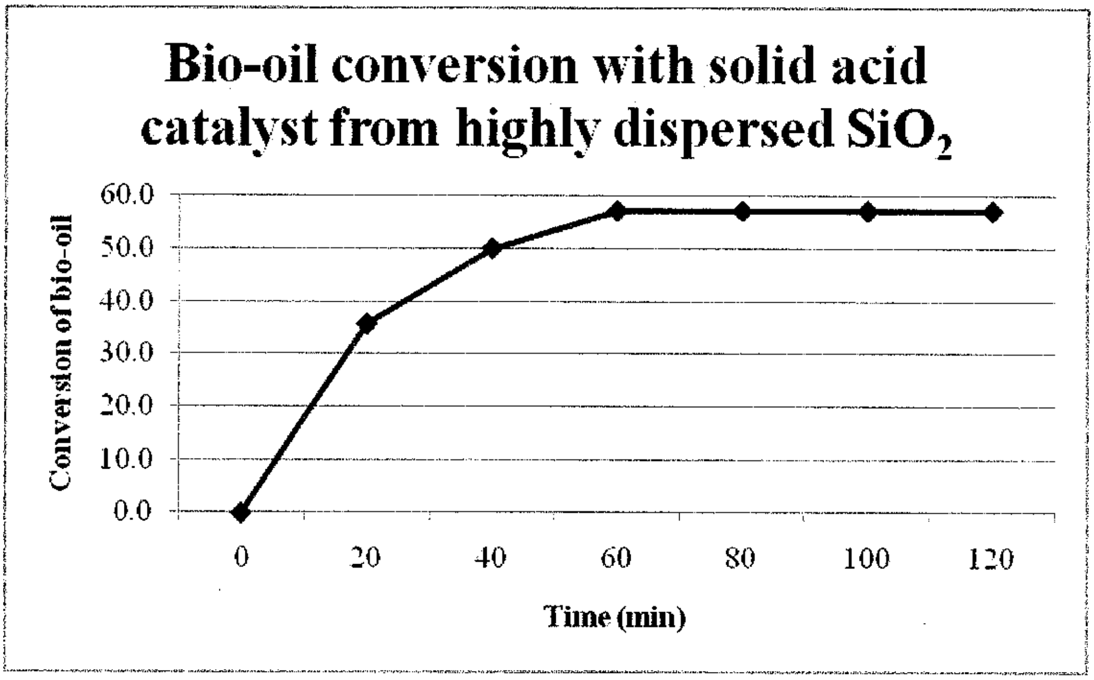

Figure 4.7: Graph for bio-oil conversion with solid acid catalyst from highly dispersed SiO_2

4.2.8 Ethanol and bio-oil with solid base catalyst

Table 4.8: Bio-oil conversion catalyzed by solid base

Time (min)	V NaOH (mL) during titration	Conversion of bio-oil (%) $(1 - V/V_0) \times 100\%$
0	0.7 (V_0)	0
20	0.6	14.28571
40	0.5	28.57143
60	0.5	28.57143
80	0.5	28.57143
100	0.5	28.57143
120	0.5	28.57143

