PREPARATION OF SOLID ACID CATALYST FROM RICE HUSK AND INVESTIGATION OF ITS CATALYTIC PERFORMANCE IN ESTERIFICATION

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This is to certify that the thesis prepared by Abel Aklilu, entitled: Preparation of solid acid catalyst from rice husk and investigation of its catalytic performance in esterification and submitted in partial fulfillment of the requirements for the degree of Master of Sciences (Process Engineering) complies with the regulations of the University and meets the accepted standard with respect to originality and quality.

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DECLARATION

I declare that this thesis entitled "*Preparation of solid acid catalyst from rice husk and investigation of its catalytic performance in esterification* "has not been submitted in any form for another degree, diploma or an award at any university or other institution of the tertiary education. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature and discussions. Information taken from published and unpublished work of others has been acknowledged in the text and a list of references is given. The work was under the guidance of Professor Belay Woldeyes, instructor of AAiT in Addis Ababa University, School of Chemical and Bio Engineering.

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ABSTRACT

The fundamental reaction in organic synthesis is esterification of carboxylic acid and alcohol which can produce high value of material in the areas of cosmetics, plastics, food, medicines, intermediates, etc. Furthermore, this reaction is used in the pretreatment step for biodiesel production from low cost, lower quality feedstocks (with high free fatty acid content) to improve the economics of production. The cost of utilization of virgin oil (higher feedstock with lower FFA content) as a raw material for biodiesel production constitutes 70% of the total biodiesel production cost. Homogeneous acid catalysts, such as sulfuric acid and phosphoric acid, are conventional catalysts for esterification. However, the uses of these homogeneous acid catalysts are limited in a practical application due to corrosion, environmental pollution, side reactions and a more tedious separation process. Alternatively, a number of prospective heterogeneous acid catalysts, which are easily separated from the reactants and products through suction filtration, get attractive routes for biodiesel production and could eliminate the problems mentioned above. A sulfonated carbon-based solid acid catalyst was prepared by sulfonating rice husk char with concentrated sulphuric acid and the catalytic activity was validated through the esterification of oleic acid with ethanol for biodiesel production. Characterization methods of X-ray diffraction (XRD),Fourier transform infrared spectroscopy(FT-IR), thermogravimetry analysis and acid density tests was carried out to reveal the physical and chemical characteristics of the prepared catalyst. The effects of catalyst preparation conditions and esterification reaction conditions on the performance of the catalyst were investigated using the esterification of oleic acid and ethanol as the probe reaction. The results showed that 450^0C and 110^0C were suitable carbonization and sulfonation temperatures respectively. The catalyst prepared at these conditions exhibited high catalytic performance and 98% conversion of oleic acid was obtained under the optimal reaction conditions with a catalyst loading of 5.73%, ethanol to oleic acid molar ratio of 10.6:1, and a reaction time of 2.65 hr. The conversion still reached 94.89% after five cycles of successive reuse, which indicated that the catalyst stability was excellent. These results clearly show that the rice husk-derived catalyst is promising, economic and eco-friendly for biodiesel production from low-cost feedstocks and potentially substituted for homogeneous sulfuric acid catalyst for esterification in industries in the near future.

Key words: *Esterification, solid acid catalyst, rice husk, biodiesel*

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Acronyms

ANOVA	Analysis of variance
ASTM	American Society for Testing and Material
AV	Acid value
CO_2	Carbon dioxide gas
DEM	diethylmalonate
ER	Eley-Rideal
FAAEs	fatty acid alkyl esters
FAME	fatty acid methyl ester
FFA	Free fatty acid
FT-IR	Fourier-transform infrared spectroscopy
H^+	Hydrogen ion
HPAs	Heteropoly acids
KBr	Potassium bromide
KZ	Potassium zirconia
LH	Langmuire Hinshelwood
NOx	Nitrogen oxides
PET	Poly ethylene
RSM	Response surface methodology
SNNPR	South nations and nationalities people region
SZ	Sulfated zirconia
TCD	Thermal conductivity detector
TG	Triglycerides
TiZ	Titania zirconia
UCO	Used cooking oil
WCO	Waste cooking oil
WZ	Tungstated zirconia
XRD	X-ray diffraction

CHAPTER 1 INTRODUCTION

1.1 Background

Usage of the renewable energy, such as biodiesel, has received extensive attentions worldwide in recent years with depletion of the fossil fuel and deterioration of the environmental conditions. Biodiesel is renewable, biodegradable and environmental benign, which brings about a series of economic, environmental and social advantages [1]. It can be blended with petroleum diesel to arbitrary proportion or used directly for the similar viscosity and solidification point. Biodiesel is mainly composed of less viscous fatty alkyl methyl esters (FAMEs) and commonly obtained by transesterification of triglycerides (high-quality oils, such as vegetable oils of soybean oil, and sunflower oil) with short-chain alcohol (methanol or ethanol) catalyzed by sodium hydroxide, sodium methoxide or Calcium Oxide[2]. However, in the primary stage, the main restricting factor for biodiesel commercialization is raw material cost. Some low-cost and low-quality feedstock, including waste cooking oils (WCOs) and animal fats also can be used, where large amounts of free fatty acids (FFAs) in the low-quality feedstock usually result in base catalysts surface deactivation arising from the saponification reaction. So, conversion of FFAs into FAMEs or FAEEs through esterification is an obligatory pre-treatment process before transesterification [3].

Traditionally, concentrated sulfuric acid used for acid value reduction could perform excellent catalytic activity. Nevertheless, the drawbacks of equipment corrosion, environmental pollution and difficult recyclability caused by this homogeneous acid catalyst are prerequisite to be overcome. Alternatively, a number of prospective heterogeneous acid catalysts, which are easily separated from the reactants and products through suction filtration, get attractive routes for biodiesel production and could eliminate the problems mentioned above. Several types of heterogeneous acid catalysts have been reported, such as heteropolyacids, zeolite, anion exchange resin, and zirconium oxide but they are generally subjected to one or more problems of low acid density, bad operational stability, expensive preparation cost and deactivation under rigorous conditions [4].

The economics of biodiesel production are strongly linked to the feedstock cost, catalyst cost, and wastewater treatment[4]. The raw material cost of the feedstock (e.g., soybean oil) for biodiesel production is significantly more than that of petroleum based diesel and represents the largest fraction of the cost for biodiesel production [4]. Thus, the high cost of refined vegetable oil, the inability to recover/reuse the catalysts, and waste formation due to use of homogeneous catalysts (e.g., H_2SO_4 and KOH) are all barriers to biodiesel commercialization.

Reusable solid acid catalysts would eliminate these barriers by allowing biodiesel production from low-quality feedstocks high in free fatty acids (FFAs), reducing catalyst cost, and eliminating the need for costly treatment of high and low pH streams. Solid acid catalysts could be used to esterify FFAs in inexpensive sources of triglycerides, such as yellow or brown grease, rendered fat, and soap stock, followed by base catalysis to transesterify the glycerides.

This awareness has resulted in research on the synthesis and testing of heterogeneous acid catalysts for esterification. There have been recent reports on the generation of solid acid catalysts. Anion exchange resins (e.g., Polystyrene sulfonic acid) have been used to esterify FFAs with a range of alcohols, yet are expensive and potentially unstable at high pH [5]. Perfluorinated alkanes supported on silicon oxides catalyze esterification [6], but again are expensive, environmentally unfriendly, unstable at high pH, and are generated from non-renewable carbon sources. Hetero poly acids impregnated or attached onto zirconia have also been developed but this support material (i.e., zirconia) is very expensive [7].

An option that has great possibility, but which has not been fully explored is the generation of acid catalysts supported on carbon for catalysis. Carbon supported catalysts have several distinct advantages over alumina or silica supported systems; they are stable under acidic basic conditions, can have very high surface area [200–1500 m^2/g], renewable biomass sources can be used to generate the carbon, and the non-polar nature of the support matrix

may reduce adsorption of polar molecules (e.g., water or glycerol) that can deactivate the catalyst.

On the other hand, methanol is commonly used in esterification and transesterification for the low price, short carbon chain and strong polarity. However, methanol is primarily generated through the pressurized catalytic hydrogenation of carbon monoxide and is toxic. On the contrary, ethanol is obtained from agricultural products and is renewable and environmentally acceptable [8]. Moreover, ethanol has much superior intersolubility with oils than methanol and mass transfer limitation between reagents is thus abated to prompt the esterification or transesterification process. At the same time, ethyl esters present higher cetane number and calorific value, and better cold properties such as cold filter plugging point, cloud point and pour point than methyl esters [9]. Due to these advantages, ethanol has recently been paid more attention for biodiesel production and it has been used in the research.

According to Nandiwale and Bokade [44], the esterification of long chain carboxylic acids such as oleic acid can represent well the biodiesel production process, because this compound is present in most of oil crops (jatropha curcas, soybean, sunflower, rapeseed, palm, etc). Therefore, in the present study, oleic acid was preferred as a model compound for evaluating the effectiveness of the prepared catalyst in esterification reaction as it is the most common FFA found in plant oil and extensively exists in the low-cost biodiesel feedstock.

1.2 Statement of the Problem

Biodiesel is a key player in the renewable energy sector for the 21st century. Increasing attentions have been devoted to the biodiesel production, as it is a promising alternative fuel to cope with global warming, environmental pollution and depletion of fossil resources. Biodiesel is a fuel comprised of monoalkyl esters of long-chain fatty acids derived from renewable feedstocks, such as plant oils, waste oil or animal fats. The high oxygen content, aromatic-free, and sulfur-free nature of biodiesel render it much cleaner burning which dramatically reduces the emissions of environmentally detrimental species than fossil fuels.

However, biodiesel is not economically competitive with petroleum-based diesel fuel at the present stage. Without government support through tax, biodiesel has nearly double price of traditional diesel. One significant cause of the high price of biodiesel is attributed to the expensive cost of feedstock, which comprises about 70% of the production cost in commercial biodiesel production[10]. Usage of the low-cost feed stocks such as waste cooking oils and inedible oils thus appears. Reported catalysts for the production of biodiesel have included homogeneous strong bases such as alkali metal hydroxides and alkoxides, homogeneous acids such as sulfuric acid and enzymes such as lipases. However, the cheap feedstock (such as waste oil or grease) generally have high levels of free fatty acid (FFA) which will react with the alkaline catalysts to form soap that eventually emulsify the oil. The soap formation process will lower the yield of esters and make the separation of esters difficult. Therefore, a pretreatment step is essentially required by converting FFAs to esters.

On the other hand, although the lipases are generally effective and non-polluting, they are usually expensive and there are problems associated with both FFAs and short chain alcohols (such as methanol and ethanol), which denature the lipase to some extent as well as substantially decreasing the operational stability of the enzyme. Compared to basic catalysts, acid catalysts are not affected by FFAs in the raw materials, especially sulfuric acid, which is used to catalyze the esterification reaction because its acid strength is responsible for the release of more H^+ species to protonate the carboxylic moiety of the fatty acid [11]. Nevertheless, traditional homogeneous acid catalysts are depressed by some drawbacks such as undesirable side reactions, corrosion of equipment, and a great deal of waste water for purification, which arguably contribute to environmental pollution. Therefore, heterogeneous acid catalysts, gaining the advantages of recovered and reused characteristic and environmental benign property, have been investigated as substitutes for homogeneous acid catalysts.

Recently there has been renewed interest in the synthesis of solid acid and base catalysts for producing biodiesel – primarily driven by the need to find environmentally benign catalysts to replace waste generating homogeneous acids and bases [12]. The renewed research

appears to be driven by a need to replace sulfuric acid and sodium methoxide in the production of biodiesel from free fatty acids (FFAs) and triglycerides.

In the production of biodiesel, the use of acids and bases as unrecoverable catalysts generate large volumes of waste that must be treated, significantly adding to costs and the environmental impact of production. The use of these catalysts requires energy-inefficient processes for separation, recycling, and treatment of the spent acids. Neutralization of the homogeneous acids produces sulfate wastes, and thus, the acids do not fulfill the general requirement of a catalyst as a reusable material that can repeatedly accelerate a chemical reaction. By this method, more than 15 million tons of H_2SO_4, for example, are consumed as an unrecyclable catalyst each year[13]. A green approach to chemical processes has stimulated the use of recyclable strong solid acids as replacements for such unrecyclable liquid acid catalysts. Therefore, the development of solid acid catalysts, which have recently gained much attention in view of their ease of separation and lack of corrosion or toxicity problems, is a desirable goal.

1.3 Objectives

1.3.1General Objective

The general objective of this research is to synthesize a solid acid catalyst based on rice husk and investigate its performance for esterification reaction.

1.3.2 Specific Objectives

The specific objectives of this research are:

- To prepare a rice husk supported solid acid catalyst for biodiesel production using different catalyst preparation conditions.
- To characterize the physico-chemical, surface functional group and crystalline properties of prepared catalyst.
- To determine the optimum catalyst preparation conditions(carbonization temperature and sulfonation temperature) for obtaining the maximum catalytic performance

- To investigate the performance of the rice husk based catalyst in terms of conversion of FFA to biodiesel and find out the optimum reaction conditions using response surface methodology.
- To investigate the stability of rice husk based catalyst

1.4 Significance of the Study

The fundamental reaction in organic synthesis is esterification of carboxylic acid and alcohol which can produce high value of material in the areas of cosmetics, plastics, food, medicines, intermediates, etc. Furthermore, this reaction is used in the pretreatment step for biodiesel production from low cost, lower quality feedstocks (with high free fatty acid content) to improve the economics of production. The cost of utilization of virgin oil (higher feedstock with lower FFA content) as a raw material for biodiesel production constitutes 70% of the total biodiesel production cost [14]. Homogeneous acid catalysts, such as sulfuric acid, p-toluene sulfonic acid and phosphoric acid, are conventional catalysts for esterification.

However, the uses of these homogeneous acid catalysts are limited in a practical application due to corrosion, environmental pollution, side reactions and a more tedious separation process, less likely catalyst recovery, sensitivity to water and so on. Enzyme catalysts, such as lipases which remain active even under unfavorable conditions, have been employed to catalyze esterification [15]. Nevertheless, it should be emphasized that use of enzymatic esterification is mainly limited by the high cost of the lipases. Besides that, the issues of the lipase stability, selectivity, mass transfer and other factors limited practical application in the esterification process.

Because of environmental concerns and need for sustainable development, heterogeneous acid catalyst for esterification have been proposed during the past few years. Sulfonated carbon-based catalysts have been proposed as low cost renewable “green catalysts” able to be prepared from either biomass or from household waste. Therefore, the use of solid catalysts in esterification reactions is very important in developing cleaner and economically improved processes for a wide variety of fine chemicals.

The significance of this research could be seen with regard to environment protection, natural resource utilization and the economy. With regard to the environment protection, it solves the problem of corrosion of equipment, environmental pollution and difficult recyclability caused by the use of homogeneous acid catalyst. Moreover, usage of heterogeneous catalysts avoid the environmental burden of treatment of large volumes of waste that result with the use of homogeneous catalysts. Although sulfuric acid is used during the preparation of the rice husk based catalyst, the catalyst itself is relatively non-toxic and can be re-used many times. It therefore represents a greener solution to biodiesel production than concentrated sulfuric acid.

With regard to economy, the high cost of feedstock which has been the bottleneck for commercialization of biodiesel will be resolved with the possible utilization of low quality feedstocks such as waste cooking oil, animal fats with high amount of FFA for biodiesel production.

The other significance of the research is with regard to natural resource utilization. The backbone of Ethiopia's economy has been the agriculture over the past decades. The government of Ethiopia is planning to change this agriculture based economy to industry led economy. In doing so, the agriculture will play a dominant role as a source of valuable raw materials. Very important products could be generated from agricultural byproducts and residues such as rice husk in this case. This research will be beneficial with regard to utilization of Ethiopian natural resources in that a novel carbon solid acid catalyst has been prepared from rice husk.

1.5 Scope of the study

This thesis work covers the synthesis of a sulfonated heterogeneous catalyst from rice husk and structural characterization of the prepared catalyst. The performance of the prepared catalyst was evaluated with the esterification reaction between oleic acid and ethanol. The detailed reaction kinetics study and development of kinetic model for the esterification catalyzed by the prepared catalyst has not been included.

CHAPTER 2 LITERATURE REVIEW

2.1 Current problem and recent research results

Biodiesel, a type of green fuel, has the advantages of a low sulfur content, being non-toxic and biodegradable, lack of aromatics, excellent lubricity, a high flash point, and a high cetane value. The most widely used industrial method for the commercial production of biodiesel is the transesterification process, in which a triglyceride, the main ingredient of vegetable oils or fats, undergoes an alcoholysis reaction with a lower alcohol and produces the corresponding fatty acid ester,i.e.,biodiesel. The major obstacle to the development of the biodiesel industry is the high cost of feedstock, which accounts for 70%-95% of the total cost according to some statistics. The use of low-priced feedstocks such as waste cooking oil, inedible oils, animal fats, and soapstock is the key to achieving industrialization and commercialization of biodiesel.

However, these feedstocks usually contain considerable amounts of free fatty acids, which adversely affect the transesterification process (for which an acid value of 1.5 mg KOH/g of feedstock is favorable), and must be converted to their corresponding esters through pre-esterification. This process is generally catalyzed using concentrated sulfuric acid, but sulfuric acid is difficult to recycle, causes serious corrosion problems, and leads to discharge of large amounts of effluents.

Recently, among the heterogeneous acid catalysts, the carbon based ones have attracted abundant attentions for their low preparation cost, high catalytic activity and pollution-free, etc. These catalysts, which possess polycyclic aromatic carbon sheets in amorphous carbon structure with large amounts of $-SO_3H$ groups, can be simply prepared by partial carbonization and then sulfonated with concentrated sulfuric acid or fuming SO_3. Zong et al [16] prepared the carbon-based heterogeneous acid catalyst from D-glucose, which showed strong catalytic activity for biodiesel production from high fatty acids. Rao et al. [17] synthesized a carbon-based acid catalyst by sulfonation of the partially carbonized de oiled canola meal and this catalyst possessed enough acidic sites of $-SO_3H$ groups to guarantee the excellent catalytic activity in esterification, where conversion of 93.8% was achieved after 24 h at 65 ^{0}C using 1:60 molar ratio of FFAs to methanol and 7.5 wt.% catalyst dosage.

Further, carbon-based materials, such as glycerol, PET-derived activated carbon and bagasse are applied for the heterogeneous acid catalyst preparation. Carbon-based solid acid is ideal for esterification reactions owing to such advantages as chemical inertness, mechanical stability, structural diversity and surface hydrophobicity. Carbon materials are relatively cheap and widely available. After easily functionalized with -SO_3H groups, the derived carbon-based heterogeneous acids have been reported as the promising esterification catalysts for biodiesel production. Hara et al. [18] prepared the carbon-based heterogeneous acid catalysts from naphthalene through the in situ partial carbonization and sulfonation method. However, their activity was drastically weakened for the aromatic molecules leaching during liquid-phase reactions.

To overcome this drawback, Toda et al. [19] obtained the carbon-based heterogeneous acid catalysts through sulfonation of incompletely carbonized D-glucose to consolidate the physicochemical interaction of the carbon structure and the sulfonic acid group and the achieved catalyst exhibited high acidic active sites density and strong catalytic stability in esterification. Additionally, Malins et al. [20] synthesized the 4-sulfophenyl activated carbon based solid acid catalyst using diazonium salt and obtained a similar catalytic performance for biodiesel production with Amberlyst-15. Subsequently, biomass resources, such as wood, oilseed cake, oil palm trunk and sugarcane bagasse, have been taken as the carbon precursors for the carbon-based heterogeneous acid catalysts preparation.

Recently, a carbon-based solid acid catalyst prepared from saccharides and biomasses by incomplete carbonization followed by sulfonation has attracted much attention from numerous researchers because of its low preparation costs and high catalytic activity. Toda's group[21] studied the esterification of acetic acid and oleic acid catalyzed by solid acid catalysts prepared by sulfonation of incompletely carbonized glucose and sucrose. The results showed that the catalytic activity in the esterification of acetic acid and oleic acid with ethanol was 1/7 and ½, respectively, compared with that of concentrated sulfuric acid, but it was superior to that of niobic acid.

Chen et al.[22] prepared a solid acid catalyst from a glucose-starch mixture and used it to catalyze the esterification of oleic acid and methanol. The results showed that the conversion of oleic acid was 96% using a methanol to oleic acid molar ratio of 10: 1 and a reaction temperature of 80^0C for 6 h. Lou et al.[23] prepared four kinds of solid acid catalysts from glucose,sucrose,starch and cellulose and explored their esterification and transesterification activity. The starch-derived catalyst showed the highest activity, rivaling that of concentrated sulfuric acid. Kastner et al.[24] synthesized solid acid catalysts by sulfonating biochar from peanut hull and wood chip pyrolysis processes. The catalysts displayed good catalytic performance for esterification of palmitic acid and stearic acid, and the conversion of palmitic acid approached nearly 100%. In a similar manner, Zhu et al[48] prepared a solid acid catalyst from rice husk char and 98.7% conversion of oleic acid was obtained under optimal reaction conditions using esterification reaction between oleic acid and methanol as a probe reaction.

2.2 Present research with regard to the current problem

Liquid acids such as sulfuric acid, phosphoric acid and hydrofluoric acid are the most widely used acid catalysts in chemical industry over the past decades. However, the usage of these homogeneous acids cause lots of serious problems such as hazards in transportation, difficulties in separation, waste acid pollution and equipment corruption. The development of environmentally friendly chemical processes has boosted the use of solid acid catalyst due to its convenience in separation and recyclability. Up to now, significant attention has been given to the solid acids such as silica-alumina, zeolites and sulfated metal oxides. But the catalytic activity and acidic strength of these acids are still lower than those of homogeneous acids. These disadvantages greatly limited their application in industrial process.

Recently, some carbon-based solid acids prepared from naphthalene or natural products such as sugar were studied by many researchers. As environmentally benign catalysts, the carbon-based solid acids show excellent efficiency on the biodiesel production and other esterification reactions. But unfortunately, the structure, acid type and strength of the acid sites on the carbon-based solid acids are still poorly understood. Thus, the acid properties of the solid acid are necessary to be investigated in detail for further industrial application. As

an agricultural byproduct with low cost and sufficient supply, rice husk is an excellent source for preparing solid acid catalyst of high quality.

Rice husks(or rice hulls) are the hard protecting coverings of grains of rice. The husk protects the seed during the growing season, since it is formed from hard materials including opaline silica and lignin, the hull is mostly indigestible to humans. Winnowing, used to separate the rice from hulls, is to put the whole rice into a pan and throw it into the air while the wind blows. The light hulls are blown away while the heavy rice fall back into the pan.

In Ethiopia, rice is among the target commodities that have received due emphasis in promotion of agricultural production, and as such it is considered as the "millennium crop" expected to contribute to ensuring food security in the country. Rice could suitably grow in many parts of the country. The predominant potential areas are:- West central highlands of Amhara Region (Fogera, Gonder Zuria,Dembia,Takusa,Wereta and Achefer); North West low land areas of Amhara and Benshangul Regions (Jawi, Pawi, Metema and Dangur);Gameblla regional state (Abobo and Etang Woredas); South and South West Lowlands of SNNPR (Beralee, Weyito, Omorate Gura Ferdaand Menit); Somali Region (Gode); South Western Highlands of Oromia Region (Illuababora, East and West Wellega and Jimma Zones)[25].

Every year huge amount of rice husk is produced in Ethiopia. So far, such a resource is mainly considered as a waste, and consequently burnt without any profit, except in a few cases of domestic uses for cooking and heating. In this work, a solid acid catalyst was prepared from rice husk and its catalytic activity was evaluated using esterification reaction of oleic acid and ethanol as a probe reaction. The stability of the as-prepared catalyst was also investigated to further evaluate the catalyst. The rice husk which has been used in this research was obtained from Wereta area and is shown the following figure.

Figure 2.1: Rice husk obtained from Wereta

2.3 Heterogeneous catalysis in biodiesel production

Today's commercial production of biodiesel is based on homogeneous catalysts. The cost of biodiesel production is still high, i.e. 1.5-3 times more expensive than petroleum based diesel. Two main factors that contribute to the cost of production are the cost of feedstock and the cost of processing. The cost of feedstock in the form of virgin vegetable oils is significantly higher 70-95% of the total cost of the biodiesel production [26]. The use of non-edible and waste cooking oils can lower the feedstock cost by 2-3 times. Experiences obtained from different industrial processes show that heterogeneous catalysts have proved to be cost effective and render convenient production process as an eco-friendly method. The use of heterogeneous catalysts for biodiesel production from different feedstock has been studied by many researchers. Many of these findings showed promising results for performance of heterogeneous catalysts in biodiesel production compared with homogenous catalysts.

Heterogeneous catalysts are relatively tolerant to high FFA and water content. Development of efficient and low cost heterogeneous catalysts for transesterification of low cost vegetable oils can lead to a much lower total production cost of biodiesel. Heterogeneous catalysts can be grouped as basic, acidic or biological (enzymatic) types. Selection of a catalyst from these groups depends on the type of feedstock, operating conditions, required catalyst activity, cost and availability[27]. Solid acids favor both esterification and transesterification reactions simultaneously for biodiesel with high FFA such as non-edible oils. Inorganic heterogeneous catalysts are mainly used because they are cheap and available, stable at high temperatures and pressures, have longer durability, can be tailor-made and implemented in the desired morphology and are easy to regenerate.

The disadvantages of these catalysts are the requirements in some cases harsh reaction conditions (temperature and pressure) and high temperatures for the preparation and modification of the active phases. Commercialization of inorganic heterogeneous catalyst for biodiesel production is still in the early stage. In 2006, a 160,000 tone/year commercial biodiesel plant started up using a heterogeneous catalysis developed by Axens, Institute Franc¸ais du Petrole (IFP) [28]. The plant has two continuous fixed bed reactors with zinc and aluminum oxide catalysts and use various type of vegetable oils. This plant technology is now spreading to different parts of the world such as US, Sweden, Malaysia.

The development of new and cost effective heterogeneous catalyst can further promote the commercialization of biodiesel production from different resources for direct onsite production and consumption. The need for high temperature and pressure reaction conditions for these types of catalysts increases the overall energy input for a biodiesel production process. Power integration using biomass residue from the biodiesel production plant can make biodiesel more carbon free with less energy requirement.

2.3.1 Reaction mechanisms

Understanding the reaction mechanisms and kinetics can help to design a suitable catalyst under the reaction conditions. The production of alkyl esters depends on the type of catalyst used, oil to alcohol ratio, reaction temperature, reaction time and impurities of the vegetable oil [29]. Reaction mechanisms are indispensable information to select and design effective catalytic materials for biodiesel production. The main mechanism of heterogeneous catalysis follows similarly the principle of homogeneous catalysis of either acid or base systems.

The concept of nucleophilic and electrophilic properties of carbonyl group of both triglyceride and alcohol helps to understand esterification and transesterification reaction mechanisms. The important factor in homogeneous base catalyzed reaction is to create nucleophilic alkoxide from the alcohol to attack the electrophilic part of the carbonyl group of the triglycerides. Because of the polarization created by oxygen atoms bonded with the carbon atom, the carbon atom becomes positively polarized and electrophilic. The breakdown of triglyceride requires three steps. The first step is to produce an intermediate tetrahedral from the attack of electrophilic carbon atom by nucleophilic alkoxide and the second step is break down of unstable intermediate tetrahedral to diglyceride ion and fatty acid ester. The last step is the recovery of the catalyst by proton transfer. These three mechanisms are repeated for cleavage of each fatty acid ester and then finally three fatty acid esters and a glycerol are formed. In base catalyzed transesterification, FFA should be kept low in order to avoid the formation of soap.

In homogenous acid catalysis, the carbonyl group in triglycerides is protonated by the acid catalyst and the alcohol attacks the protonated carbon to create a tetrahedral intermediate. The unstable tetrahedral intermediate cleaves the fatty acid alkyl group from the diglycerides. Like base catalyzed transesterification, acid transesterification reaction has three consecutive, reversible reactions. Unlike base catalysis, the carbon atom of the carbonyl group of the triglyceride becomes more electrophilic by the catalyst and more susceptible to be attacked by alcohol. This process is slower than the base mechanism. This

key difference in the reaction mechanism has made the two different homogenous catalyzes to be discernible and to proceed through different reaction rates.

Both acidic and basic reactions can be promoted either on Brønsted or Lewis catalyst sites. The mechanism of transesterification reaction of liquid phase methyl salicylate and phenol on acidic sites of ZrO_2 (Z), SO_4^{-2}/ZrO_2 (SZ) and Mo(VI)/ZrO_2 (MZ) solid acid catalysts was studied [30]. Heterogeneous esterification reaction mechanism of gas phase acetic acid via single Brønsted acid sites on silica-supported Nafion (SAC-13) solid acid catalyst was discussed[31].Like homogeneous catalysis, acidic and basic characteristics of heterogeneous catalysis are important properties for transesterification of triglycerides. Unlike homogeneous systems, in heterogeneous catalysis adsorption of reactants and desorption of products has to take place on the surface of the solid catalyst for the reaction to proceed at a faster rate.

In solid acid catalysts, triglyceride is adsorbed on the surface of the catalyst by protonation of the carbon in carbonyl group which is to be attacked by alcohol in the liquid phase. This mechanism can be based on Brønsted or/and Lewis solid acids. But the literature fails to give clear mechanism on how the reaction takes place on the surface of the catalyst materials or particles. Two hypotheses have been proposed for solid acid catalyzed transesterification and esterification reaction mechanisms: a single site (Eley-Rideal (ER) type) or dual-site mechanisms (Langmuire Hinshelwood (LH) model). In the single site reaction mechanism, the carboxyl of triglyceride is adsorbed to the catalyst active site and protonized so that alcohol in the liquid phase attacks it.

The dual-site mechanism is acceptable from the chemical point of view that the two reactants (triglyceride and alcohol) are adsorbed on the catalyst active sites so that the reaction occurs with the adsorbed species. Suwannkarn et al. [32] suggest that the type of reaction mechanism depends on the alcohol used. Though no justification has been given, it was found out that higher carbon alcohol prefers dual-site mechanism where as low carbon alcohols such as methanol prefer single site mechanisms. Low carbon alcohols are usually used in the

synthesis of biodiesel from vegetable oils and therefore, the ER model is the likely model for methanol based transesterification reaction.

ER mechanism based on Brønsted acid site type by protonation of the carbonyl group is shown Figure 2.2a and (ER) mechanism by solid Lewis acid is shown in Figure 2.2b. The mechanism has three main steps: the first is the physicosorption and chemisorption of triglyceride in to the catalyst site. The oxygen atom with the double bond of triglyceride interacts with the catalyst site due to electrophilic property. The intermediate association creates electrophilic carbon in the carboxyl of the triglyceride. The second step is the attack of the electrophilic carbon by alcohol which creates an intermediate tetrahedral. The final step is the cleavage of the fatty acid ester and diglyceride from the catalyst followed by desorption from the site.

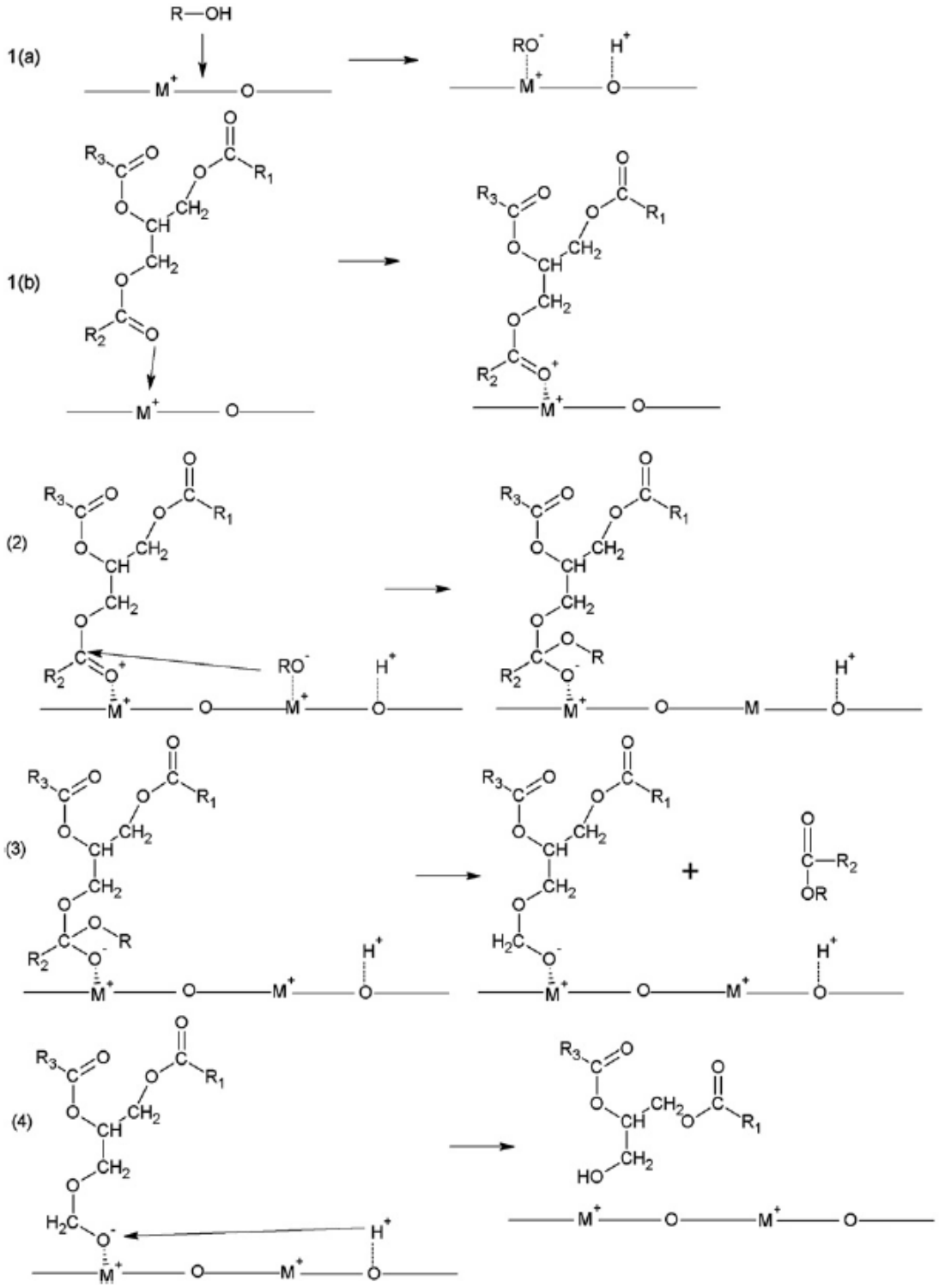


Figure 2.2: Eley-Rideal(ER) mechanism of (a) Bronsted acid and (b) Lewis solid acid catalysts[45]

Stronger Lewis acid doesn't favor product desorption easily which makes the reaction slow. The process is repeated for each fatty acid alky ester production. Like solid acid catalysts, basic solid catalysts can be Brønsted or Lewis base types. The mechanism of both Brønsted and Lewis bases catalysts for the transesterification reaction was reported [33]. The mechanism is based on the ER mechanism where the alcohol is adsorbed on the catalyst site and the alkoxides ion on the surface attacks the positively polarized carbon of triglyceride in the liquid phase.

LH model for the transesterification of ethyl acetate with methanol by magnesium oxide catalyst was studied by Dossin et al[34]. Both reactants are adsorbed on two sites of the catalyst and react. Fig. 2.3 shows how LH model describes the transesterification reaction. The reaction mechanism has four main steps. The first stage 1(a) and 1(b) is the adsorption of both reactants on the catalyst surface. The second step (2) produces a tetrahedral intermediate from the alkoxide group and the protonized carbonyl group. A fatty acid alkyl ester is produced in the third stage (3) and diglyceride is the product of the final stage (4). The ER model lacks a good justification how the second reactant alcohol in acidic solids and triglyceride in the basic solids is inhibited from attaching to the catalyst site.

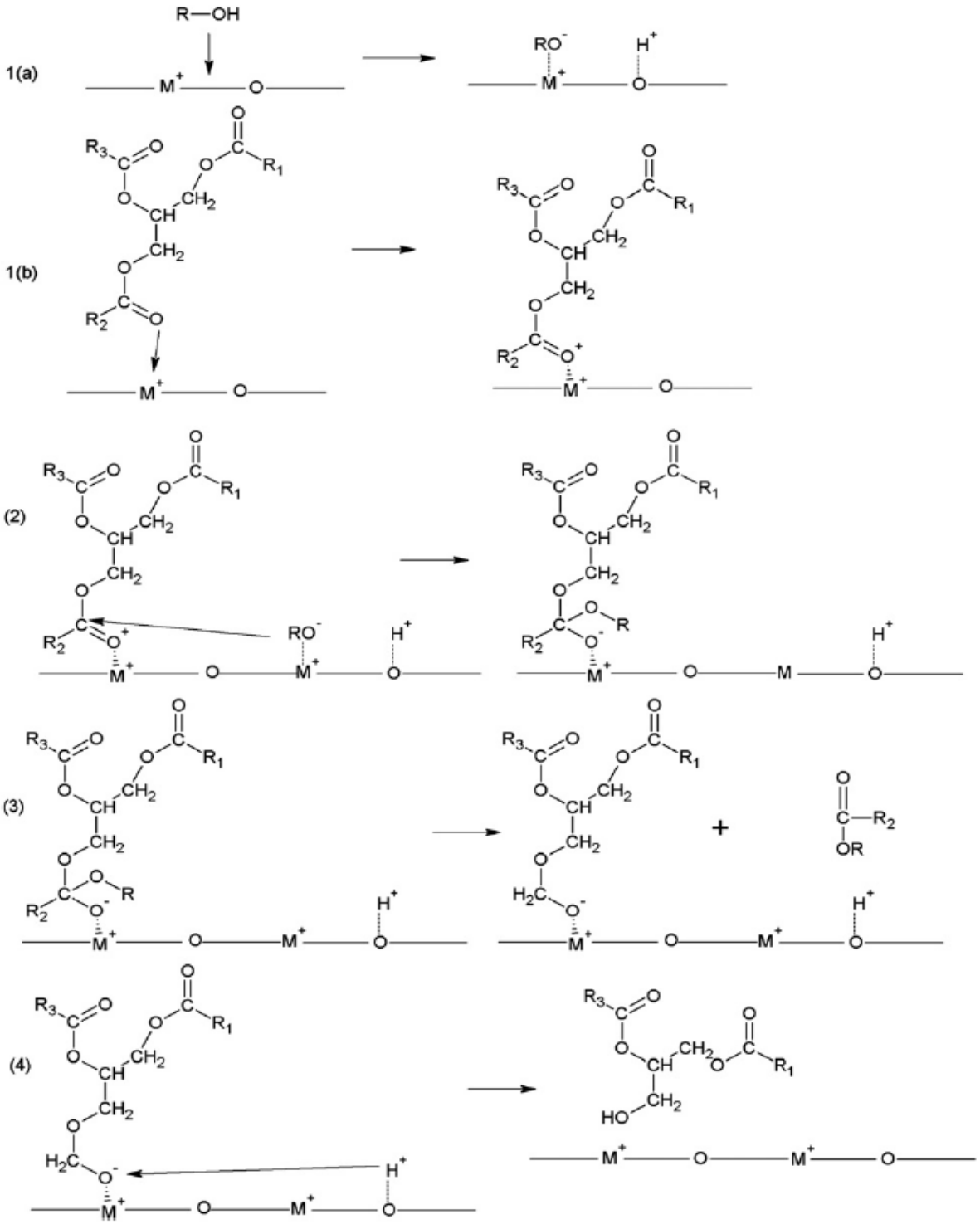


Figure 2.3: Langmuire Hinshelwood(LH) mechanism for transesterification of TG with alcohol[45]

2.3.2 Solid acid catalysts

Solid acid catalysts have been the most common heterogeneous catalysts used in petrochemical industries especially for organic reaction such as Friedele Crafts reactions. Solid acids can be described based on Brønsted or Lewis acidity, the strength and the number of these sites and morphology of the support. Activity and selectivity of the catalyst can depend on how these properties are tuned. Some organic reactions require high Brønsted, Lewis acid or both types of acid sites together. The synthesis of pure Lewis acid is quite difficult due to Brønsted association with Lewis acid-base complications. The size of pore in the catalyst supports is quite important to attain the required selectivity in organic reactions. This is due to the fact that organic molecules are mostly large in size and the pore size is an important issue in the design of highly selective catalyst.

The availability of controlled pore-size mesoporous materials such as silica alumina makes possible for the development of new solid acid catalysts for liquid phase reactions. Solid acid catalysts have advantages in being water and FFA tolerant in transesterification of triglyceride. Moreover, they can perform esterification and transesterification reactions simultaneously. However, solid acid catalysts in transesterification reaction have slow reaction rate and adverse side reactions. In the design of solid acid catalyst for transesterification of vegetable oil, hydrophobic surface has advantages in promoting the adsorption of oily hydrophobic species on the catalyst surface and to avoid deactivation of the catalyst by polar byproducts such as glycerol and water.

a. Zeolites solid acid catalysts

Nowadays, zeolites are becoming the most widely used industrial catalysts because of their inexpensive, environmentally benign processes and generous surface area. Zeolites are built of tetrahedral AlO_4^{-5} and SiO_4^{-4} bonded by Fi oxygen atom and having a general formula of $M_x/n[(AlO_2)_x(SiO_2)y] \cdot zH2O$, where M is an extra-framework cation that balances the anion charge of the framework.

Different type of properties can be tailored by manipulating the structure, silica-aluminum ratio, pore size and density. Extensive variety of acidic, surface properties and morphology

can be synthesized. The use of zeolite acid catalysts in esterification and transesterification reaction of vegetable oil has been studied [35]. The major problem of zeolites in organic reaction is the small pore size that limits diffusion of reactant and products to or out of the catalyst site. The acidic property of zeolites depends on the ratio of silica to aluminum. The lower is the ratio; the higher is the acidity while the opposite holds for basicity.

Most of the acid zeolites showed a low reaction rate that took long reaction time for simultaneous esterification and transesterification. Zeolites with low Si/Al ratio favor higher catalytic activity due to their higher acidity. Apart from catalyst preparation method, the activity of zeolites depends on the polarity, shape and size of the substrate and the reaction conditions. High reaction temperature favors higher activity. The volume of triglyceride molecule is mostly greater than the pore diameters of zeolites which create a diffusion limitation for adsorption of triglyceride to acid sites. Due to comparable lower molecular size of FFA, zeolites showed better activity for esterification than transesterification reaction. Zeolites are also reported to have low number of acid sites at external surface compared to internal surface which results in weak acid strength at external surface where possible catalytic activity takes place for large organic molecule such as triglycerides. This can result in a slow reaction rate.