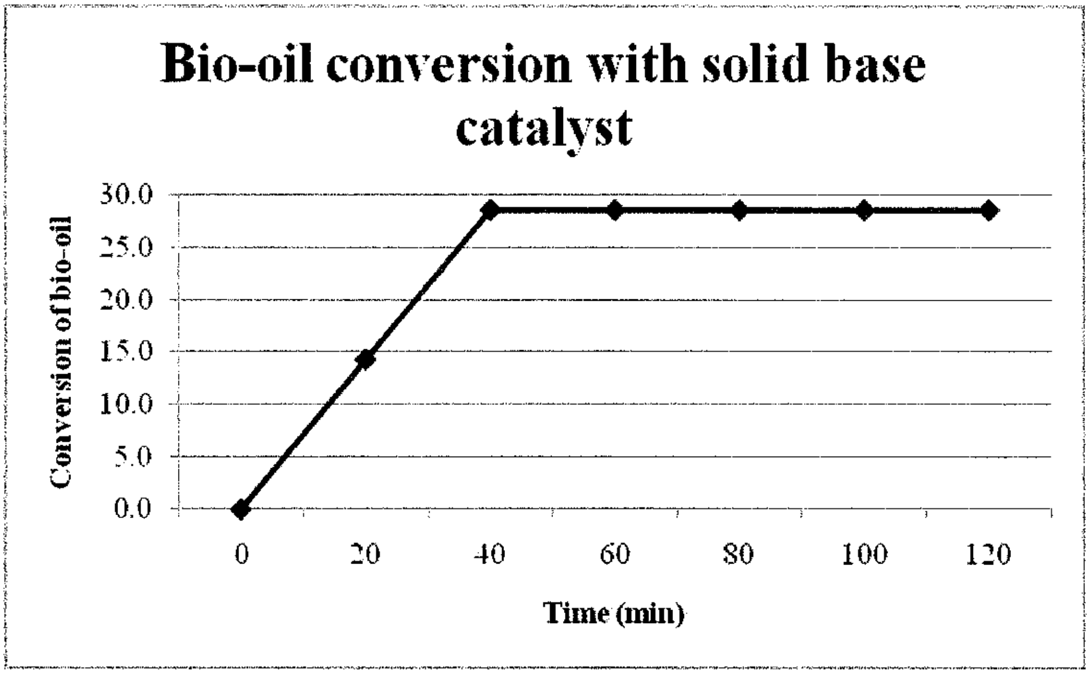

Figure 4.8: Graph for bio-oil conversion with solid base catalyst

Based on the results of all the eight (8) reactions of esterification using bio-oil and acetic acid, the conversion over different catalysts is described in Figure 4.7.

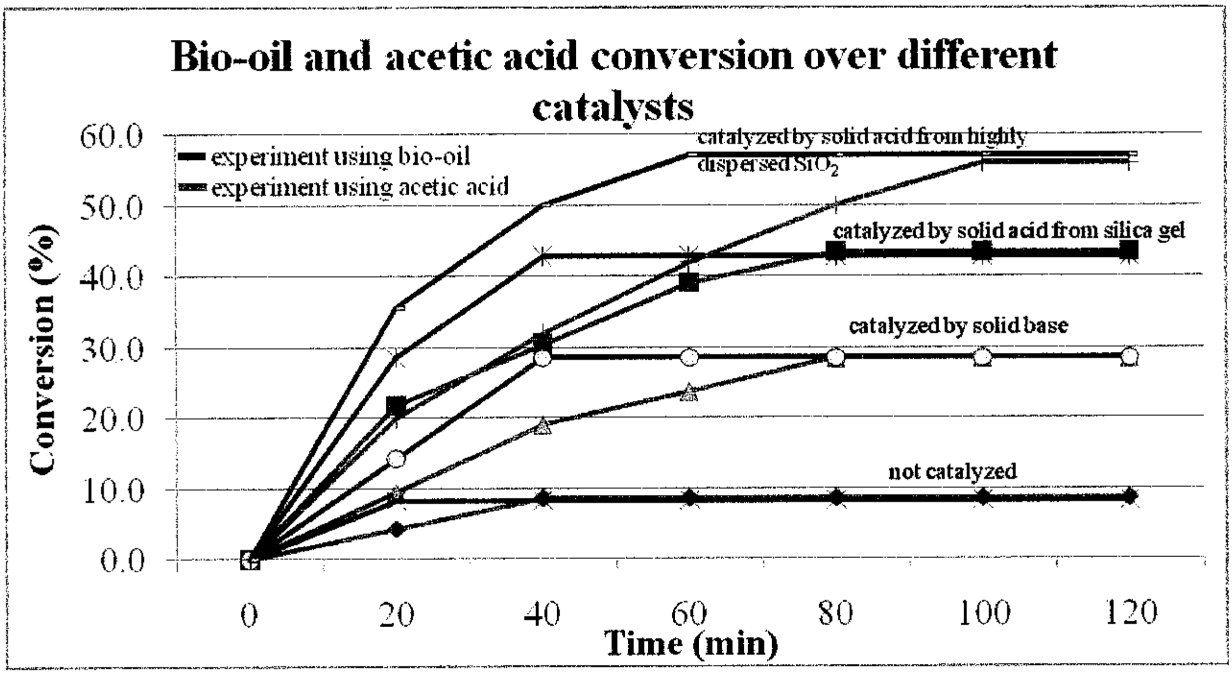

Figure 4.9: Graph for bio-oil and acetic acid conversion over different catalysts