The design of mesoporous zeolites to avoid the diffusion limitations can open a great opportunity for transesterification of vegetable oils as zeolites can be tailored to high activity for FFA esterification and as water tolerant. Shah et al. [36] were able to synthesize a mesoporous silica SBA-15 molecular sieve with high pore diameter, surface area and pore volume which can accommodate large organic molecules. The catalyst has been tested for transesterification of diethylmalonate (DEM) with butanol with tin impregnated on it. At 100 ^{0}C reaction temperature, 1:3 DEM to alcohol ratio, 16.25 wt.% catalyst loading with DEM and 24 h reaction time a 90% conversion was obtained with 100% selectivity of DEM. The reused activity of the catalyst has been checked and showed very small decrease of the activity.

b. Hetropoly acids

Heteropoly acids (HPAs) are complex proton acids formed from heteropoly anions having metal-oxygen octahedral as a basic unit. Keggin-types are the first used types in the design of a variety of acidic HPAs catalysts. Kozhevnikov and Timofeeva reviewed acid solid catalysis by HPAs and gave details about the catalytic activity of HPAs compared with conventional acidic catalysts in different organic reactions. The general formulas of HPA classes are: $H_{8-x}X^{x}M_{12}{}^{VI}O_{40}$ and $H_{8-x+n}X^{x}M_{12-n}{}^{VI}V_{n}{}^{V}O_{40}$ where X_x = ¼ Si^{IV}, Ge^{IV}, P^{V}, As^{V}; M =Mo^{VI}, W^{VI}. These classes of catalysts have shown very stable thermal properties at high temperatures and good mechanical properties. However, in recent years new HPAs with strong Brønsted acidic sites have been synthesized mainly by substituting X^{x} =Ti^{IV}, Zr^{IV}, Th^{V}.

The activity of HPAs depends on the composition and the type of reaction but more dependent on structure which depends on the type of preparation used. Dawson's structure give the highest activity and the lowest is by Dexter-Silverston's structure while Keggin's structure in between of these two. HPAs are stronger than the usual inorganic acids such as HCl, H_2SO_4 and $HClO_4$. The physicochemical properties of HPAs can be controlled by the structure and composition of the heteropoly anions, extent of hydration, type of support and thermal pretreatment. The acidity doesn't depend much on the composition but on the type of solvent or reactant used.

c. Functionalized oxides

Mixture of oxides from zirconia, silica, alumina, tungsten oxide and tin oxide can produce high surface area and stable functionalized solid acidic catalysts for transesterification and esterification of vegetable oils. Surface treatment of these oxides with acids such as sulfuric and phosphoric acids can also produce functionalized solid acid catalysts. Solid superacids can be prepared from sulfated ion promoted metal oxides such as SO_4^{-2}/ZrO_2 and SO_4^{-2}/TiO_2 and can give high activity toward simultaneous esterification and transesterification of low quality vegetable oils.

Deactivation due to coke formation and leaching were reported to be the main causes for reduced yield during the reuse of the catalysts. Lo`pez et al.[37] reported that the activity of SZ decreased from 61% to 36% after five cycle of esterification reaction while the activity of WZ has decreased from 22% to 13% after equally long cycles. However, the activity of TiZ hasn't been affected by the reuse. The regeneration of catalysts from carbonaceous deactivation was found possible at a temperature >500 ^{0}C. Garcia et al. [38] have tested SZ for transesterification of soybean oil with methanol at a reaction temperature and catalyst calcination temperature of 120 ^{0}C, 650 ^{0}C, respectively with 5 wt.% catalyst loading. A FAME yield of 99.5 % was obtained. However, some solid acid catalysts such as zeolite and Niobic acid have small pores and are not suitable for biodiesel production because of the diffusion limitation of large fatty acid molecule.

2.3.3 Carbon materials for catalysis

Both organic and inorganic carbons play a key role in catalysis. Organic molecules form the huge and very complex discipline of organic chemistry, and they are, in most catalytic applications, the substrates and the products of the process under consideration. In homogeneous catalysis, carbon is often the main constituent of the organic ligands surrounding the metallic center. In enzymatic catalysis it constitutes the backbone of the active species. In heterogeneous catalysis, carbon materials are unique catalyst supports, allowing the anchoring of the active phase, and can also act as catalysts or catalyst poisons (carbon deposits) by themselves.

The physical and chemical properties of carbon materials, such as their tunable porosity and surface chemistry, make them suitable for application in many catalytic processes. Traditionally, carbon materials have been used as supports for catalysts in heterogeneous catalytic processes, although their use as catalysts on their own is becoming more and more common. Although several kinds of carbon materials have been studied, activated carbon (AC) and carbon black (CB) are the most commonly used carbon supports. The typically large surface area and high porosity of activated carbon catalysts favor the dispersion of the active phase over the support and increase its resistance to sintering at high metal loadings. The pore size distribution can be adjusted to suit the requirements of several reactions. The

surface chemistry of carbon catalysts influences their performance as catalysts and catalyst supports. Carbon materials are normally hydrophobic and they usually show a low affinity towards polar solvents, such as water, and a high affinity towards solvents such as acetone.

Although their hydrophobic nature may affect the dispersion of the active phase over the carbon support, the surface chemistry of carbon materials can easily be modified, for example by oxidation, to increase their hydrophilicity and favor ionic exchange. Apart from an easily tailorable porous structure and surface chemistry, carbon materials present other advantages: (i) metals on the support can be easily reduced; (ii) the carbon structure is resistant to acids and bases; (iii) the structure is stable at high temperatures (even above 1023 K under inert atmosphere); (iv) porous carbon catalysts can be prepared in different physical forms, such as granules, cloth, fibers, pellets, *etc*.; (v) the active phase can be easily recovered; and (vi) the cost of conventional carbon supports is usually lower than that of other conventional supports, such as alumina and silica. Nevertheless, carbon supports also present some disadvantages: they can be easily gasified, which makes them difficult to use in high temperature hydrogenation and oxidation reactions, and their reproducibility can be poor, especially activated carbon based catalysts, since different batches of the same material can contain varying ash amounts.

A. Activated carbons

The term activated carbon (also known as activated charcoal) defines a group of materials with highly developed internal surface area and porosity, and hence a large capacity for adsorbing chemicals from gases and liquids. The adsorption on the surface is essentially due to Van der Waals or London dispersion forces. This force is strong over short distances, equal between all carbon atoms and not dependent on external parameters such as pressure or temperature. Thus, adsorbed molecules will be held most strongly where they are surrounded by the most carbon atoms. The area presenting a high density of graphitic basal structural units will favor a high adsorption. High temperature treatment (>1500 K) of AC can favor the adsorption sites by increasing the density of "π-sites" present on partly graphitized structure. Almost all precursors containing a high fixed carbon content can potentially be activated. The most commonly used raw materials are coal, coconut shells,

wood (both soft and hard),peat and petroleum based residues or agricultural residues. Most carbonaceous materials do have a certain degree of porosity and an internal surface area in the range of 10–15 m^2g^{-1}. There are many activation methods to produce an AC that can basically be categorized into two: physical and chemical activation. In the same way, the manufacture of AC involves two main stages, the carbonization of the starting material and the activation of the resulting char. The choice of the activation method is dependent upon the starting material and whether a low or high density, powdered or granular carbon is desired.

b. Carbonization. The first step is a thermal treatment of the raw material that implies dehydration and where most of the non-carbon elements, such as dust and volatile substances, are eliminated by heating the source under anaerobic conditions. The aim of the carbonization stage is to conserve the carbonaceous structure of the material, which is achieved by burning off the material at a range of temperatures from 673 to 1123 K. The char is constituted when carbon atoms regroup themselves into sheets forming rigid and dense clusters of microcrystals, each one consisting of several layers of graphitic planes. Each atom inside one stack is bonded to four adjacent carbon atoms. Thus, the carbon atoms on the edges of the planes have a high adsorption potential available. The internal structure is neither homogeneous nor regular; leaving free interstices that constitute the porosity of the char. These interstices may be filled or blocked by disorganized carbon resulting from deposition and decomposition of tars making them not always accessible and reducing the porosity.

$$C_x(H_2O)_y \longrightarrow C(s) + yH_2O \quad \text{Carbonization}$$

There are three stages in the carbonization process. First of all, is the loss of water in the 373–473 K range. The second stage is the primary pyrolysis, which takes place in the 473 - 773 K temperature range and is characterized by a large generation of gases and tars due to the elimination of volatile matter and tars, causing a remarkable reduction of weight. This also forms the basic structure of the char. The third step is the consolidation of char structure in the range of temperatures from 773 to 1123 K, with a very small weight loss. The small reduction in bulk density with increasing carbonization temperature, coupled with the large reduction in weight (especially in the second stage) implies a contraction of the precursor

material; such contraction continues above 773 K, since the density slightly increases in the third stage temperature range.

C. Physical activation. The objective of the activation process is to enhance the pore structure. The physical activation is the partial gasification of the char with steam, carbon dioxide and air, or a mixture of these, at temperatures around 1073–1473 K (lower for air). Once the non-desirable materials have been removed, the char is accessible. The main change is an increase in pore volume exposing the crystallites to the action of the activating agent (oxidizing gases) for further development of porosity with increasing burn-off. The oxidizing gases employed, steam or CO_2, are reactive agents that react with the raw material and also remove volatile material from the solid. For a given temperature, the reactivity with steam is larger than that with carbon dioxide. Many authors have shown that the most important variables in the gasification process from the point of view of porosity development are: the choice of activating agent, the final burn-off temperature reached, the presence of inorganic impurities that catalyze or inhibit the gasification reaction.

D. Chemical activation. During chemical activation, carbonization and activation are accomplished in a single step by carrying out thermal decomposition of the raw material impregnated with certain chemical agents such as H_3PO_4, H_2SO_4, HNO_3, NaOH, KOH or $ZnCl_2$. In this way, a carbonized product with a well-developed porosity may be obtained in a single operation. The activating agents employed function as dehydrating agents that influence pyrolytic decomposition, inhibiting the formation of tar and thereby enhancing the yield of carbon. The yield and properties of AC depend on the impregnation conditions, such as impregnation ratio (weight of activating reagent/weight of carbon precursor), time of pre-drying of impregnated materials, as well as pyrolysis conditions, such as temperature, soaking time (period of time that the sample and chemical are in contact) and atmosphere. All these process variables vary with the type of carbon precursor and the activating agent. The temperatures used in chemical activation are lower than that used in the physical activation process. As a result, the development of a porous structure is better controlled in the case of chemical activation. In spite of the above mentioned advantage, the chemical

method has its own inherent drawbacks, such as the need for washing of the product to remove the residual inorganic material.

E. Carbon as a Catalyst Support

Among their many interesting applications, carbon and graphite materials have been considered over the last decades for their utilization in several processes involving heterogeneous catalytic reactions. Most of these catalysts consist of metals or metallic compounds supported on several materials, the role of which is not only to maintain the catalytic phase in a well dispersed state but also affect the catalytic activity, by means of direct participation in any of the steps of the reaction mechanism, or by favoring the interactions between active phase and support. This participation and their interaction with the active phase make catalyst supports more than just simple active phase carriers. Some of the properties desirable in a support are its inertness towards unwanted reactions, stability under regeneration and reaction conditions, adequate mechanical properties, tunable surface area, porosity, and physical form, *i.e.* the possibility of being manufactured in granulates or conformates of different size and shape to suit different chemical reactor configurations. Only a few out of a wide range of potential materials totally fulfil this set of desirable properties and combine them in an optimal way.

To date the most important carbon supports from an industrial point of view are activated carbon and carbon black. The main reason for the success of those materials is their commercial availability and variety of different grades, so that the final catalyst can be tailored to the end user's requirements. Other carbon supports like carbon aerogels and CNTs are the focus of modern catalytic research, but so far have not been used in commercial processes. Carbon supported metal catalysts are employed in a number of applications including hydrodesulfurization of petroleum, hydrodenitrogenation, dehydrohalogenation, hydrogenation of carbon monoxide, hydrogenation of halogenated nitroaromatics compounds and nitro compounds, hydrogenation of unsaturated fatty acids, hydrogenation of alkenes and alkynes, oxidation of organic compounds and organic pollutants, and for fuel cells. However, the number of industrial processes using carbon or graphite materials as catalyst or catalyst support is still relatively limited. The large scale synthesis of vinyl acetate

and vinyl chloride, and the desulfurization of natural gas on AC impregnated with ZnO, CuO, or Fe_2O_3 are important technical applications.

Additionally, in the Catalytic Reaction Guide published by Johnson Matthey, of 69 reactions of industrial interest catalyzed by noble metals, 50 used carbon materials as catalyst support (*e.g.* fatty acid hydrogenation, selective nitrobenzene hydrogenations, reductive alkylation, hydrogenation of dinitrotoluene, butanediol synthesis, purified terephthalic acid, *etc.*).In the past, the lack of fundamental understanding of many aspects of the use of carbon in catalysis and the irreproducibility of the results obtained when employing AC supported catalysts caused a limited application of carbon as catalyst and more so as catalyst support. But the continuous studies to better understand all aspects of the physical and chemical characteristics of carbon material, especially for activated carbom (surface area and porosity) and, even more so, the possibility of controlling the surface chemistry of such materials is the origin of much important research carried out in industrial chemistry over the last decade.

2.4 Main factors affecting esterification reaction

Esterification is the process of forming esters from carboxylic acids and alcohol. In the esterification reaction, in the presence of an acid catalyst and heat, the hydroxyl (-OH) from the carboxylic acid is removed and, after that, the hydrogen from the alcohol is removed. The hydroxyl and the hydrogen combine to form water as byproduct of the reaction and ester as a main product (biodiesel).The esterification reaction between oleic acid and ethanol in the presence of solid acid catalyst can be represented as follows:

Oleic acid + Ethanol $\xleftrightarrow{\text{catalyst}}$ Ethyl oleate + Water

The conversion of oleic acid can be calculated according to the following equation:

$$\text{Conversion}(\%) = 1 - \frac{AV_1}{AV_0} * 100 \qquad (2.1)$$

Where AV_0 and AV_1 are the acid values of feed and products, respectively, and the relative acid value is determined by titration method.

2.4.1 Catalyst loading

The FFA conversion can be affected by the dosage of the applied catalyst. However, the esterification is a reversible reaction; an adequate amount of catalyst is required to push the reaction forward. Besides that, the by-product water might decompose (inactive) catalyst through catalysis reaction. Hence, catalyst amount should be sufficient in order to drive the reaction forward, to produce desired product. An excess amount of the catalyst increases the number of active sites through catalysis which consequently increases the FFA conversion in a shorter reaction time. On the other hand, further amount of catalyst increases the viscosity of the reaction mixture because; it reduces the surface contact between catalyst active sites and reactants [30]. Thereby, the maximum FFA conversion can be achieved in presence of an optimum amount of catalyst.

2.4.2 Ethanol/oleic acid molar ratio

The esterification of high FFAs oils requires high ethanol to oil molar ratio to drive the reaction toward the products side. Moreover, solid acid catalysts needed higher ethanol to oil molar ratio compared to homogenous acid catalysts. However, this depends greatly on the FFAs content in the parent oil. Ethanol to oil molar ratio is an important factor affecting esterification reaction. It is well known that esterification reaction is an equilibrium reaction. Thus, excess of ethanol is required to drive the reaction toward the formation of ester.

2.4.3 Reaction temperature

Reaction temperature is another important parameter which affects the rate of reaction. The activity of the applied catalyst highly depends on reaction temperature. It causes the cracking of the hydrogen atoms on the surface of the catalyst. The detached hydrogen atoms will be bonded with the free fatty acids. Beside, raising the reaction temperature increases the particles movement and increases the solubility of the reactants, resulting in higher ester yield. A higher reaction temperature can decrease the viscosities of oils and result in an increased reaction rate. A shortened reaction time found that when the reaction temperature increases beyond the optimal level, there is more chance of loss of ethanol. Esterification reaction has been reported to be influenced positively with increase in temperature. Depending on the oil used, the optimal temperature ranges from 60 °C to 120 °C.

2.4.4 Reaction time

Reaction time is another key operating parameter that highly affects the yield of final product. In the case of shorter operating time, the FFA particles cannot be converted to ester. Increased the reaction time will accelerates, the movement of the particles. The movement of the particles causes heat transfer between particles and results in higher reaction temperature [31]. Previous work shows that the conversion rate increases with reaction time. At the beginning, the reaction is slow due to the mixing and dispersion of alcohol into the oleic acid. After a while, the reaction proceeds very fast. Normally, the yield reaches a maximum at optimum reaction time and then remains relatively constant with a further increase in the reaction time. Moreover, excess reaction time will lead to a reduction in the product yield due to the backward reaction of esterification [37].

2.4.5 Stirring speed

Biodiesel reaction mixture (consists of catalyst, feedstock, and alcohol) is an immiscible mixture. In absence of stirring condition, the free fatty acid conversion process goes on fairly slow at the surface of the particles. Thereby, continuous stirring is needed in order to improve mass transfer between three different immiscible phases[32,33]. Since esterification reaction can only occur in the interfacial region between the liquids and also due to the fact that free fatty acids and alcohols are not totally miscible, esterification is a relatively slow process. As a result, vigorous mixing is required to increase the area of contact between the two immiscible phases [13].

The agitation intensity appears to be of a particular importance for the alcoholysis process. The mass transfer of FFA from the oil phase towards the ethanol-oil interface could be a critical step limiting the rate of alcoholysis reaction because the reaction mixture is heterogeneous, consisting of two immiscible phases. Poor mass transfer between two phases in the initial phase of the reaction results in a slow reaction rate, the reaction being mass transfer controlled. Therefore, variations in mixing intensity are expected to alter the kinetics of the esterification reaction [24].

CHAPTER 3 MATERIAL AND METHODS

3.1 Time and place of the study

The study was conducted from January 2017 to August 2017 at Addis Ababa Institute of Technology, chemical Engineering laboratories except the catalyst characterization experiments which had been conducted at Addis Ababa University, college of natural science, Chemistry department laboratory and Leather industry Development Institute (LIDI) laboratory.

3.2 Chemicals and Instruments

The raw material for the preparation of catalyst, rice husk, was collected from Wereta, Amhara region located between $11^0$55'0''N and $37^0$42'0''E at a distance of 607 Kms from Addis Ababa. The temperature of the region varies from mean monthly minima of 10.4 to 14.4^{0}C and mean monthly maxima of 24.9 to 30.6^{0}C while the mean relative humidity varies from 40.9% to 74.5%. The rice husk was harvested during November 2016.

The equipments needed for preparation of the catalyst are tubular furnace(carbolite, maximum temperature 1100°C), vacuum filter, analytical balance (precision is ± 0.01 mg), pH meter(Jenway model 3510 digital), muffle furnace, siever, crucibles, desiccator, oil bath, drying oven, stirrer, litmus paper, aluminum foil, different size of beakers, graduated cylinder, digital micro-pipet and volumetric pipet, filter paper, stirring rods, spatulas, mechanical and magnetic stirrer,FTIR spectroscopy, X-ray Diffractrometer(XRD) ,Flash CHNS/O- analyzer and thermogravimetric analyzer, different size of conical and Erlenmeyer flasks, different styles of burette stopcocks, sonicator(Bandelin sonorex RK 106s),different size volumetric glass flasks, three neck round bottom flask, stirrer, water bath, vacuum filter, condenser, filter paper, thermometer and chiller.

The chemicals and reagents that were used for preparation of catalyst are concentrated sulfuric acid(sigma), distilled water, acetone(sigma), vanadium pentoxide catalyst, copper and copper oxide (sigma),nitrogen gas, sodium hydroxide(sigma),sodium chloride(sigma) oleic acid(sigma),ethanol(sigma),potassium hydroxide(sigma), phenolphthalein powder, diethyl ether(sigma). All the chemicals were analytical grade and they were bought from different chemical stores in Addis Ababa.

3.3 Characterization of rice husk

3.3.1 Proximate analysis of the rice husk

As defined by ASTM D5373-02 (2003), proximate analysis separates the products into four groups: moisture, volatile matter, consisting of gases and vapors driven off during pyrolysis, fixed carbon, the nonvolatile fraction of biomass, and ash, the inorganic residue remaining after combustion.

I. Moisture Content

Sample was measured and taken in a petri dish. It was then heated at 105°C for 12hr. The petri-dish was left open during the heating process. After heating, the petri-dish was cooled in desiccator and then weighed. The amount of moisture content present in the sample was determined as:

$$\textbf{Moisture}, \% = \frac{W_1 - W_2}{W_1} * 100 \quad (3.1)$$

Where: W_1 = weight of sample before drying (gram), W_2 = weight of sample after drying (gram).

II. Ash Content

The sample was put in a crucible and the crucible was ignited in a muffle furnace at 650^0C for 3 hour period. Then the crucible was put in to a desiccator and it had been cooled to room temperature and then weighed. The ash content was determined as:

$$\textbf{Ash content}, \% = \frac{W_2}{W_1} * 100 \quad (3.2)$$

Where: W_1 = weight of sample before heating (g), W_2 = weight of ash (g).

III. Volatile matter content

The sample was measured and placed in a closed crucible. It was then heated up to 900°C for 7 minutes in a furnace. The crucible was then cooled in a desiccator and weighed. The percentage of Volatile Matter had been calculated from the loss in mass of the sample as:

$$\textbf{Volatile matter}, \% = \frac{W_1 - W_2}{W_1} * 100 \quad (3.3)$$

Where W_1= weight of sample before heating, W_2= Weight of sample after heating.

IV. Fixed carbon content

The fixed carbon content, Fc had been determined by subtracting the sum of percentage compositions of moisture content, volatile matter content, and ash content form 100.

$$\text{Fixed carbon}(\%) = 100 - (\text{moisture}, \% + \text{ash}, \% + \text{volatile matter}, \%)(\text{wet basis}) \quad (3.4)$$

3.4 Pyrolysis of the rice husk

Pyrolysis or cracking involves the thermal decomposition of organic material to smaller molecules through the application of heat without the addition of supplemental air or oxygen. The laboratory set up for the pyrolysis of rice husk is shown in Appendix B .The rice husk sample was placed in a horizontal stainless steel tubular reactor equipped with horizontal tubular furnace (Carbolite), temperature controller, and N_2 gas inlet. The carbonization had been performed at five different carbonization temperatures of 400, 450,500, 550, 600^{0}C with heating rate of 8, 9, 10, 11 and 12 ^{0}C/min respectively for a period of 3 hr under nitrogen flow rate of 250 mL/min. The rice husk char generated was cooled and temporarly stored in a dessicator for 1 hour. Sieve analysis of the rice husk char was then performed after it was crushed using mortar and pestle. Then, leaching with 1 M NaOH at 90 ^{0}C for 5 h at the ratio of solid to liquid of 1 g: 10 ml was conducted to remove silica in the rice husk. Then, it was continuously washed using distilled water in order to remove impurities and its weight was measured. Finally, the rice husk char had been dried in oven overnight and stored in air tight plastic bags until it is needed for sulfonation. The yield of pyrolysis process was calculated as the ratio of the weight of washed rice husk char obtained after carbonization to the weight of rice husk before carbonization.

3.4.1 Ultimate analysis of rice husk char

The Ultimate Analysis of a sample determines the elemental composition of the sample. It is based on the principle of Dumas method which involves the complete and instantaneous oxidation of the sample by flash combustion. The results are in percentage composition of Carbon, Hydrogen, Nitrogen and Sulphur. From these results the oxygen composition is

determined by subtracting the sum of Carbon, Hydrogen, Nitrogen, and Sulphur compositions from 100. The Ultimate Analysis was carried out in EA 1112 Flash CHNS/O-analyzer under the condition of carrier gas (He-gas) flow rate of 120 ml/min, reference flow rate of 100 ml/min, and oxygen flow rate of 250 ml/min with furnace temperature of 900° C and oven temperature of 75 °C. The sample was fed into the analyzer along with excess supply of oxygen. The reaction of oxygen with other elements (namely carbon, hydrogen, nitrogen, and sulphur) present in the sample produces carbon dioxide, water, nitrogen dioxide, and sulphur dioxide respectively. The combustion products were separated by a chromatographic column and were detected by the thermal conductivity detector (TCD), which gives an output signal proportional to the concentration of the individual components of the mixture. This determines the equivalent compositions of elements in the sample.

3.5 Sulfonation of the rice husk char

Numerous research studies involving sulfonated carbon catalysts have reported that the optimum sulfonation temperature strongly depends on the type of carbon and its source [24]. The rice husk char was sulfonated at different sulfonation temperatures of 70, 90,110,130 and 150^{0}C for a duration of 2 hour in an oil bath under nitrogen flow. The laboratory set up for sulfonation of rice husk char is shown in Appendix B. The ratio of rice husk char(RHC) to concentrated sulphuric acid volume(98% concentration) is 1g:10 ml. After cooling to ambient temperature, the mixture was added to distilled water, stirred, and filtered. The precipitate was then washed repeatedly with hot distilled water until the filtrate was free from sulfate ions. Following filtration, the sample was dried at 80 ^{0}C for 24 h in a drying oven,bagged,and placed in a desiccator. Lou et al. [4] found that carbonization and sulfonation duration exerted a weak effect on catalytic activity and this phenomenon could be explained by the slight differences in FTIR spectra of the carbon precursors carbonized for various durations and the catalysts sulfonated for different durations. Moreover, it is indicated the sulfonation process for introducing the -SO_3H groups into the rice husk char is relatively fast and could be completed within 2 h which is superior to the 6 h sulfonation duration for the oil palm trunk and sugarcane bagasse derived heterogeneous acid preparation[17]. Hence, in this study, carbonization and sulfonation temperatures are

designated as the main factors influencing the catalytic activity, where 3 h and 2 h are selected as the suitable carbonization and sulfonation duration for subsequent experiments.

The effect of carbonization temperature on the catalytic activity were firstly evaluated with sulfonation temperature of 90 ^{0}C. Further examinations were performed to compare influence of sulfonation temperature on activity of the rice husk-based heterogeneous acid in catalyzing esterification of oleic acid with ethanol at the carbonization temperature with the highest esterification efficiency. The prepared catalyst is denoted as Cx-Sy, where C and S indicate carbonization and sulfonation, and x and y represent the carbonization and sulfonation temperature, respectively. Esterification efficiency and total acid density have been selected as a screening parameter for determining high performing catalyst.

3.6 Characterization of rice husk based solid acid catalyst

3.6.1 Determination of acidity

Total acid density of the prepared catalysts, consisting of carboxylic, phenolic, and sulfonic groups, was measured using the standard acid-base back titration method. The catalyst samples were pre-dried in the oven at 105°C for two hours prior to analysis, then 0.05 g of catalyst were placed in a flask, and mixed with 15 mL 2 mol/L NaCl solution. As H^+ ion existed in -SO_3H of sulfonated catalyst, it exchanged with Na^+ ion by ultrasonic oscillation for 30 min. Afterwards, the solid was filtered. With phenolphthalein as an indicator, 0.02 mol/L NaOH solution was used to titrate filtrate. When the color of the filtrate turned from colorless into slightly red, the end point of titration was reached. The accurate acid density N_{total}) was calculated as follows:

$$N_{total}\left(\frac{mmol}{g}\right) = \frac{\text{Concentration of NaOH} * \text{Volume of NaOH consumed in titratation}}{\text{mass of catalyst sample}} \qquad (3.5)$$

The material and methods for determining esterification efficiency has been outlined under section 3.7. All the reactions performed for determining the esterification efficiency in the investigation of catalyst preparation conditions had been conducted using reaction conditions of catalyst loading 3%, ethanol to oleic acid molar ratio of 6:1, agitation speed of 300 rpm, reaction temperature and times of 90^{0}C and 2hr respectively.

3.6.2 X-ray Diffraction(XRD) Spectroscopy

This analysis is one of the most commonly used techniques for either crystalline or amorphous phase identification. In this technique, the catalyst sample is irradiated with X-ray of a known wavelength (λ). The X-ray diffraction (XRD) patterns of sulfonated catalyst were obtained using MiniFlex 300/600, Japan operated at 40 kV and 15 mA, using Ni-filtered Cu-Kα radiation (1.54059-1.54441). The samples were placed on a sample holder made up of silicon wafer and the measurements were taken continuously from 10^0 to 80^0 angles over the range of 2θ. The resultant intensity data was processed by using in-built diffraction software Match! 3 to graph and analyze the peak position. A custom-made sample holder with a shallow well was used for the samples, and rotated to improve particle statistics. The equipment used for performing XRD analysis has been shown in Figure B6 of the Appendix, and the analysis has been carried out in the following manner. The sample was loaded in to the sample holder and it was slipped into clip. The MiniFlex Guidance software was started and the x-ray tube warmed up. From the flow chart that appeared when the software started, general measurement was selected. The measurement conditions was filled in to the pop up window and the measurement started instantly. Finally, the sample were removed and the guidance software logged off.

3.6.3 Fourier Transform Infrared (FT-IR) Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. Fourier transform infrared spectroscopy will be used to examine the framework vibration. Functional group of the catalyst was tested by Fourier transform infrared spectroscopy(FTIR) on Spectrum 65 FT-IR(PerkinElmer) with the resolution of 4 cm^{-1} and scanning range from 400 cm^{-1} to 4000 cm^{-1} using the conventional KBr technique. The functioning group was determined based on the interpretation of the infrared spectrum obtained by comparing it with the standard spectrum group frequencies. The procedure followed to perform this analysis is as follows: First the sample for the analysis was milled in a ceramic pestle and mortal to powdery conditions. The powder was then mixed with KBr particles to make it suitable to infrared analysis. The mixture was then pressed to a small thickness, slightly below 1mm, required for FTIR analysis. Then the power of the instrument was turned on and the initialization

started. Then the sample holder was cleaned by acetone with Kimwipes and the spectrum software was launched. From the window that appeared, the instrument setup button was selected and 'Scan and instrument setup' dialog popped up. The sample name, scan range and scan number was inputted. The sample was placed on the sample holder and the 'apply' and 'start' buttons were pressed to collect the spectrum. Finally, the data was saved and the instrument was switched off. The FT-IR data was be graphed by using Microsoft Excel 2013.

3.6.4 Ultimate analysis

Ultimate analysis(elemental C,H,N,S,and O(by difference) in %(w/w)) of the raw rice husk and the catalyst derived from it were conducted using a device EA 1112 Flash CHNS/O-analyzer following ASTM D3176. The conditions of the analysis used were carrier gas flow rate of 120 ml/min, reference flow rate of 100 ml/min, oxygen flow rate of 250 ml/min; furnace temperature of 900 °C and oven temperature of 75 °C. Five calibration points for every component were used. Samples were run in duplicate and the average values are to be taken to minimize the data error.

The general theory of operation is as follows: Dried and powdered samples were combusted in a tin sample crucible with vanadium pentoxide catalyst, purified by a reactor packed with electrolytic copper and copper oxide, separated on a gas chromatographic column, and analyzed using a thermal conductivity detector (TCD). When the tin crucible with sample is dropped into the reactor, the oxygen environment triggers a strong exothermic reaction. Temperature rises to ~1800°C, causing the sample to combust. The combustion products were conveyed across the reactor, where oxidation gets completed. Nitrogen oxides and sulfur trioxide were reduced to elemental nitrogen and sulfur dioxide and oxygen excess was retained. The gas mixture containing N_2, CO_2, H_2O, and SO_2 flows into the chromatographic column, where separation takes place. Eluted gases were sent to the TCD where electrical signals were processed by the Eager 300 software which provide percentages of nitrogen, carbon, hydrogen, and sulfur contained in the sample.

3.6.5 Thermo gravimetric Analysis

Thermal stability of the catalyst was investigated through thermogravimetric analysis (TGA) on thermogravimetric analyzer(TA instrument, SDT Q600 V20.9 Build 20) in the temperature range of 25-800 ^{0}C with a heating rate of 10 ^{0}C/ min where nitrogen (with the

highest purity) was used as both the protection gas and reaction gas. For the thermo gravimetric analysis to be carried out, small amount of the sample (22-30mg) was placed in a vial, which was present in the TGA analyzer. This vial is connected to sensors which detects the weight of the sample at all times. Testing was carried out under inert atmosphere (N_2) with a flow rate of 2 ml/min to remove all corrosive gases and avoid thermoxidative degradation and the retention time of the sample at the maximum temperature. The thermal degradation onset temperature and the thermal degradation weight loss of composites were recorded and analyzed using origin pro 8.0 software.

3.7 Catalytic Performance Evaluation of rice husk based catalyst

3.7.1 Catalytic reaction procedure

Catalytic performance of the rice husk-based heterogeneous acid was evaluated by esterification of oleic acid with ethanol. For esterification, certain molar ratios of ethanol to oleic acid were mixed in a 1000 mL three-necked round bottomed flask with a reflux condenser and stirring rod. And the catalyst with varying dosages was added into the reaction system. The mixture was then heated at defined temperature in the oil bath for the given duration and the stirring speed was set at 300 rpm. The experimental set up for the esterification reaction is shown in Appendix B. In this test, oleic acid dosage was fixed to be 100 g and the catalyst loading was calculated based on the oleic acid amount. After esterification, the liquid products and heterogeneous acid catalyst were separated under vacuum filtration. The generated water and un-reacted ethanol were then removed from the liquid product using rotary evaporator. The conversion of oleic acid into biodiesel, which is used to evaluate catalytic performance of the rice husk based heterogeneous acid catalyst in esterification, has been determined according to the changes of acid value in the oil phase and calculated as follows:

$$\text{Conversion}(\%) = \frac{\text{AVo} - \text{AV1}}{\text{AVo}} * 100 \qquad (3.6)$$

Where AV1 is final acid value and AVo is acid value of oleic acid and it is measured to be 201.6 mg KOH g^{-1}.

3.7.2 Acid value analysis

The acid values of product has been determined according to standard methods. Standard alcoholic KOH solution (0.1 M) was prepared by dissolving 5.6 g of KOH (pellet) to one liter of (95%) ethanol. The solution was filtered and stored in brown bottle for five days. A phenolphthalein 10 g per liter of 95% v/v ethanol was used as indicator. A mixture of 1+1 v/v ethanol 95% v/v and diethyl ether was prepared by mixing 100 ml diethyl ether and 100 ml of ethanol. The solution was neutralized in a presence of 0.3 ml of indicator per 100 ml of mixture by means of ethanolic KOH solution.

A weighed quantity of the sample (5 gm) was dissolved in 150 ml of 1+1 mixture of ethanol and diethyl ether previously neutralized. The solution was titrated with 0.1N ethanolic KOH solution in presence of phenolphthalein indicator. The end point was recognized by a dark pink color. The volume of 0.1 M KOH (V) for the sample titration was noted. The total acidity (acid value) in mg KOH/ gm was calculated using equation 3.7.

$$\text{Acid value} = \frac{V * N * 56.1}{M} \tag{3.7}$$

Where:-

V - Volume expressed in milliliter of 0.1M solution of ethanolic KOH

M - Mass in gram of test portion

N - Concentration of ethanolic KOH

3.7.3 Catalyst Stability

Catalyst reusability in esterification of oleic acid with ethanol was conducted by consecutive batch cycles under optimal conditions. Catalyst used after each cycle was separated by suction filtration, washed with ethanol thoroughly, and then dried in oven at 105 ^{0}C for 4 h before it is reused.

3.8 Experimental design and Statistical Analysis

Response surface methodology (RSM) is an efficient statistical technique used for modeling experimental data and evaluation of the influence of parameters on the response process. This methodology allows obtaining much information by performing a small number of experiments and permits the evaluation not just of the single experimental parameters but

also of their interactions. Response surface methodology (RSM) was thus employed to analyze the operating conditions of esterification and to obtain a high percent conversion. The experimental design was carried out by three chosen independent process variables at three levels, and the studied factors were catalyst loading(3%,4.5%,6%), molar ratio of ethanol to oleic acid(6:1,9:1,12:1), and reaction time(1h,2h and 3h). The reaction temperature and rotation speed were set at optimum point of 90^0C and 300 rpm respectively at constant atmospheric pressure where the maximum conversion could be achieved based on literature data. The selection of the levels was defined according to results obtained in preliminary tests. The percent conversion of oleic acid was taken as the response of the design experiment. A Box Behnken center united design was employed to design the experiments. This design consisted of seventeen randomized runs with five replicates at the central point to minimize the error.

Coefficients of the single-response model were evaluated by regression analysis and tested for their significance. Insignificant coefficients were eliminated stepwise on the basis of their P-values after testing the coefficients. Therefore, the best-fitting model was determined by regression and stepwise elimination. The software of Design Expert 10.0 was used for designing and analyzing the experimental data. The independent variables (factors) and their levels, real values as well as coded values were presented in Table 3.1. The model equation was used to predict the optimum value and subsequently to elucidate the interaction between the factors, and the quadratic equation model for predicting the optimal point was expressed according to the following equation

$$Y = \lambda_o + \sum_{i=1}^{3} \lambda_i x_i + \sum_{i-1}^{3} \lambda_{ii} {x_i}^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \lambda_{ij} x_i x_j \qquad (3.8)$$

Where λ_o, λ_i, λ_{ii} and λ_{ij} are regression coefficients (λ_o is constant term, λ_i is linear effect term, λ_{ii} is squared effect term, and λ_{ij} is interaction effect term), and Y is the predicted response value.

Table 3.1: Coded levels for independent factors used in the experimental design.

Factors	Symbol	Coded levels		
		-1	0	1
Catalyst loading(%)	A	3	4.5	6
Molar ratio of ethanol to oleic acid	B	6	9	12
Time,hr	C	1	2	3

The adequacy of the model was determined by evaluating the lack of fit, coefficient of determination (R^2) and the Fisher test value (F-value) obtained from the analysis of variance that was generated by "Design-Expert®" Version 10.0 (Stat-Ease, Inc., Minneapolis, MN, USA) software. Statistical significance of the model and variables were determined at 5% probability level ($P < 0.05$).

CHAPTER 4 RESULT AND DISCUSSION

4.1 Characterization of rice husk

4.1.1 Proximate analysis of rice husk

Proximate analysis, which is a standardized procedure that gives an idea of the bulk components that make up a substance, was done to determine the average of the percentage volatile matter content, percentage ash content, moisture content and percentage content of fixed carbon of rice husk. The procedures of the ASTM standard D5373-02 (2003) was adopted to obtain the parameters and the result is shown in the following figure (wet basis).

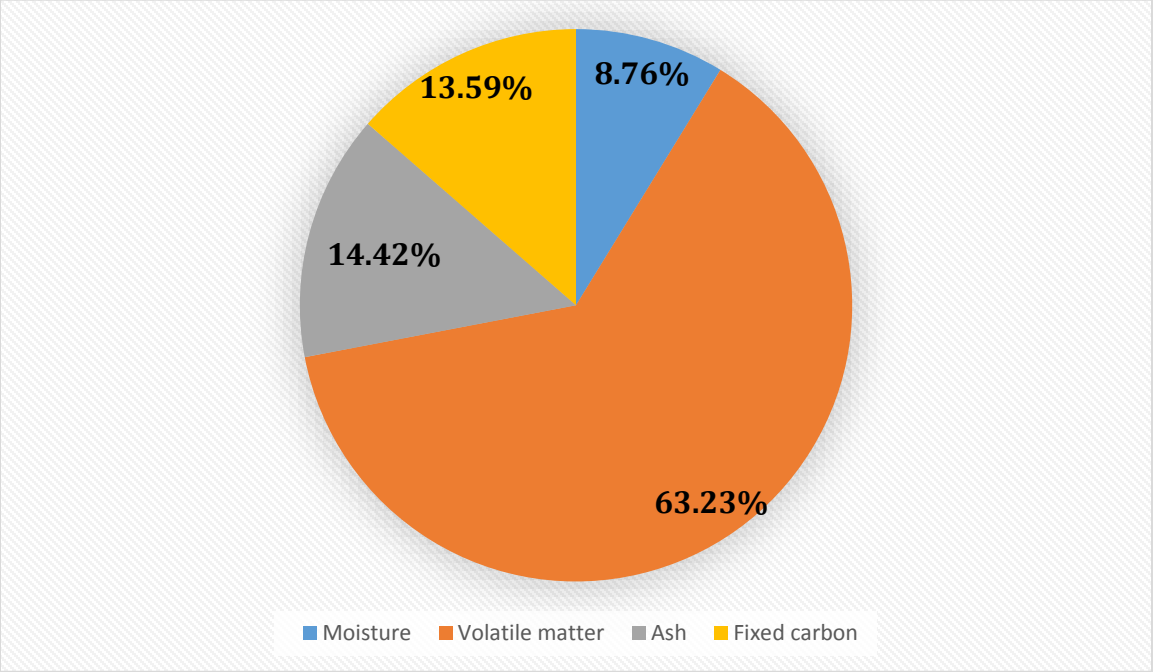


Figure 4.1 Proximate analysis of rice husk

The proximate analysis result of rice husk determines the distribution of its contents. It may be noted that the volatile matter present in the rice husk, contributes maximum to its contents. The moisture content present in the sample can also be considered as water vapor when it is heated to high temperatures. Hence, about 71.99% of the contents tend to leave the sample when heated, of which 63.23% is volatile matter and 8.76% is moisture content.

The ash content of the sample is 14.42% and the fixed carbon content of the sample is 13.59%. This gives an overview about the components of the rice husk.

4.1.2 Ultimate analysis of rice husk char

The elemental analysis of rice husk char was conducted using EA 1112 Flash CHNS/O-analyzer under the condition of carrier gas (He-gas) flow rate of 120 ml/min, reference flow rate of 100 ml/min, and oxygen flow rate of 250 ml/min with furnace temperature of 900° C and oven temperature of 75 °C. For every component, five calibration points were calibrated. Samples were run in duplicate and the average values are to be taken. The percentage of oxygen content was estimated by difference as follows: O (%) = 100 - (C + H + N + S).

The elemental content of the rice husk char is presented in Table 4.1 and it showed that carbon content increased with temperature, but the loss of O, and H was recorded. The increase in carbon content with temperature is due to increasing degree of carbonization. However, these decline in O and H elements may be attributed to breaking of weaker bonds in biochar structure and highly carbonaceous materials yielded with increased temperature[47]. Char is a porous carbon structure that remains after the hydrogen and oxygen fractions have left the fuel. It is generally assumed that char completely exists of carbon, but since char is often defined as the solid residue after pyrolysis, it is often polluted with other components. Char is usually polluted with mineral fractions and after incomplete pyrolysis large fractions of hydrogen and oxygen can still exist.

Table 4.1: Elemental analysis of rice husk and rice husk char obtained at different temp.