As shown in the graph, both solid acid and solid base catalysts successfully converted the bio-oil and acetic acid into esters. This can be proven through Gas Chromatography – Mass Spectrometry analysis. Based on the graph, the solid acid catalyst generated by highly dispersed SiO_2 converted the bio-oil and acetic acid into esters the most, presenting high activities whereas the bio-oil and acetic acid conversion rose to 57.14% and 56% respectively. The solid acid catalyst generated by silica gel presented high activity as well whereas the bio-oil and acetic acid conversion rose to 42.86% and 43.48% respectively. The solid base catalyst exhibited better activity than no catalyst, although it was not as high as the solid acid catalysts.

4.3 CHARACTERIZATION OF BIO-OIL

After conducting the esterification experiments, characterization was done to study the properties of the upgraded bio-oil such as density, viscosity, water content and acidity. The results are shown in the following table.

Table 4.9: Properties of the upgraded bio-oil

Bio-oil	**Properties**		
	Density (gr/cm^3)	**Dynamic viscosity (mm^2/s)**	**Acidity, pH**
Upgraded by solid acid*	0.8330	4.174	1.045
Upgraded by solid base	0.8508	5.340	5.819
Upgraded without catalyst	0.836	5.250	3.013

**generated by silica gel*

The density of the upgraded bio-oil was measured by taking account the mass per 5 cm^3 of volume. In this case, the mass of upgraded bio oil using solid acid, solid base and no catalyst per 5 cm^3 of volume is 4.166, 4.254 and 4.179 gr respectively. Hence, using these values the density was calculated by dividing the mass by volume. The result showed that the upgraded bio-oil with solid base catalyst has the highest density compared to those with solid acid and no catalyst, although the differences are not significant. The same case happened in terms of viscosity whereas the upgraded bio-oil with solid base catalyst has the highest dynamic viscosity compared to the other two. This satisfies the theory that the dynamic viscosity is proportional to the density, which is shown by the following equation:

$$\rho = \frac{\mu}{\upsilon}$$

Where, ρ = density (kg/m^3)

μ = dynamic viscosity (Pa.s)

υ = kinematic viscosity (m^2/s)

The acidity of the upgraded bio-oil varies differently, affected by the type of catalyst used. As shown in Table 4.7, the pH value of upgraded bio-oil with no catalyst is 3.013 which is considered quite acidic. This is due to the large amount of acid in the artificial bio-oil itself. As the solid acid catalyst was used, the pH value of the upgraded bio-oil becomes more acidic which is 1.045. On the other hand, the usage of solid base catalyst increased the value of pH which indicates less acidic.

4.4 CASE STUDY

For a case study, Table 4.8 shows the data from the esterification experiment using bio-oil as compared with the previous project by Zhang et al (2006) in terms of catalysts materials, conversion and equilibrium time.

Table 4.10: Data comparison with previous project

Parameter	**Previous project (Zhang et al. 2006)**			**This project**			
	No catalyst	**Solid acid**	**Solid base**	**No catalyst**	**Solid acid**		**Solid base**
Materials for catalyst	N/A	• SiO_2 (Degussa A-380) • TiO_2 powder	• K_2CO_3 • Al_2O_3	N/A	• **Silica gel** • TiO_2 powder	• **Highly dispersed SiO_2** • TiO_2 powder	• K_2CO_3 • Al_2O_3
Bio-oil conversion (%)	15	88	23.7	8.3	42.9	57.1	**28.6**

Equilibrium time (min)	N/A	80	> 100	20	**40**	**60**	**40**

Source: Zhang, Q., Chang, J., Wang, T. and Xu, Y. (2006). Energy Fuels, 20, pp. 2717-2720.

In terms of catalyst material, as shown in the table above, this project used silica gel and highly dispersed SiO_2 as new approaches in generating solid acid catalyst for upgrading bio-oil through esterification reaction. Although the bio-oil conversion was not as much as using the solid acid from SiO_2 Degussa A-380, silica gel and highly dispersed SiO_2 are considerable since they are more available and easier to purchase compared to SiO_2 Degussa A-380. The silica gel purchased in this project is also very cheap compared to any other solid acid catalyst materials, costing only RM 30.57 per 500 gr of amount. This is highly beneficial since the same amount of other solid acid materials can cost above RM 300.