	Mass fraction(%)				
Sample	C	H	O	N	S
Rice husk	48.57	5.79	44.94	0.63	0.07
C-400	65.89	4.21	28.44	1.41	0.05
C-450	66.51	4.16	27.87	1.41	0.05
C-500	68.38	4.01	25.13	1.42	0.06
C-550	69.23	3.59	25.70	1.42	0.06
C-600	71.42	3.14	23.96	1.43	0.05

4.1.3 Rice husk char yield of pyrolysis

The yield of pyrolysis process obtained has been provided in table 4.2. The pyrolysis of biomass usually produces about 10%-25% of solid char. The process can be adjusted to favour biochar, bio-oil, or gas production with a fuel to feed efficiency of up to 95%. Biochar like rice husk char is also an excellent candidate for a source of low price carbonaceous catalyst support. Its effective and high-value use will significantly improve the bio-oil economy. Since it is expected to obtain yield above 10%, the expectation is satisfied.

Table 4.2: Pyrolysis yield results

No.	Temp.,^{0}C	Weight of sample before carbonization,g	Weight of sample after carbonization,g	Dried weight after washing,g	Yield,%
1	400	50	21.3	6.25	12.5
2	450	50	23.8	6.79	13.58
3	500	50	28.1	7.35	14.7
4	550	50	31.5	7.46	14.92
5	600	50	34.5	8.14	16.28

4.2 Catalyst characterization

4.2.1 Determination of acidity

The total acid site density and especially density of sulfonic groups, is a crucial factor for catalytic activity. The total acid density consisted of three different acidic groups of sulfonic, carboxylic and phenolic. However, only the sulfonic group has enough acid strength to participate in esterification reaction. Carboxylic and phenolic groups do not have enough acidity to catalyze the esterification reaction. These two groups are the result of oxidization of aliphatic groups due to strong sulfonation and incomplete carbonization of the supporting material. These groups contribute very little to catalytic esterification due to their insufficient acidity, but their hydrophilicity should favor the dispersion of catalysts.

Titration method was described in section 3.6.1. Each sample was tested in triplicate. The total acid site density, consisting of carboxylic, phenolic, and sulfonic groups, was measured via back titration method and the results reported in the following table.

Table 4.3: Total acid density of prepared catalyst

Catalysts	Total acid density(mmol g^{-1})	Catalysts	Total acid density(mmol g^{-1})
C400-S90	1.326	C450-S70	1.269
C450-S90	1.381	C450-S90	1.381
C500-S90	1.296	C450-S110	1.436
C550-S90	1.273	C450-S130	1.372
C600-S90	1.145	C450-S150	1.294

4.2.2 Ultimate analysis

Ultimate analysis is a serviceable measure to obtain useful information about the chemical composition in the rice husk based heterogeneous acid catalyst. Ultimate analysis of the samples reveal the presence of carbon, hydrogen, oxygen, nitrogen and sulfur in the rice husk based heterogeneous acid catalyst, as showed in Table 4.4. Compared to the raw rice husk, the content of hydrogen dropped after carbonization, indicating the dehydration and decomposition process during carbonization. Furthermore, both oxygen and sulfur contents get increment distinctly after sulfonation, demonstrating the successful attachment of $-SO_3H$ groups into carbon structure. Meanwhile, more surface oxygen containing functional groups, such as lactone, carboxyl and phenolic hydroxyl are generated under the concentrated sulfuric acid effect during sulfonation. This result shows the effective utilization of concentrated sulfuric acid and validates the existence of acid sites mainly as $-SO_3H$ groups, which confirms the consequence of acid strength. Similar results have been obtained by Jiang et al.[45]

Table 4.4: Ultimate analysis of rice husk, rice husk char and rice husk based catalysts

Sample	Mass fraction (%)				
	C	H	O	N	S
Rice husk	48.57	5.79	44.94	0.63	0.07
C-450	66.51	4.16	27.87	1.41	0.05
C-450 S-110	36.64815	2.3356	56.94745	0.8217	3.2471

4.1.2 X-ray Diffraction(XRD) spectroscopy

The XRD pattern of the solid acid catalyst obtained from rice husk char is shown in figure 4.2. Compared with that of raw rice husk, the peak of the impurities ($2\Theta = 18^0$, silica) disappeared in the spectrum of rice husk char and the solid acid. This indicates that the solid acid and rice husk carbon consist of a single layer of polyhexagonal carbon atoms after leaching, implying that the BET surface area of the solid acid may be dramatically high. As can be seen in the figure, the X-ray diffraction (XRD) pattern of the rice husk based catalyst exhibited abroad diffraction peak ($2\Theta = 10–30^0$) and a weak diffraction peak ($2\Theta = 35–50^0$), which can typically be attributed to amorphous carbon. This indicates that the rice husk based catalyst had an amorphous structure, which may be important in the catalyst's activity during esterification reactions [41]. This structure is far from crystal and is reported to be favorable for anchoring the $–SO_3H$ groups. In contrast, catalysts prepared by sulfonation of familiar carbon materials such as graphite, carbon black, graphitized carbon fiber, activated carbon and glassy carbon, displayed no catalytic activity in the esterification reaction[42].

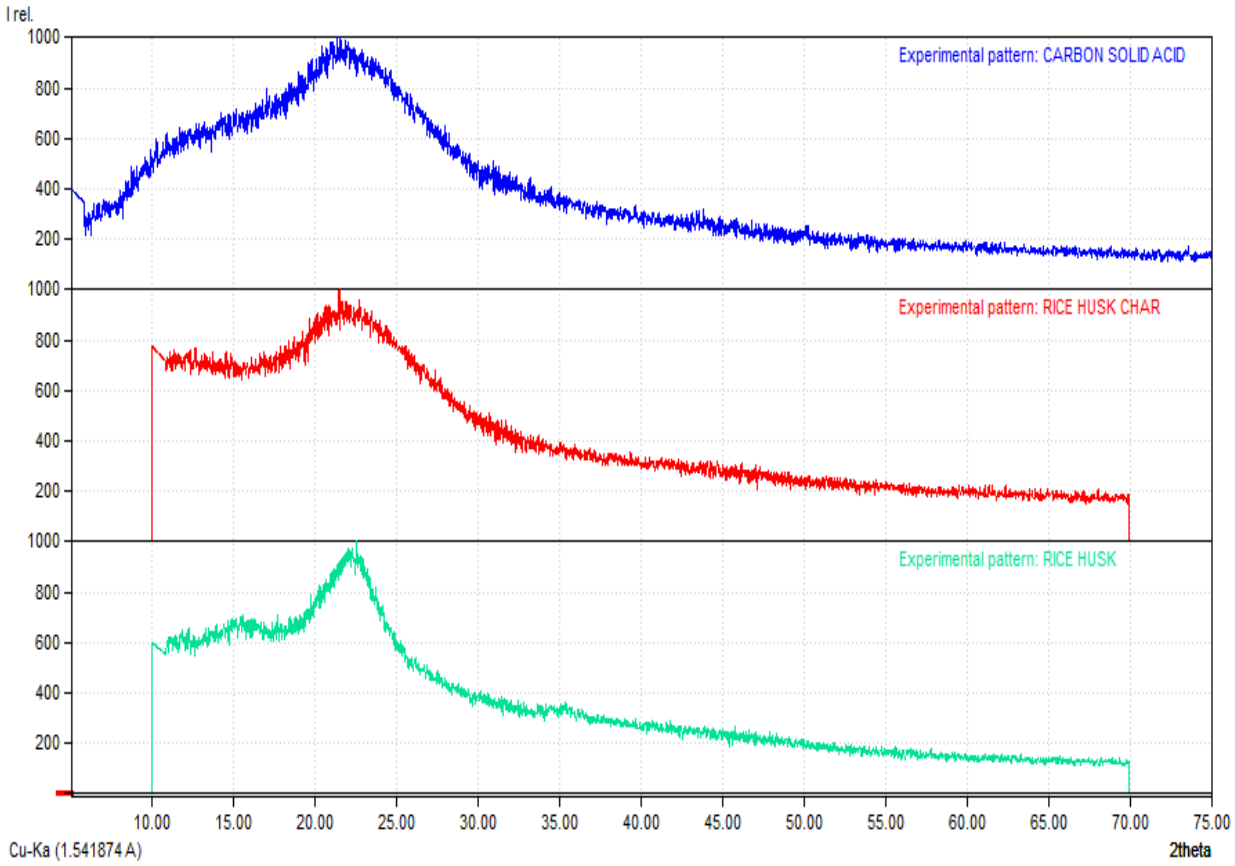


Figure 4.2: XRD pattern of rice husk, char and rice husk based solid acid catalyst

4.1.2 Fourier Transform Infrared (FT-IR) Spectroscopy

The vibrational spectrum of a molecule is considered to be a unique physical property and is characteristic of the molecule. As such, the infrared spectrum can be used as a fingerprint for identification by the comparison of spectrum from an unknown but previously recorded reference spectrum. Fourier Transform Infrared Spectroscopy (FTIR) spectra is a useful tool to identify functional groups in a molecule, as each specific chemical bond often has a unique energy band and can obtain structural and bond information on a complex to study compounds.

FT-IR spectroscopy was employed to explore the changes in functional groups induced by preparation process. In the present study, FTIR spectroscopy was, therefore done for qualitative analysis of major functional groups responsible for solid acid catalyzed

esterification process and explore the changes in functional groups induced by preparation process. It shows that the difference of the spectroscopy is mainly the bands of oxygen functionalities in the samples (Figure 4.3). The bands at 1074 cm^{-1} and 1162 cm^{-1} are identified as the O=S=O symmetric and asymmetric stretching vibrations in $-SO_3H$ groups, respectively, which clearly demonstrate the successful incorporation of $-SO_3H$ groups in to the rice husk based heterogeneous acid catalyst. This group were the active sites of the catalyst. The band at 1636 cm^{-1} can be attributed to the C=O stretching mode of the -COOH groups, while the broad band centered at 3456 cm^{-1} was assigned to the -OH stretching mode. The band at 1381 cm^{-1} can be attributed to the C=C stretching mode of the samples. Therefore, -COOH, $-SO_3H$ and -OH were found as the functional groups on the solid acid. Similar results have been reported by Hara et al.[18].

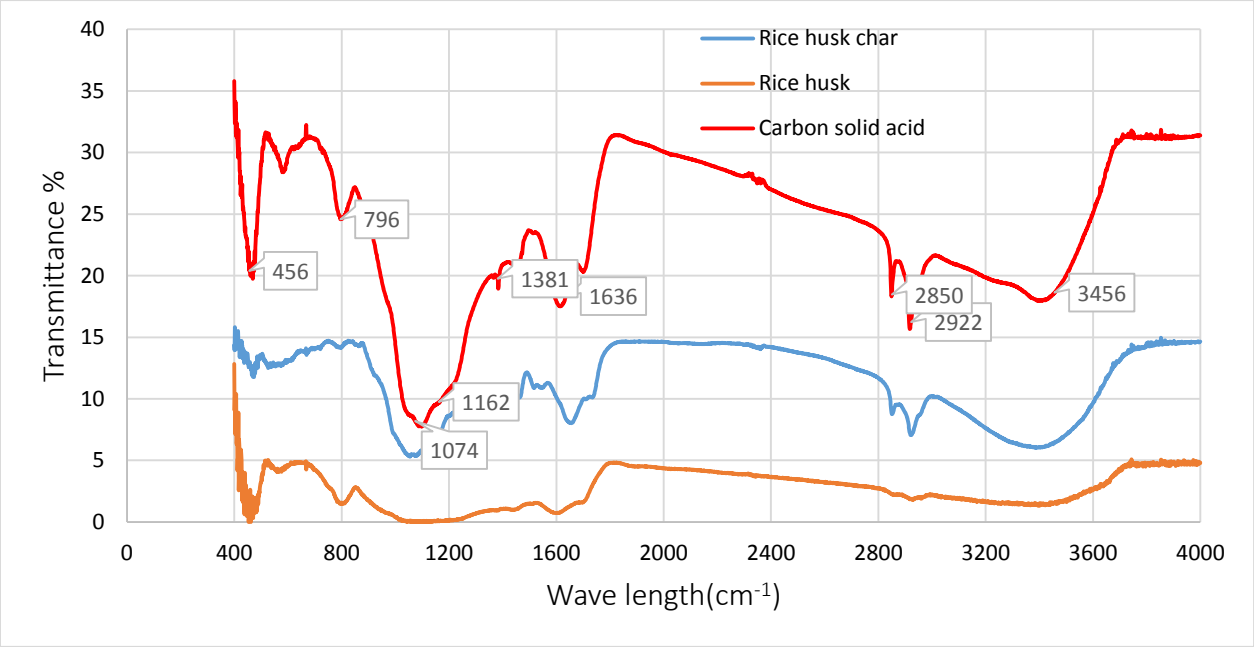


Figure 4.3: FT-IR spectra of rice husk, rice husk char and carbon solid acid catalyst

4.1.3 Thermo gravimetric Analysis

The thermal stabilities of rice husk based catalyst were investigated via thermogravimetric analyzer (TGA) SDT Q600. TG curves showed that the weight loss for the catalyst were about 1.6% in the range from room temperature to 120 ^0C, which is mainly due to the physically absorbed water. However, the weight loss occurred at a higher temperature because $-SO_3H$

is hydrophilic and favors the adsorption of water[43]. As a result, water molecules in rice husk based catalyst are absorbed more firmly.

TG curve for the rice husk based catalyst is divided into three stages. The first stage from the initial temperature to 240^{0}C involves evaporation of the free water and physical adsorbed water, where the TG curve is basically kept flat. Mass loss of the second stage 240^{0}C to 570 ^{0}C is 61.57% and is mainly attributed to the thermal decomposition of hemicellulose, cellulose and partial lignin for the rupture of the chemical bonds, like H-O, C-H, C-O-C, etc. Thus, the relative stable polycyclic mesh aromatic structure forms for the thermal polycondensation reaction. Mass loss of the third stage, which is from 570 ^{0}C to 800 ^{0}C, becomes slow, for the further decomposition of oxygenic groups and the more stable carbon network compounds are formed. In succession, the curve is basically kept as plateaus in 100–220 ^{0}C and a rapid mass loss is then observed from 220 ^{0}C to 570 ^{0}C. This result confirms that the carbon-based heterogeneous acid catalyst derived from rice husk exhibits satisfying thermal stability under esterification condition, especially below 100 ^{0}C.

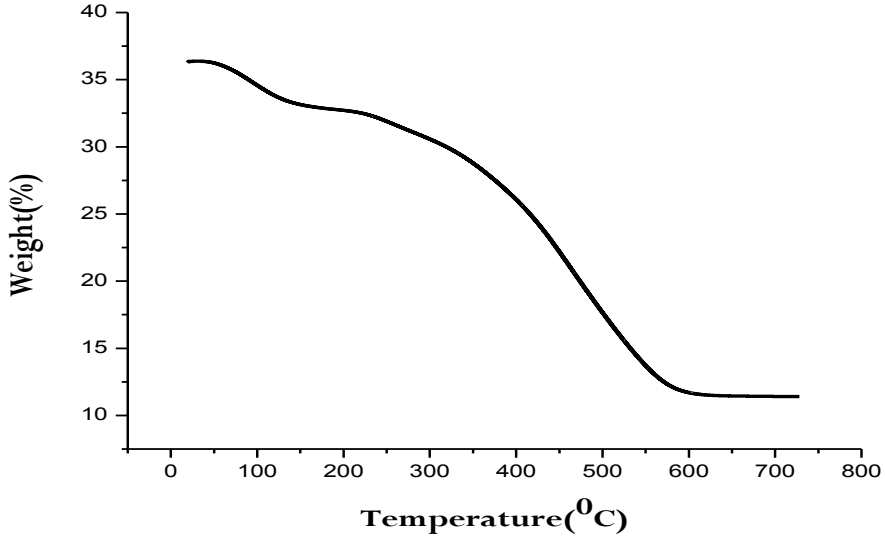


Figure 4.4 TG curve of rice husk based catalyst

4.3 Influence of preparation conditions on catalyst activity

4.3.1 Effect of carbonization temperature

Pyrolysis is a thermo-chemical process that converts biomass into liquid (bio-oil), char and non-condensable gases by heating biomass to high temperatures in the absence of oxygen. Carbonization temperature dominates the catalytic performance of the materials prepared by this method. Low carbonization temperatures only provide complex polymers containing aromatic compounds. Sulfonation of such pyrolysates results in soluble sulfonated species. In contrast, high carbonization temperatures largely decrease the catalytic performance due to growth of the carbon network. Sulfonation of carbon materials with electrical conductivity, such as graphite, cannot form carbon sheets that bond high densities of SO_3H groups, because carbon sheets with conducting electrons lose aromaticity.

As shown in figure 4.5, effect of carbonization temperature on the catalytic activity is firstly evaluated with sulfonation temperature of 90^0C. The initial esterification efficiency is heightened with the carbonization temperature until the maximum value of 92.23% is achieved at 450 ^{0}C, and then decreased to 85.42% when the temperature is further increased to 500^0C. More seriously, a continued decrement in esterification efficiency to 82.47% and 80.73% is observed at 550 ^{0}C and 600 ^{0}C respectively, which is in accordance with the acid density variation trend listed in Table 4.3. Carbonization temperature is of great concern, for carbonization process is accompanied with release of oxygen-containing groups, such as -OH and -COOH, from the carbon material. Namely, vast oxygen-containing groups would remain on the carbon channel and thus impede introduction of $-SO_3H$ groups at lower carbonization temperature.

However, too high temperature would aggravate the formation and stacking of large polycyclic aromatic carbon sheets, leading to a more rigid structure in the carbonized products with a lower density of $-SO_3H$ groups. Consequently, the applicable carbonization temperature is selected as 450 ^{0}C and the resulting catalyst manifests the highest catalytic activity and acid density.

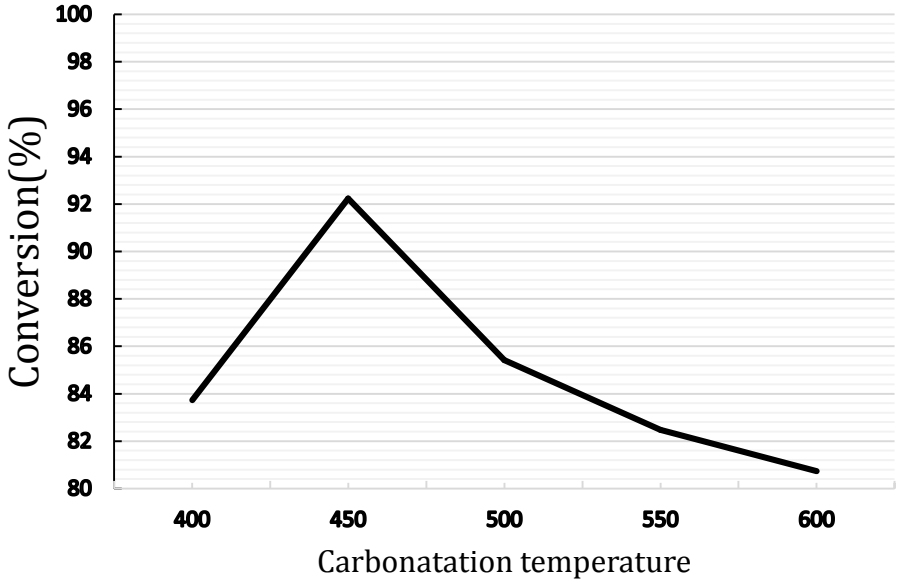


Figure 4.5: Effect of carbonization temperature on esterification efficiency

4.3.2 Effect of sulfonation temperature

The sulfonation temperature affected greatly the concentration of -SO_3H groups on these carbon-based catalysts. Examinations were performed to compare influence of sulfonation temperature on activity of the rice husk-based heterogeneous acid in catalyzing esterification of oleic acid with ethanol at carbonization temperature of 450 ^{0}C. As presented in figure 4.5, the esterification efficiency rises gradually as sulfonation temperature is increased from 70 ^{0}C to 110 ^{0}C and attains the peak value of 94.18% at 110 ^{0}C. Similar to carbonization temperature, a further augment of sulfonation temperature results in a depressed esterification efficiency. It is also observed that the catalytic activity is in correlation with the acid density displayed in Table 4.3. Toda et al. [19] reported that sulfonation temperature would affect position and stability of the introduced -SO_3H groups into the poly cyclic aromatic carbon structure. Thus, sulfonated product generated at lower temperature is unstable and easily to be hydrolytic. But exceeding temperature might lead to oxidation reaction between concentrated sulfuric acid and carbonized product, which would dilute concentrated sulfuric acid and reduce the catalytic activity. Moreover, increasing the sulfonation temperature resulted in a decrease in that concentration of SO_3H group.

At high sulfonation temperatures, side reactions such as condensation, oxidation and dehydrogenation played a dominant role and a small amount of polycyclic aromatic moieties with attached SO_3H groups was obtained. As a consequence, 110 ^0C is regarded as the optimal sulfonation temperature for the heterogeneous acid catalyst preparation.

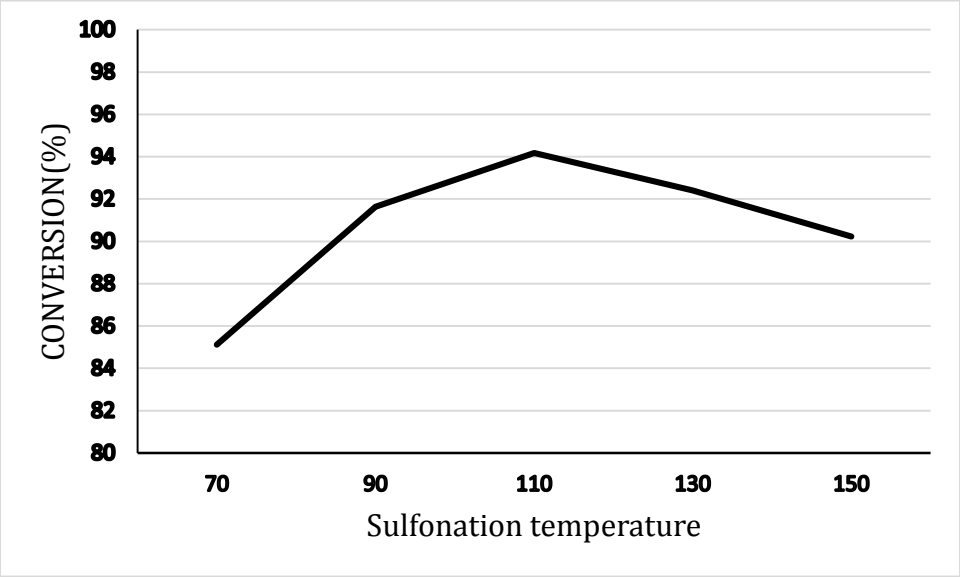


Figure 4.6: Effect of sulfonation temperature on esterification efficiency

4.4 Catalyst performance evaluation in esterification reaction

To illustrate the efficiency of the catalyst in the production of a representative component of biodiesel, the catalytic activity of the sulfonated catalyst in the esterification of oleic acid with ethanol was investigated. The esterification reaction had been carried out in 1000 mL three-necked round bottomed flask with a reflux condenser and stirring rod. And the catalyst with varying dosages was added into the reaction system. After esterification, the liquid products and heterogeneous acid catalyst were separated under vacuum filtration. The generated water and un-reacted ethanol were then removed from the liquid product using rotary evaporator. The conversion of oleic acid into biodiesel, which is used to evaluate catalytic performance of the rice husk based heterogeneous acid catalyst in esterification, has been determined according to the changes of acid value in the oil phase(Eq.3.7). Control studies clearly indicated that sulfonation of the carbons was required for catalytic activity and esterification did not take place without the catalysts. Controls consisted of a method blank

(ethanol plus oleic acid) and catalyst blank (non-sulfonated rice husk char). Reactions (3 g rice husk char, 160 g ethanol, and 100 g of oleic acid) conducted at 90^0C for 2 h indicated no formation of ethyl esters.

4.4.1 RSM experiments and fitting the models

A Box–Behnken center-united design was employed to design the experiments, and the results obtained after running the 17 trials for the statistical design were shown in Table 4.5. The best-fitting models were determined by multi-regression and tested for significance. Table 4.5 also presented the experimental value of conversion and the fitting value of conversion, and then the results indicated a good fit.

Table 4.5: Box Behnken experimental design, experimental and estimated data for three-level-three-factors response surface analysis

Run	Catalyst loading(%)	Molar ratio of ethanol to oleic acid	Reaction time, hr	Conversion(%)		
				Experimental	Estimated	Residual
1	4.5	9	2	95.3	95.48	-0.18
2	4.5	6	1	87.23	87.35	-0.12
3	4.5	12	3	95.75	95.63	0.12
4	4.5	12	1	93.87	93.43	0.44
5	3	12	2	89.03	89.10	-0.069
6	6	12	2	96.5	96.99	-0.49
7	4.5	9	2	95.63	95.48	0.15
8	6	9	1	97.37	95.32	0.049
9	4.5	9	2	95.12	95.48	-0.36
10	3	6	2	80.92	80.43	0.49
11	6	9	3	97.84	97.47	0.37
12	3	9	1	83.32	83.69	-0.37
13	6	6	2	94.66	94.59	0.069
14	4.5	9	2	95.58	95.48	0.098
15	4.5	6	3	90.21	90.65	-0.44
16	3	9	3	87	87.05	-0.049
17	4.5	9	2	95.78	95.48	0.30

The ANOVA for the response surface quadratic model is provided in Table 4.6. It showed that three linear coefficients (A, B, C), three quadratic coefficients (A^2; B^2 ;C^2), one interaction effect(AB) were highly significant and no items were very insignificant($P > 0.5$). A p-value showed that all of the quadratic and linear coefficients were more highly significant than their cross-product terms. However, in order to minimize error, all of the coefficients were considered in the design. According to the ANOVA analysis of factors, we noted a low lack of

fit. This indicates that the model does indeed represent the actual relationships of reaction parameters, which are well within the selected ranges.

Table 4.6: ANOVA for response surface quadratic model analysis of variance

ANOVA for Response Surface Quadratic model						
Analysis of variance table [Partial sum of squares - Type III]						
	Sum of		**Mean**	**F**	**p-value**	
Source	**Squares**	**df**	**Square**	**Value**	**Prob > F**	
Model	406.14	9	45.13	215.34	< 0.0001	Significant
A-Catalyst loading	*243.10*	*1*	*243.10*	*1160.07*	*< 0.0001*	
B-Molar ratio of ethanol to oleic acid	*61.22*	*1*	*61.22*	*292.13*	*< 0.0001*	
C-Time	*15.15*	*1*	*15.15*	*72.31*	*< 0.0001*	
AB	*9.83*	*1*	*9.83*	*46.90*	*0.0002*	
AC	*0.37*	*1*	*0.37*	*1.75*	*0.2279*	
BC	*0.30*	*1*	*0.30*	*1.44*	*0.2686*	
A^2	*39.00*	*1*	*39.00*	*186.11*	*< 0.0001*	
B^2	*19.66*	*1*	*19.66*	*93.83*	*< 0.0001*	
C^2	*10.19*	*1*	*10.19*	*48.65*	*0.0002*	
Residual	1.47	7	0.21			
Lack of Fit	*1.18*	*3*	*0.39*	*5.54*	*0.0658*	*not significant*
Pure Error	*0.28*	*4*	*0.071*			
Cor Total	407.60	16				

4.4.1.1 Development of Regression model equation

Using the designed experimental data, the polynomial model for the conversion of oleic acid was regressed by considering the significant terms and the equation was shown as follows:

$$Y=-2.74375+19.38733* A+6.99492* B+9.33275* C-0.34833* A * B -0.20167* A *C-0.091667* B * C -1.35267* A^2-0.24011* B^2-1.55600* C^2 \quad (4.1)$$

in which Y is the response factor, conversion (%). A, B and C are the values of the independent factors, catalyst loading, oleic acid to ethanol molar ratio, and reaction time respectively. The model coefficients and probability values (coded value) are shown in Table 4.7. The model proved suitable for the adequate representation of the real

relationship among the selected factors. The multiple regression coefficients were obtained by employing a least square technique to predict quadratic polynomial model for the oleic acid conversion (Table 4.7). Hence, the best fitting model was determined. The model was selected based on the highest order polynomial where the additional terms were significant and the model was not aliased as suggested by the DOE software.

Table 4.7: Regression coefficients and significance of response surface quadratic model

	Coefficient		Standard	95% CI	95% CI	
Factor	**Estimate**	**df**	**Error**	**Low**	**High**	**VIF**
Intercept	95.48	1	0.20	95.00	95.97	
A-Catalyst loading	5.51	1	0.16	5.13	5.90	1.00
B-Molar ratio of ethanol to oleic acid	2.77	1	0.16	2.38	3.15	1.00
C-Time	1.38	1	0.16	0.99	1.76	1.00
AB	-1.57	1	0.23	-2.11	-1.03	1.00
AC	-0.30	1	0.23	-0.84	0.24	1.00
BC	-0.27	1	0.23	-0.82	0.27	1.00
A^2	-3.04	1	0.22	-3.57	-2.52	1.01
B^2	-2.16	1	0.22	-2.69	-1.63	1.01
C^2	-1.56	1	0.22	-2.08	-1.03	1.01

The results in Figure 4.7 demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit and splits evenly by the 45 degree line. This result indicates that it was successful in capturing the correlation between the three esterification process variables to the conversion of oleic acid.

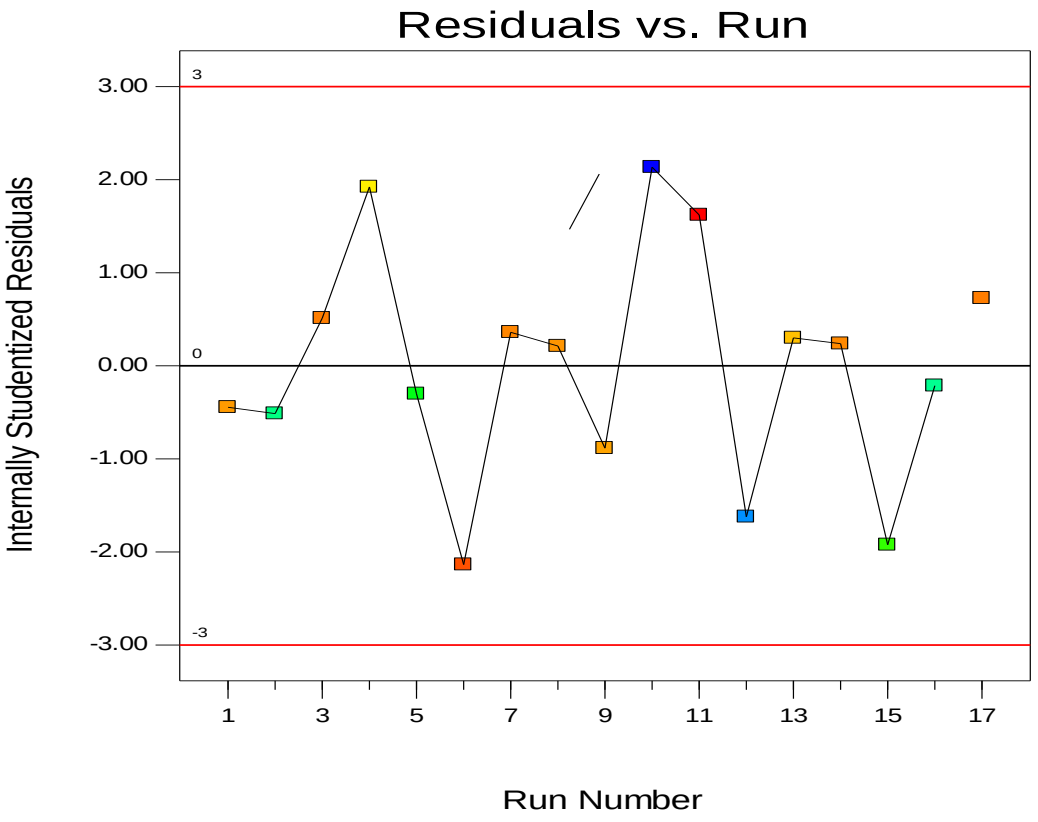
4.4.1.2 Model adequacy check

The model was tested for adequacy by analysis of variance (ANOVA). The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared, adjusted R-Squared and predicted R-Squared (Table 4.8) having a value of 0.9964, 0.9918, and 0.9525 respectively. The Predicted R-Squared of 0.9525 is in reasonable agreement with the Adjusted R-Squared of 0.9918; i.e. the difference is less than 0.0393,

then the model is fitting the data and can reliably be used to interpolate. Adequacy Precision measures the signal to noise ratio. A ratio greater than 4 is desirable i.e. the model has a strong enough signal to be used for optimization. The signal to noise ratio of 48.526 in this case indicates an adequate signal. This model can be used to navigate the design space.

Table 4.8: Sequential model fitting for oleic acid conversion

Source	**R^2**	**Adjusted-R^2**	**Predicted – R^2**	**PRESS**	
Linear	0.7838	0.7339	0.6678	135.41	
2FI	0.8096	0.6952	0.5219	194.86	
Quadratic	0.9964	0.9918	0.9525	19.36	Suggested
Cubic	0.9993	0.9972		+	Aliased



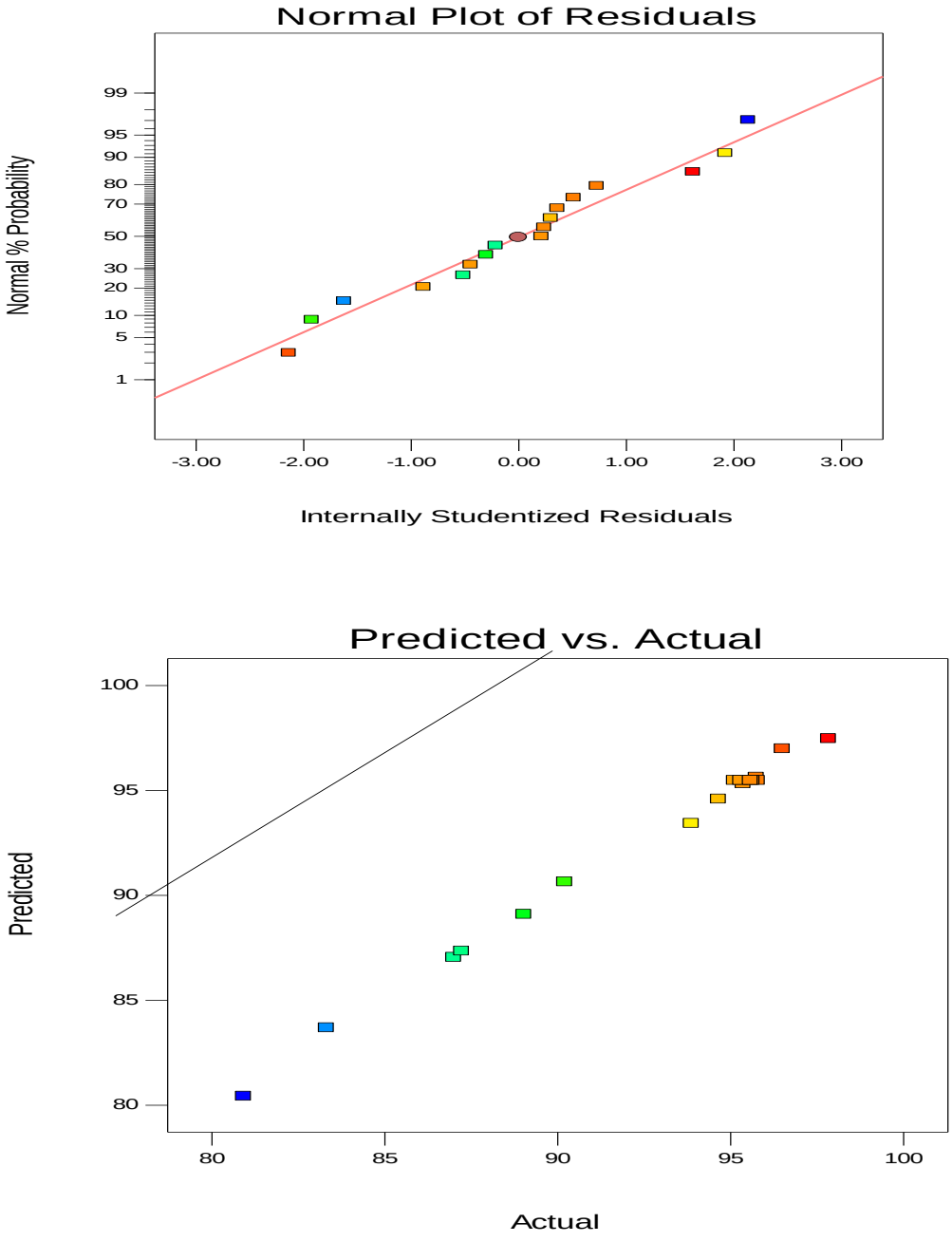


Figure 4.7 Diagnostic plots for adequacy of proposed model

4.4.2 Effect of the process variables on conversion

4.4.2.1 Effect of individual factors on conversion

A. Effect of catalyst loading

The effect of catalyst loading on esterification efficiency is shown in figure 4.8. Esterification reactions usually have low equilibrium constants and require the addition of a catalyst in order to obtain high yields. Catalyst reduces the reaction activation energy, which thus promotes esterification toward the products, and increasing catalyst dosage implies more active sites are available to catalyze the reaction for an enhancement of esterification efficiency. The increase in the reaction rate was due to the increase in the total number of acid sites available for the reaction with increasing catalyst loading. But further increase in catalyst loading does not improve the conversion. This was perhaps attributed to the blocking of the active sites due to formation of multilayer on the support, and the multilayer formation can hinder the reactant molecules to react with the active sites and intern there is only a slight increase in the conversion. Moreover, exceeding catalyst dosage would increase viscosity of the reaction mixture and interfere in the mass transfer between the catalyst and reactants. Therefore, the catalyst dosage has a significant effect on the conversion of oleic acid.

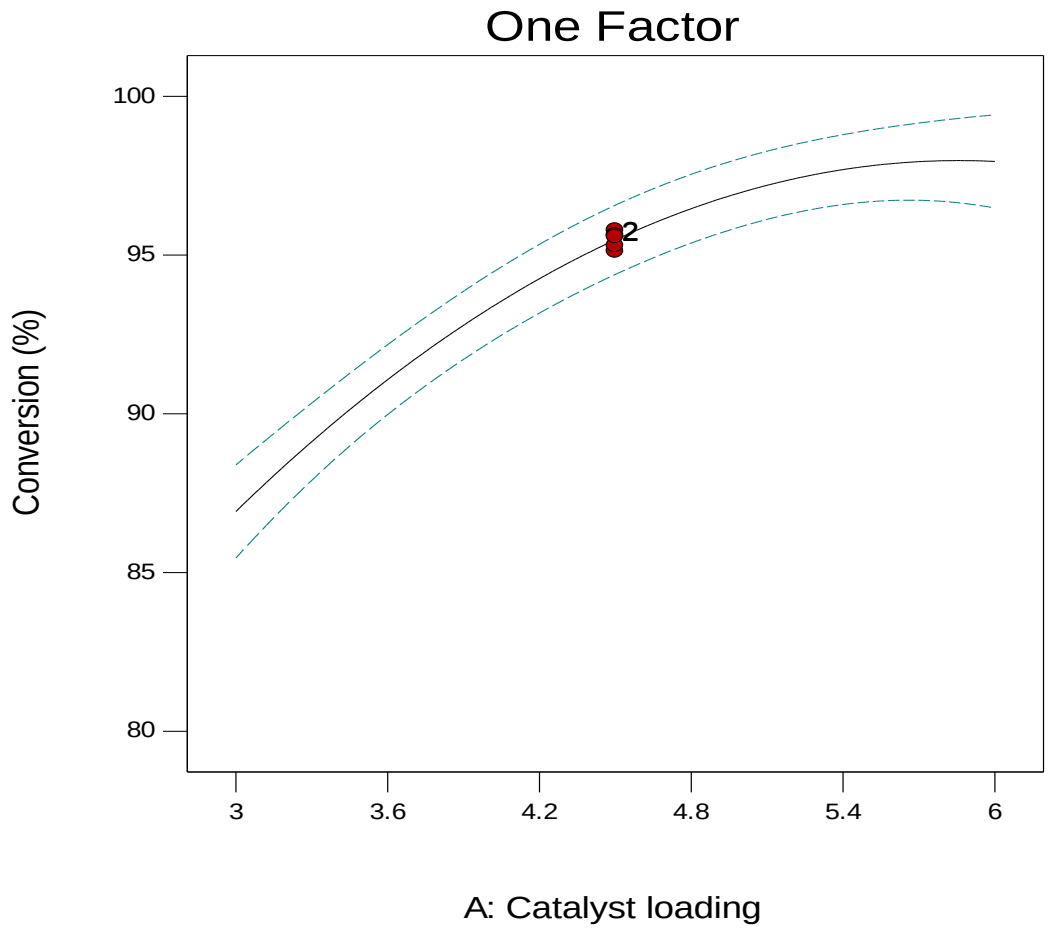


Figure 4.8: Effect of catalyst loading

B. Effect of molar ratio of ethanol to oleic acid

The esterification is a reversible reaction so that excessive alcohol was usually added in order to improve the conversion. The esterification of oleic acid is equilibrium-limited reaction. In order to overcome the equilibrium limitation, generally esterification of oleic acid is conducted by taking ethanol in excess in order to favor the forward reaction where the un-reacted ethanol could be easily separated and recycled through evaporation. In the present work, the effect of different molar ratios of oleic acid to ethanol was studied, and the dependence of oleic acid conversion on the molar ratio of alcohol to oleic acid (6:1–12:1) was then shown in figure 4.9.

It was obvious that the reaction had a faster initial reaction rate and reached a higher final conversion for lower molar ratio of alcohol to acid. The conversion of oleic acid was enhanced while increasing the amount of alcohol, because the excess of ethanol provided more opportunity for reactant molecules to collide and then shifted the reaction equilibrium towards biodiesel. Also, it was observed that the conversion increased with increasing molar ratio of the reactants. However, a slight decrease of conversion was observed when the molar ratio exceeded certain values. This result might be attributed to the saturation of the catalytic surface with ethanol. The further increase of the molar ratio did not result in an increase in the conversion, the ethanol adsorbed on the catalyst surface would accumulate when the ethanol concentration increased to a higher level, which offset the increased conversion or even deactivated the catalyst whereby the esterification was inhibited. Moreover, superfluous ethanol would dilute the esterification system and cover active site of the catalyst, which would lead to the decline in collision frequency and thereby weaken the esterification efficiency. Hence, the molar ratio of ethanol to oleic acid has a significant effect on the esterification efficiency. Moreover, the use of lower molar ratio of ethanol to FFA makes the process more economic and environmentally benign.