In terms of bio-oil conversion, Table 4.8 showed that the conversion achieved by using the solid base catalyst in this project is 28.6%. Comparing with the previous project which achieved 23.7% of conversion by using the same catalyst, this project has succesfully increased the conversion by 4.9%.

In terms of equilibrium time, the time needed to reach the equilibrium conversion by using the solid acid generated by silica gel and solid base catalysts in this project is both 40 minutes. This is significantly lower than those achieved in the previous project which is 80 and above 100 minutes for conversion using solid acid and solid base catalyst respectively. Although the equilibrium time reached by using the solid acid catalyst generated by highly dispersed SiO_2 in this project is slightly lower which is 60 minutes, it is also still faster than the previous project. Thus, it can be concluded that this project gives faster reaction rate in achieving the equilibrium conversions.

Another case study analyzed in this project is about the properties of the upgraded bio-oil. The results from the characterization are compared with the properties of standard biodiesel. The information on density, viscosity and acidity of standard biodiesel can be all obtained based on IS 15607 standard. The summary is shown in Table 4.9 below.

Table 4.11: Comparison of upgraded bio-oil properties with standard biodiesel

Properties	**Bio-oil from this project**			**Standard biodiesel (IS 15607)**
	Upgraded without catalyst	**Upgraded by solid acid**	**Upgraded by solid base**	
Density (gr/cm^3)	0.836	0.833	0.8508	0.86 – 0.9
pH	3.013	1.045	5.819	Not mentioned
Viscosity (mm^2/s)	5.250	4.174	5.34	2.5 - 6

Based on the table above, it is concluded that the properties of upgraded bio-oil is similar to standard biodiesel. The density of upgraded bio-oil is 0.836, 0.833 and 0.8508 gr/cm^3 by solid acid, solid base and no catalyst respectively. Although these values do not reach the minimum of 0.86 gr/cm^3, the errors are below 5%. As for the viscosity, the values are all between 2.5 and 6 mm^2/s. This the standard required viscosity for biodiesel.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

Both solid acid and solid base catalysts successfully converted the bio-oil into esters through esterfication experiment. For generating solid acid catalyst, **silica gel and highly dispersed SiO_2 can be used as new approaches.** These materials are highly available, easy to purchase and low cost.

The solid acid catalyst generated by highly dispersed SiO_2 converted the bio-oil the most whereas the conversion rose to 57.14%. The solid acid catalyst generated by silica gel rose the bio-oil conversion to 42.86%. Meanwhile, the solid base catalyst exhibited better activity than no catalyst, reaching 28.6% of conversion. Comparing with the previous project which used the same catalyst, this project has succesfully increased the conversion of upgraded bio-oil using solid base catalyst by 4.9%.

This project gives a fast reaction rate in achieving the equilibrium conversions. The time needed to reach the equilibrium conversion by using the solid acid generated by silica gel and solid base catalysts in this project is both 40 minutes while the equilibrium time reached by using the solid acid catalyst generated by highly dispersed SiO_2 is 60 minutes.

The characteristics of upgraded bio-oil in this project are improved to standard biodiesel properties. Based on the characterization results, the upgraded bio-oil with solid base catalyst has the highest density and dynamic viscosity while the upgraded bio-oil with solid acid catalyst has the highest acidity. All the values measured are within the limit of standard biodiesel properties except for the density values which has errors of less than 5%.

For recommendation, it is encouraged to study other parameters of the upgraded bio-oil such as ester content, water content and flash point. This can be done through Gas Chromatography – Mass Spectrometry analysis, Karl Fischer titration and flash point tester respectively. It is also recommended to carry out the esterification reaction by using SiO_2 sol Degussa A-380 in generating the solid acid catalyst so that the bio-oil conversion can be improved further.