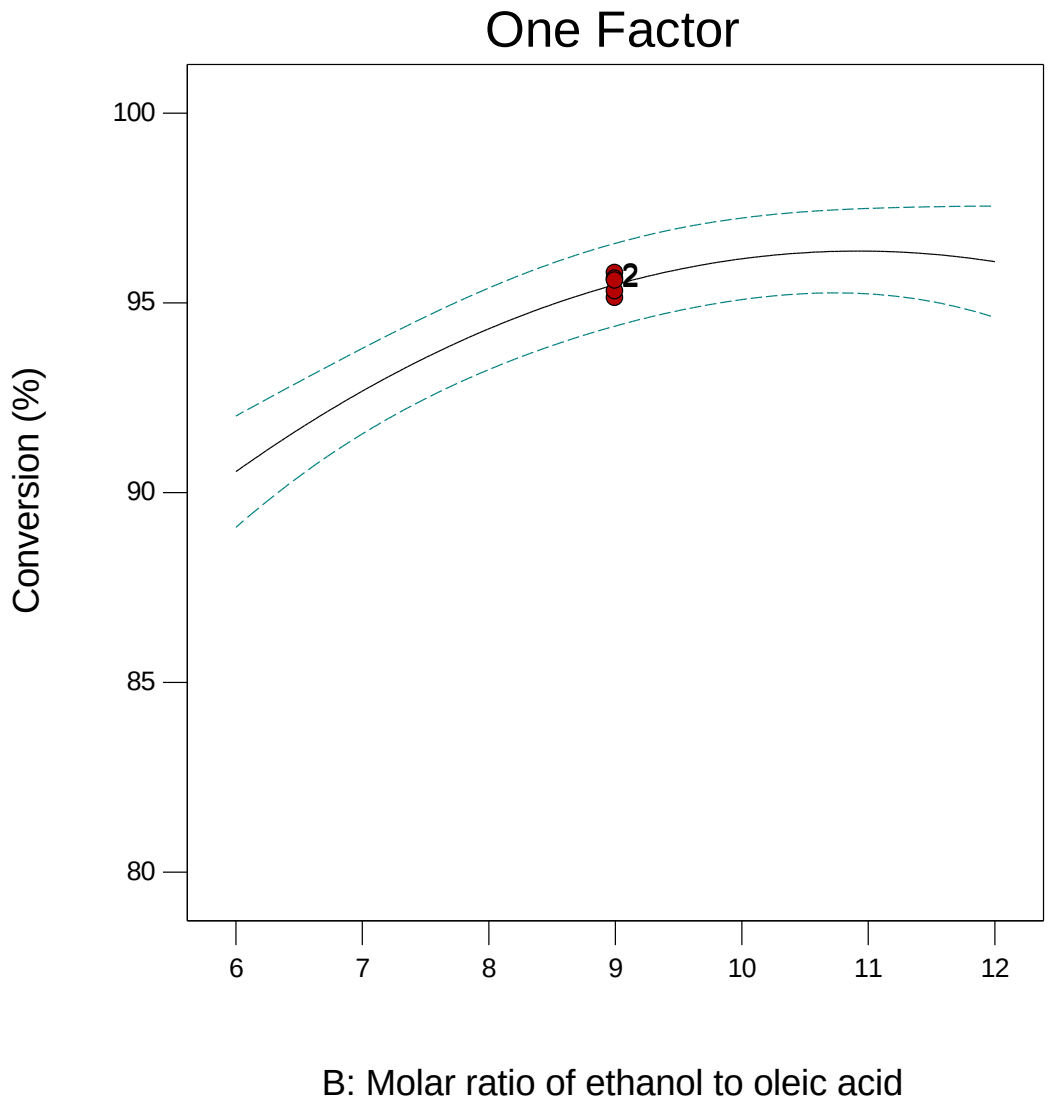


Figure 4.9: Effect of molar ratio of oleic acid to ethanol

C. Effect of reaction time

Esterification efficiency is improved rapidly with reaction duration increase. Nevertheless, the conversion climbs very slowly with duration further increased. For esterification, sufficient duration is obligatory to guarantee the mass transfer among the immiscible phases. But excess of reaction duration would not facilitate the esterification efficiency due to the equilibrium status of esterification.

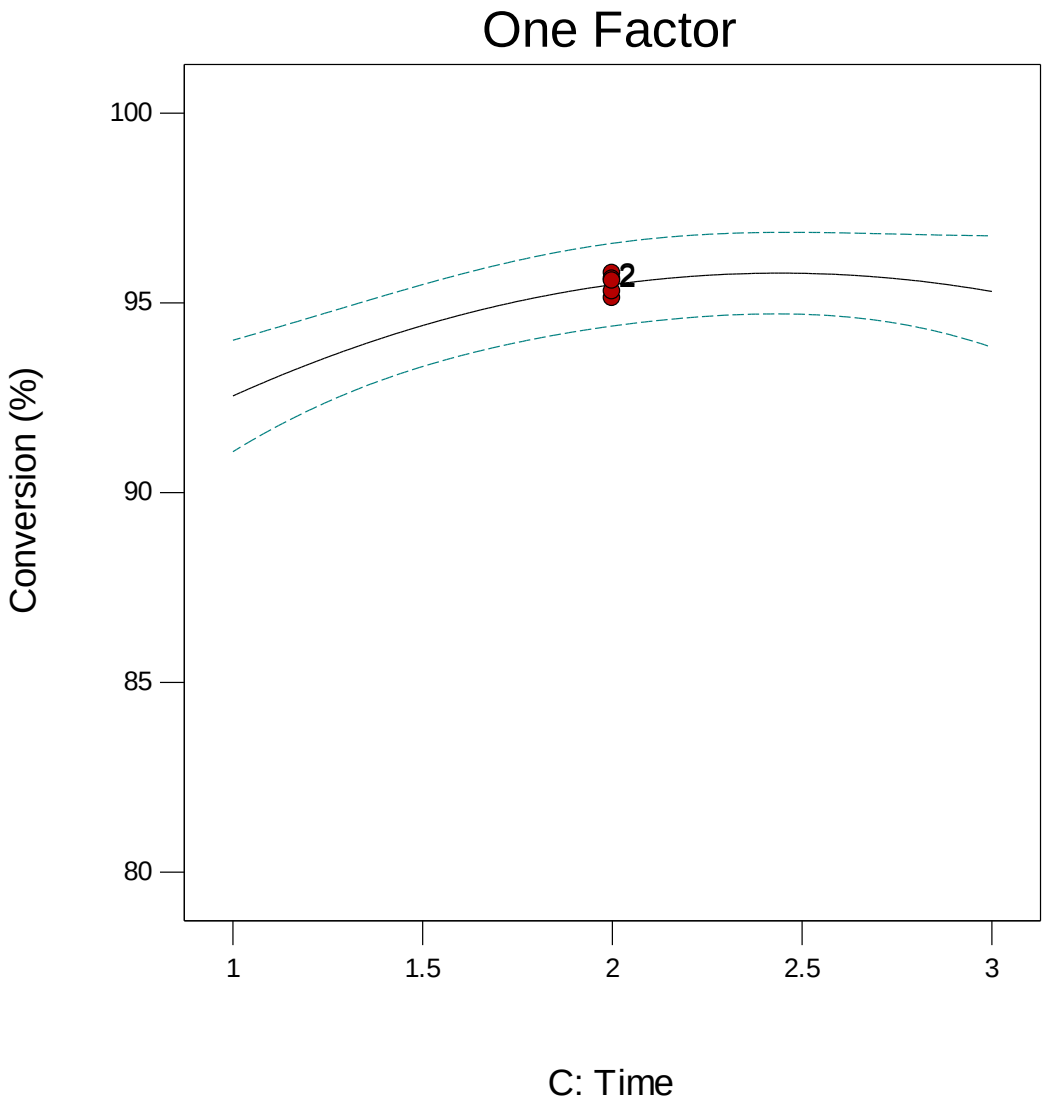


Figure 4.10: Effect of reaction time

4.4.2.2 Interaction effect of Process Variables on oleic acid conversion

The relationships between the parameters were demonstrated clearly by plotting two independent variables with the conversion rate on a three-dimensional contour map. Figure 4.11 shows the conversion rate of oleic acid with the catalyst loading and molar ratio of ethanol to oleic acid. The conversion rate of oleic acid gradually increased to the peak value at high catalyst loadings and then decreased as the molar ratio of ethanol to oleic acid

continued to increase. On the one hand, more active sites of the catalyst were provided by increasing the catalyst loading. Therefore, increasing the amount of catalyst was beneficial to improving the conversion rate of oleic acid. On the other hand, increasing the molar ratio of ethanol to oleic acid could lead to high conversion rates within certain limits. However, excess ethanol would lead to a decline of the conversion rate of oleic acid.

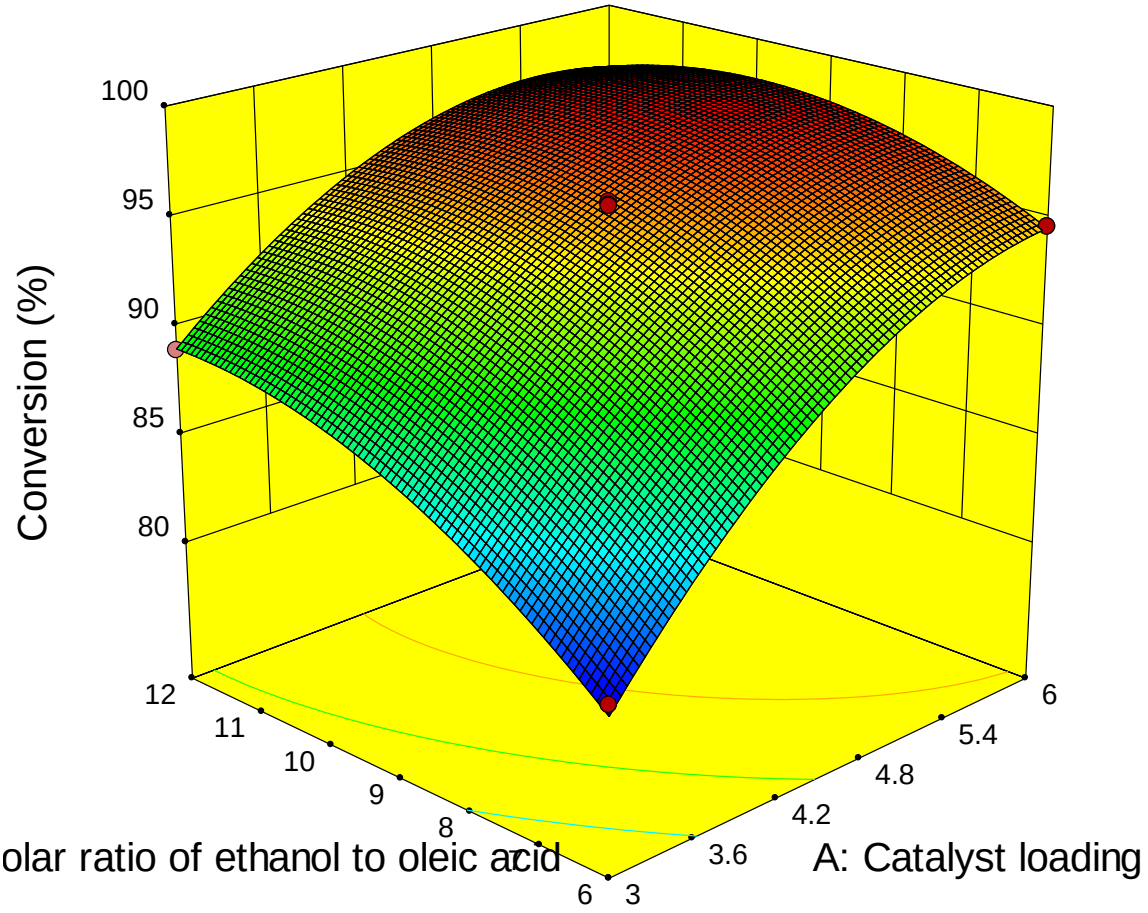


Figure 4.11: Response surface plot of the conversion of oleic acid vs. the molar ratio of ethanol to oleic acid and catalyst loading

The variations of the conversion rate of oleic acid with the molar ratio of ethanol to oleic acid and reaction time were depicted. As shown in figure 4.12, the conversion rate of oleic acid increased to the peak value at low molar ratios of ethanol to oleic acid and long reaction time. In other words, increasing the molar ratio of ethanol to oleic acid did not improve the conversion rate of oleic acid significantly due to the decreased concentration of active catalyst sites in the reaction system. In addition, the hydrogen bonds between ethanol and sulfonic group (-SO_3H) of the catalyst would form easily as a result of the polarity of ethanol, and then the ethanol molecules were adsorbed on the active sites of the catalyst. The inhibition of esterification in the system was mainly caused by the poor accessibility of the catalyst surface when the concentration of ethanol reached a certain level. So the high conversion rates were obtained at low molar ratios of ethanol to oleic acid and long reaction time.

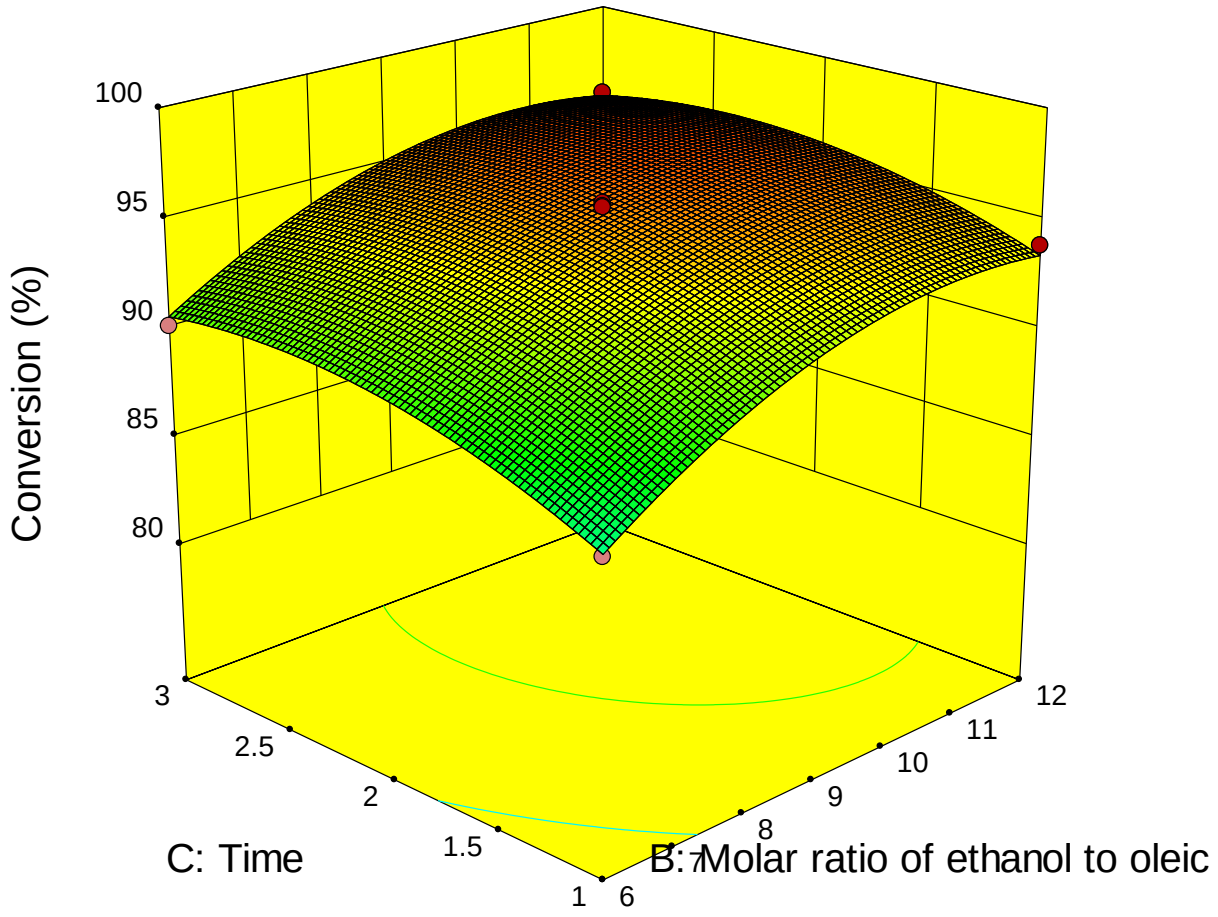


Figure 4.12: Response surface plot of the conversion of oleic acid vs. the molar ratio of ethanol to oleic acid and reaction time

Figure 4.13 presents the interaction between catalyst loading and reaction time with respect to the conversion rate of oleic acid. It is clear that high amount of catalyst and long reaction time favored high conversion rates of FFAs. The conversion rate of oleic acid decreased as the catalyst loading and reaction time reduced. This is possibly due to the decrease of catalyst loading which offered fewer opportunities to make the reactants adsorb on the active sites

of the catalyst. Moreover, prolonging the reaction time could also contribute to increasing the conversion rate of oleic acid.

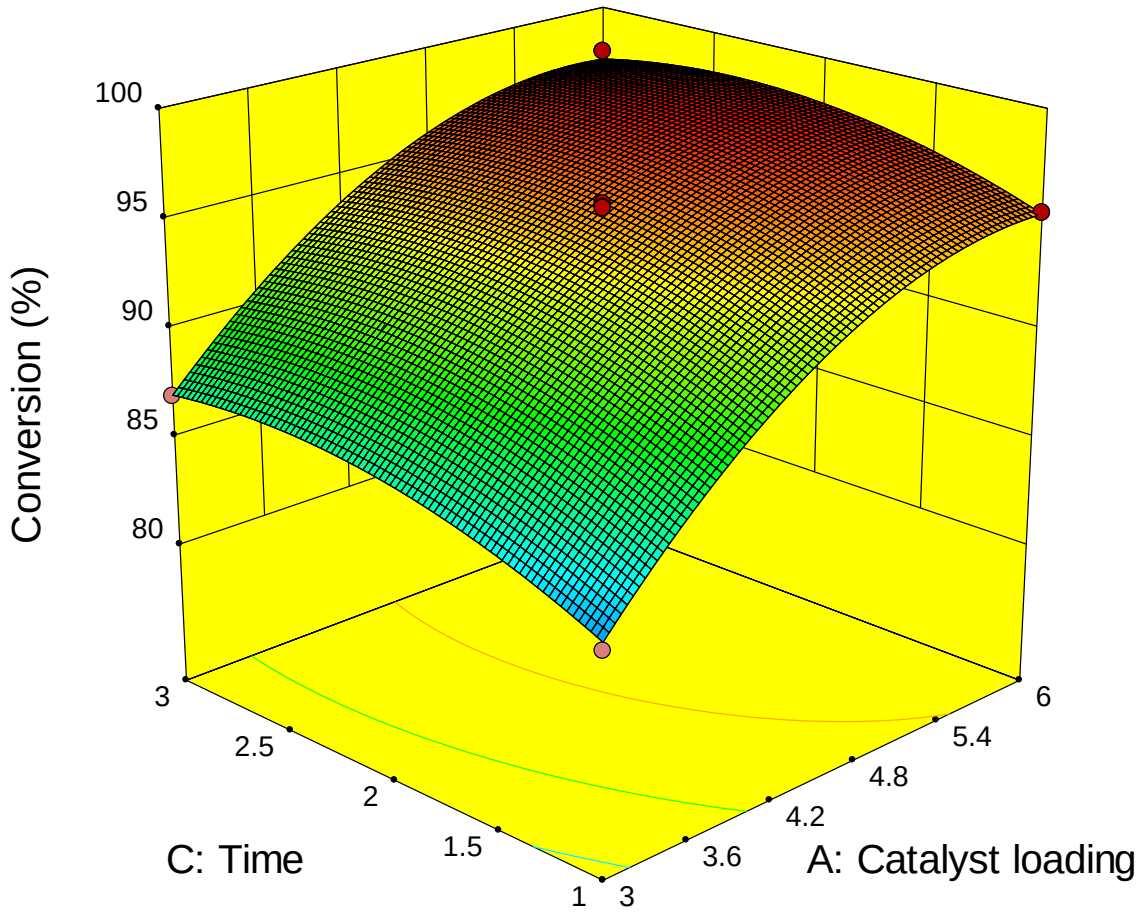


Figure 4.13: Response surface plot of the conversion of oleic acid vs. catalyst loading and reaction time

4.3.3 Optimization of reaction conditions

The optimum conditions for three factors, i.e catalyst loading (A), molar ratio of ethanol to oleic acid (B), reaction temperature(C) were determined using the numerical optimization feature of the Design expert software. The software searched for a combination of factors

that simultaneously satisfied the requirements placed on the response and each of the factors. Table 4.4 shows the optimum working conditions (ultimate goals, high and low limits) of the response (conversion) and factors, employed during the optimization analysis. The optimum conditions obtained were then evaluated by the composite desirability, which has a value from 0 to 1, to determine the degree of satisfactory of the optimum conditions for the ultimate goal of response. In order to obtain the maximum conversion of oleic acid, the predicted combination of parameters was as follows: catalyst loading of 5.73%, ethanol to oleic acid molar ratio of 10.6:1 and reaction time of 2.65 hr. Under these conditions, the model predicted of 98.114% with a desirability value of 1.0.