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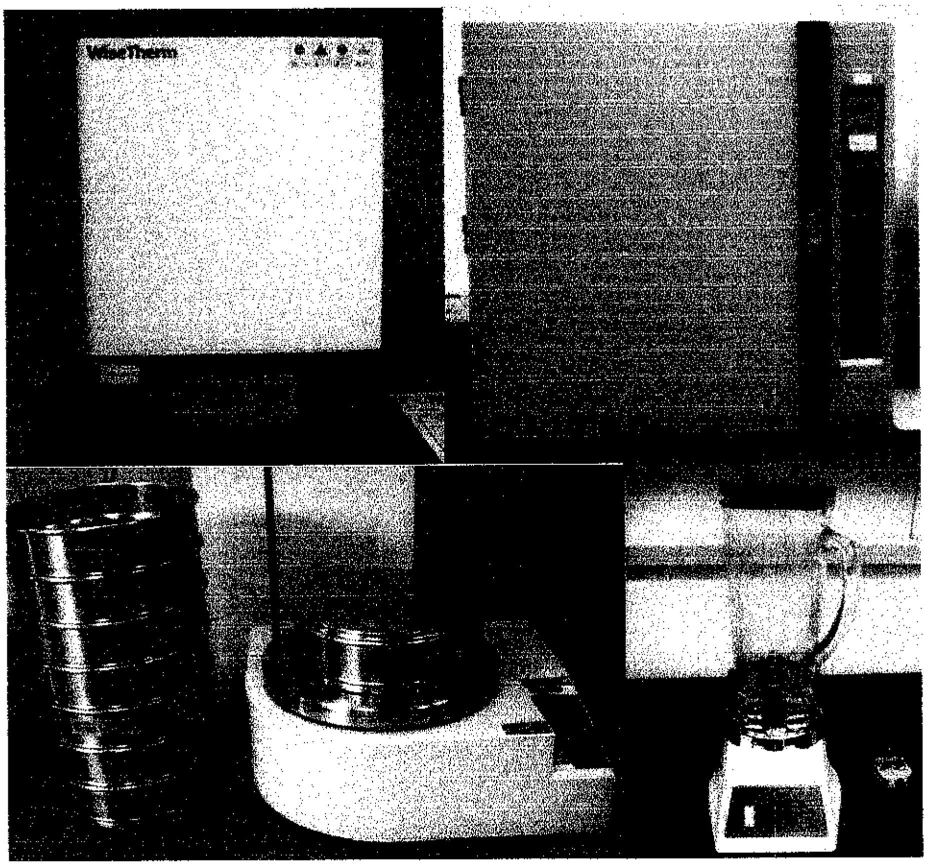
APPENDIX 1

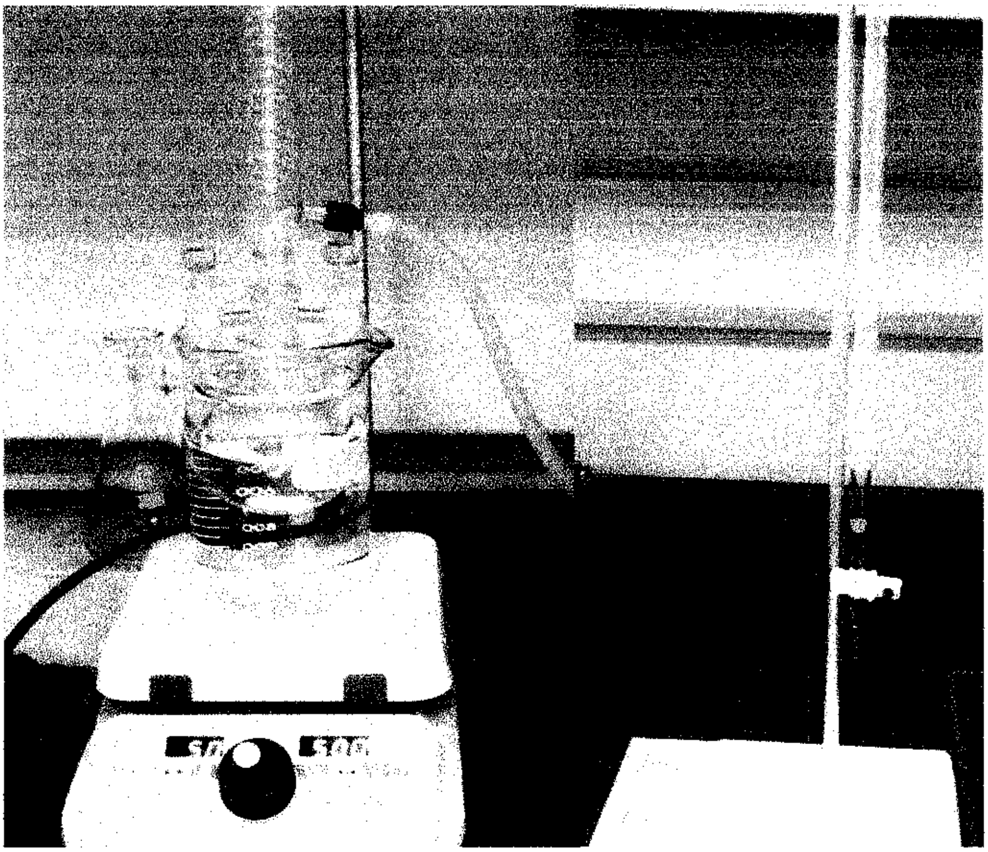
Heating and Grinding Equipments



(a) Chamber furnace; (b) Oven; (c) Sieve shaker;
(d) Mixer

APPENDIX 2

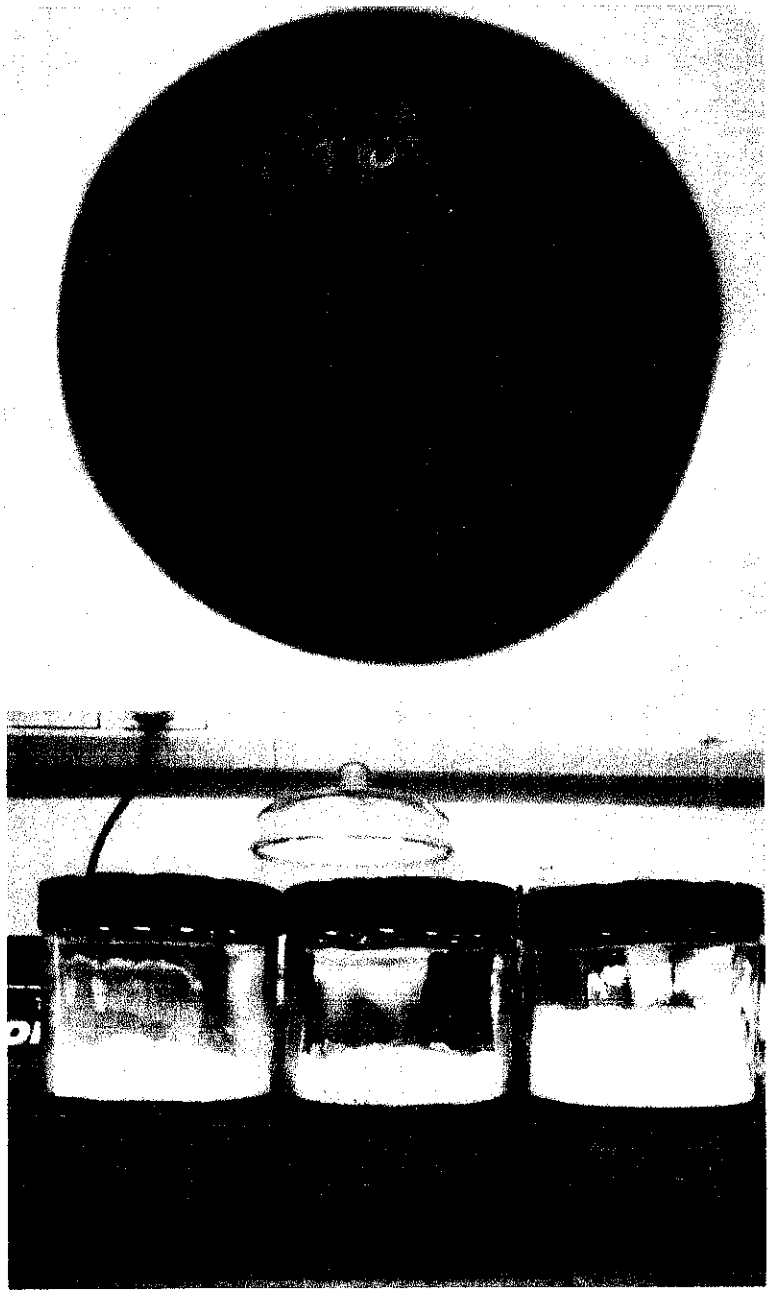
Esterification and Titration Apparatus



(a) Three-neck flask equipped with reflux condenser and magnetic stirrer; (b) Burette

APPENDIX 3

Catalyst Material and Products



(a) Silica gel (general purpose grade); (b) Solid acid and solid base catalysts