Table 4.9: Working conditions of response and factors for optimization

Variables	Ultmate goal	Experimental region	
		Lower limit	Upper limit
Catalyst loading(%)	In the range	3	6
Ethanol to oleic acid molar ratio	In the range	6	12
Reaction time(h)	In the range	1	3
Conversion(%)	Maximize	80.56	98.12

To validate the optimum conditions predicted by the model using desirability ramp, triplicate experiments were conducted using the optimized esterification process conditions and mean oleic acid conversion of 97.53% was obtained. The results are closely related with the data obtained from optimization analysis using desirability functions, indicating Box Behnken design incorporate with desirability function could be effectively used to optimize the parameters that affect conversion of oleic acid. Therefore, this research shows that rice husk based solid acid catalyst can definitely be used for esterification of free fatty acids and high conversion can be obtained from the esterification reaction using sulfonated rice husk based catalyst at optimum reaction conditions.

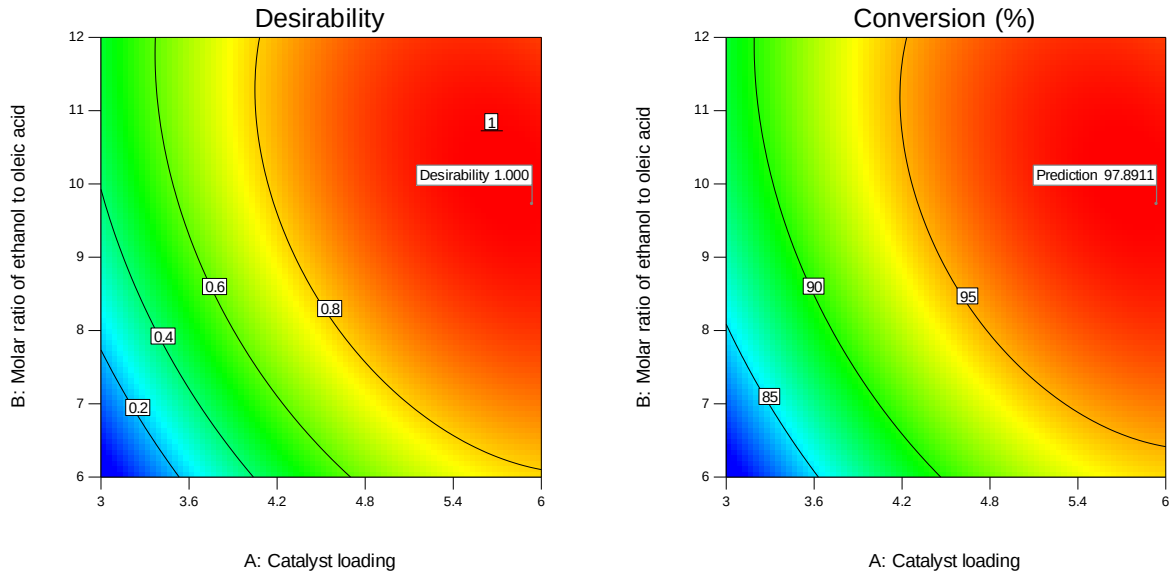


Figure 4.14 Cubic plot of the desirability and the maximum conversion of oleic acid at optimum process conditions

4.5 Catalyst stability

High-grade biodiesel was produced by esterification of the vegetable-oil constituent oleic acid with ethanol where water was also formed as a byproduct. In succession, the generated water would exacerbate the reversible reaction. The stability of a catalyst is an important factor in measuring its performance. In the pre-esterification of waste oils, using a catalyst of good stability will reduce the pretreatment cost, thus lowering the cost of the material for biodiesel production.

In order to investigate the stability of the catalyst prepared from rice husk, esterification reaction had been carried out at optimum reaction conditions and the catalyst was repeatedly used for five cycles. The result showed that there was a slight decrement in the oleic acid conversion over five cycles. This proved that the catalyst had excellent stability. Although the catalyst unfolded and the $-SO_3H$ groups in the bulk could also participate in the esterification when the catalyst was mixed with the reactants, thus enhancing its catalytic activity, leaching of $-SO_3H$ groups from the reaction system might occur. The catalyst recovered after five cycles was characterized by ultimate analysis. The result showed that the sulfur content of the recovered catalyst was 2.46%, a decrease of 24% relative to the

fresh catalyst. Accordingly, it can be inferred that the slight decline in the esterification activity of the catalyst was caused by leaching of some $-SO_3H$ groups; this is in agreement with the results of Mo et al [46].

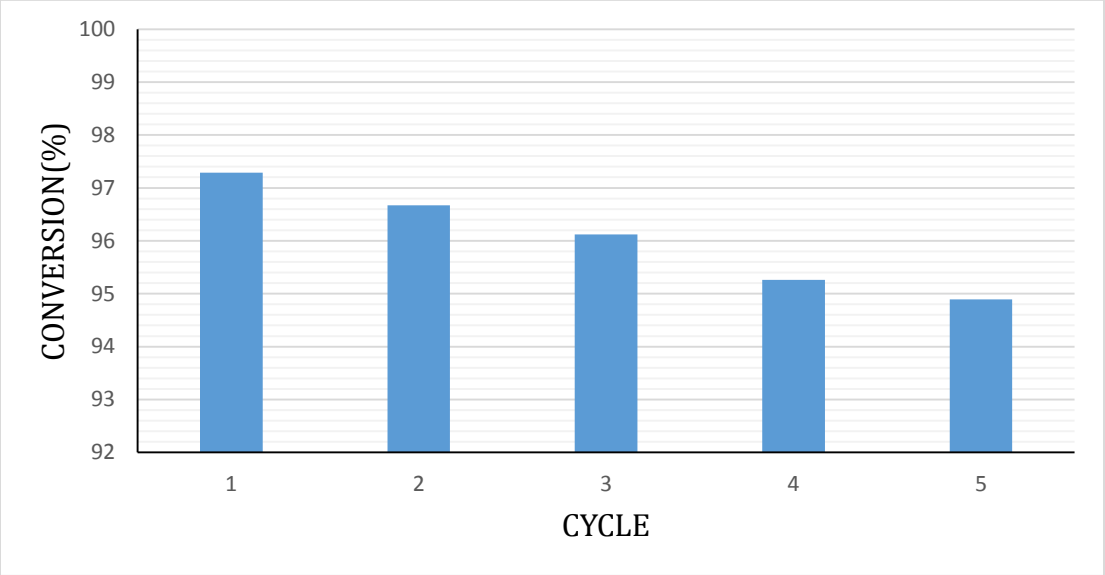


Figure 4.15: Reusability of catalyst

Table 4.10: Ultimate analysis of fresh and reused rice husk based catalyst

Sample	Mass fraction (%)				
	C	H	O	N	S
Fresh catalyst	36.64815	2.3356	56.94745	0.8217	3.2471
Reused catalyst	36.124	2.541	58.036	0.8314	2.4678

4.6 FTIR analyses of esterification product

FTIR spectrum of the esterification product after purification is demonstrated in Fig. 4.16. The weak peak at 3473 cm^{-1} is attributed to C-H bond stretching vibration for alkenes. Two strong bands at 2923 cm^{-1} and 2855 cm^{-1} and one weak peak at 719 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations as well as C-H out-of-plane bending vibration in CH_2, respectively, which confirm the saturated carbon chain in the ethyl oleate. Band at 1743 cm^{-1} is assigned to the C=O stretching vibrations and peak at 1468 cm^{-1} is for

C-H angular deformation in CH_3. The characteristic peak at 1468 cm^{-1} is corresponding to CH_3 asymmetric deformation of the ethyl ester O-C_2H_5 group and peaks at 1376 cm^{-1} and 1185 cm^{-1} are attributed to C-O-C asymmetric vibration and C-O stretching vibration in the ester groups, respectively. Moreover, FTIR spectrum of the purified esterification product is selfsame to the analytical grade of ethyl oleate, which further validates the selectivity and catalytic performance of the rice husk based heterogeneous acid in catalyzing esterification.

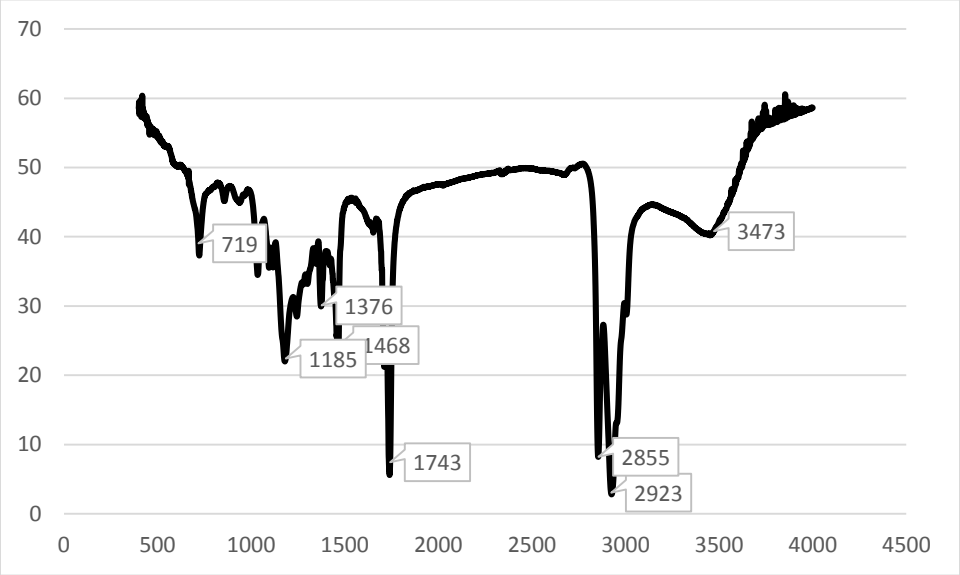


Figure 4.16 FTIR spectrum of esterification product

CHAPTER 5 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Over 15 million tons of sulfuric acid is annually consumed as ‘‘an unrecyclable catalyst’’ which requires costly and inefficient separation of the catalyst from homogeneous reaction mixtures, thus resulting in a huge waste of energy and large amounts of waste products. The ‘‘green’’ approach to chemical processes has stimulated the use of recyclable strong solid acids as replacements for unrecyclable liquid acid catalysts. Solid acid catalysts offer significant advantages, such as easy separation from the reaction system, recycling, eliminating corrosion for the equipment, and reducing the pollutants.

The preparation of the solid acid catalyst from rice husk was simple, rapid and energy efficient. Suitable carbonization temperature and sulfonation temperature were 450 ^{0}C and 110^{0}C, respectively. The catalyst prepared under the optimal conditions had amorphous carbon structure with a large number of sulfonic groups. It exhibited good catalytic activity in the esterification of oleic acid with ethanol, and the oleic acid conversion of 98% was obtained under the best reaction conditions of catalyst loading 5.73%, ethanol to oleic acid molar ratio 10.6:1 and reaction time 2.65 h. The catalyst had excellent stability. Therefore, a novel method for fatty acid ethyl ester (biodiesel) production via the esterification of higher fatty acid with ethanol was proposed, with the advantages in the recycling of waste biomass and the reduction of waste residue.

This study will give alternative approach to the deacidification of oil materials with high acid values in biodiesel production. The rice husk based catalyst presented here has great potential to be a stable and highly active solid acid catalyst and may have broader applications in other acid-catalyzed systems.

In summary, the results support the conclusions that rice husk based catalysts have much higher catalytic activity than other solid acid catalysts and as such are very promising to replace sulfuric acid and other catalysts as a green catalyst for efficient production of biodiesel from higher fatty acids and especially waste oils with a high acid value. In addition,

it is possible that environmentally benign, recyclable rice husk based catalysts may find wide applications in reactions where concentrated sulfuric acid or other acids are currently used as catalysts.

5.2 RECOMMENDATION

Biofuels are renewable solutions to replace the ever dwindling energy reserves and environmentally pollutant fossil liquid fuels when they are produced from low cost sustainable feedstocks. Biodiesel is mainly produced from vegetable oils or animal fats by the method of transesterification reaction using catalysts. Homogeneous catalysts are conventionally used for biodiesel production. Unfortunately, homogeneous catalysts are associated with problems which might increase the cost of production due to separation steps and emission of waste water. Inorganic heterogeneous catalysts are potentially low cost and can solve many of the problems encountered in homogeneous catalysts. Hence, it is recommended to use the rice husk based catalyst in the present study for the production of biodiesel from low cost feedstocks.

The issue of stability for longer catalyst life has been found to be the main problem in most of the heterogeneous catalysts studied so far, hampering their implementation and commercialization in continuous fixed bed reactors. A breakthrough in heterogeneous catalysis and design of catalysts materials necessitates a downstream without further cleaning steps, preparation methods with less complex or refined steps, sustainable and environmentally benign precursors and/or materials as well as reaction conditions, which are less severe to be competitive with today's homogeneous reaction system. Therefore, further research is required on possible causes of catalyst deactivation so that the rice husk based catalyst could be reused for more number of cycles without significant reduction of catalytic activity.

Moreover, the simultaneous esterification and transesterification (SET) catalyzed by the heterogeneous acid has been proved to be the most economic outlook and development potential technology for biodiesel production with low-grade feedstocks, where highly efficient heterogeneous acid catalysts, including zeolites, heteropolyacids, cation exchange

resins have been explored. Thus, it is recommended to study the application of rice husk based catalyst prepared in the present study in simultaneous esterification and transesterification for biodiesel production. I also recommend the textural properties of the catalyst such as surface area, pore volume and pore diameter to be conducted for further analysis.

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APPENDICES

Appendix A: Calculations

Appendix A1: Proximate analysis

1. **Moisture content of rice husk**

   Sample 1

   A. Mass of empty crucible : 36.21 g

   B. Mass of rice husk : 1.0 g

   C. Mass of rice husk and crucible after drying : 37.1316 g

   Moisture content,% = 100-[(C-A)/B]*100%

   =100% -[(37.82-36.21)/1.0]*100% = 7.84%

   Sample 2

   A. Mass of empty crucible : 35.421 g

   B. Mass of rice husk : 1.0 g

   C. Mass of rice husk and crucible after drying : 36.3294 g

   Moisture content,% = 100-[(C-A)/B]*100%

   =100% -[(36.3294-35.421)/1.0]*100% = 9.16 %

   Sample 3

   A. Mass of empty crucible : 35.425 g

   B. Mass of rice husk : 1.0 g

   C. Mass of rice husk and crucible after drying: 36.3322g

   Moisture content,% = 100-[(C-A)/B]*100%

   =100% -[(36.3322-35.425)/1.0]*100% = 9.28 %

2. **Volatile matter content of rice husk**

   Sample 1

   A. Mass of crucible, cover, and sample: 22.7492 g

   B. Mass of rice husk : 1 g

   C. Mass of crucible, cover, and de-volatilized sample:22.108 g

   Volatile matter,% = (A-C)/B = (22.7492-22.108)/1 *100%=64.12%

Sample 2

A. Mass of crucible, cover, and sample: 23.1932 g

B. Mass of rice husk : 1 g

C. Mass of crucible, cover, and de-volatilized sample: 22.5554

Volatile matter,% = (A-C)/B = (23.1932-21.5554)/1 *100%=63.78%

Sample 3

A. Mass of crucible, cover, and sample: 23.6948 g

B. Mass of rice husk : 1 g

C. Mass of crucible, cover, and de-volatilized sample: 23.0769 g

Volatile matter,% = (A-C)/B = (23.6948 -23.0769)/1 *100%=61.79%

3. Ash content of rice husk

Sample 1

A. Mass of empty crucible: 17.05 g

B. Mass of rice husk sample : 1.0 g

C. Mass of sample + crucible after burning:17.2032

Ash content = [((C-A)/B)*100%] = [((17.2032-17.05)/1)*100%]=15.32%

Sample 2

A. Mass of empty crucible: 16.9125 g

B. Mass of rice husk sample : 1.0 g

C. Mass of sample + crucible after burning: 17.0528

Ash content = [((C-A)/B)*100%] = [((17.0528-16.9125)/1)*100%]=14.03%

Sample 3

A. Mass of empty crucible: 17.0841 g

B. Mass of rice husk sample : 1.0 g

C. Mass of sample + crucible after burning: 17.2232 g

Ash content = [((C-A)/B)*100%] = [((17.2232-17.0841)/1)*100%]=13.91%

Appendix A2: Determination of acid density of catalyst

Sampe calculation for catalyst prepared at carbonization temperature of 400^0C and sulfonation temperature of 90^0C

Volume of 0.02 M NaOH: 3.315 ml

$$\text{Total acid density} = \frac{\text{concentration of sodium hydroxide} * \text{Volume of titrate}}{\text{mass of catalyst sample}}$$

$$\text{Total acid density} = \frac{0.02\,\frac{\text{mol}}{\text{l}} * 3.315\ \text{ml} * \frac{1\text{l}}{1000ml}}{0.05\ \text{g}}$$

$$= 1.326\ mmol/g$$

In a similar manner, the total acid density of catalysts prepared at different carbonization and sulfonation temperatures had been determined.

Appendix A3: Determination of Esterification efficiency

Calculation of oleic acid conversion (%)

Oleic acid + Ethanol $\xleftrightarrow{\text{catalyst}}$ Ethyl oleate + Water

282.47 g/mol 46 g/mol 310 g/mol 18 g/mol

$C_{17}H_{33}COOH + C_2H_5OH \xrightarrow{\text{Catalyst}} C_{17}H_{33}COOC_2H_5 + H_2O$

100 g ?

$$\text{Stoichiometric amount of ethanol} = \frac{100\ \text{g} * 46\,\frac{\text{g}}{\text{mol}}}{282.47\,\frac{\text{g}}{\text{mol}}} = 16.285\ \text{g}$$

Thus, the amount of ethanol for 6:1,9:1 and 12:1 molar ratio of ethanol to oleic acid are 97.71 g,146.565 g and 195.42 g respectively.

The amount of catalyst for 3%,4.5% and 6 % catalyst loading are 3 g, 4.5 g and 6 g respectively. The conversion of oleic acid has been determined according to the changes of acid value in the oil phase and calculated as follows:

$$\text{Conversion}(\%) = \frac{\text{AVo} - \text{AV1}}{\text{AVo}} * 100$$

Where AV1 is final acid value and AVo is acid value of oleic acid and it is measured to be 201.6 mg KOH g^{-1}.

The acid value of the esterification product had been determined as;

Volume of 0.1 M KOH: 8.45 ml

$$\text{Acid value} = \frac{\text{Volume of titrate} * \text{Concentration of KOH} * 56.1}{\text{Mass of catalyst sample}}$$

$$= \frac{8.45 * 0.1 * 56.1}{5} = 9.48\ mg\ \text{KOH/g}$$

Then the conversion will be calculated as:

$$\text{Conversion}(\%) = \frac{201.6\ \text{mg KOH/g} - 9.48\ \text{mg KOH/g}}{201.6\ \text{mg KOH/g}} * 100 = 95.3\%$$

The esterification efficiency for the other experimental runs had been calculated in a similar manner.

Appendix B: Laboratory work images and equipments used

1. Catalyst preparation

Figure B1: Equipments used for proximate analysis of rice husk

Figure B2: Experimental set up of the carbonization of rice husk

Figure B3: Experimental set up for Sulfonation of rice husk char

2. Catalyst characterization

Figure B4: Rigaku, mini flex 600 X-ray Diffractrometer

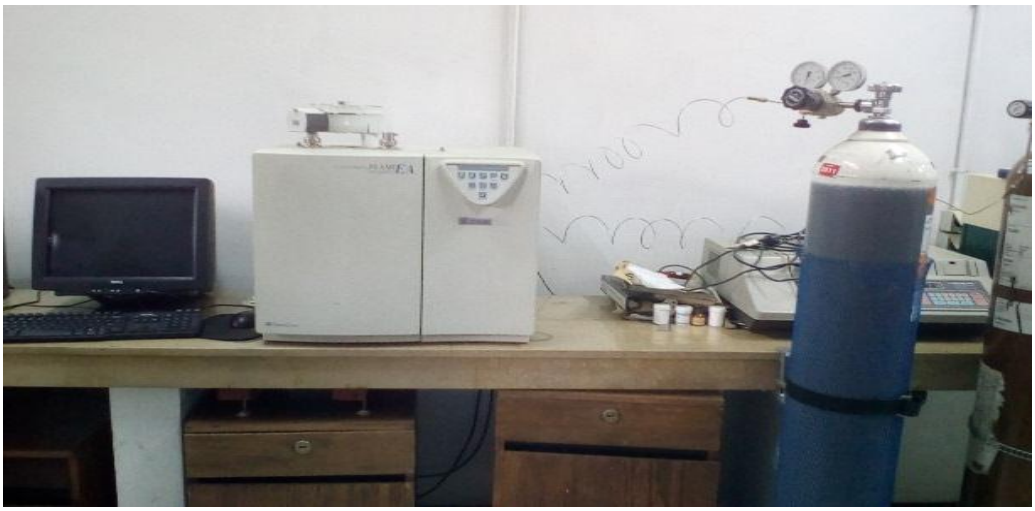

Figure B5: EA 1112 Flash CHNS/O- analyzer

Figure B6: Spectrum 65 FT-IR(PerkinElmer)

Figure B7: SDT Q600 thermogravimetric analyzer

3. Catalyst performance evaluation

Figure B8: Experimental set up for esterification reaction

Figure B9: Rotary evaporator used for product separation