

***KINETIC STUDY OF ESTERIFICATION OF FATTY
ACIDS OVER CALCIUM FERRITE CATALYST***

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ABSTRACT

Biodiesel is a promising renewable alternative fuel to fossil energy. For the biodiesel production from non-edible oil feedstocks like *Jatropha curcas* oil, a pre-treatment step is essential, which is the esterification of free fatty acids in the feedstocks in order to avoid soap formation and minimize catalyst deactivation. The FFA used in this experiment was obtained by two methods which saponification, where oil (*Jatropha* oil) is converting to soap and also acidification, where the sodium salts of free fatty acids are converted to FFA by using hydrochloric acid (HCL). In this research, Calcium Ferrite (CaFe_2O_4) catalyst was prepared for the esterification of FFA. Due to its ability as an effective catalyst and without changing its crystal structure, Calcium Ferrite can yield high conversion of FFA into biodiesel. Calcium Ferrite catalyst was synthesized by Pechini method. Pechini process was newly used in this field of catalyst production. It is a powder-synthesis process that involves the formation of a polymeric precursors (resin), using citric acid and ethylene glycol. The molar ratio for citric acid monohydrate to ethylene glycol used in this experiment was 60:40. The calcinations behavior of the precursor powders of Calcium Ferrite was studied in the temperature range of 450-1200⁰C in an air atmosphere. Characterization of the powder samples were performed using several processes including X-ray diffractometry (XRD), thermogravimetry (TGA) and Brunauer Emmett Teller (BET) analyzer. The effects of reaction temperature, methanol/FFA molar ratio, catalyst concentration on the FFA conversion were also studied. Based on the findings of this study, ethanol to FFA ratio of 30:1, 10 % weight of the catalyst, reaction time of 6 h and temperature 70 ⁰C were found as the optimum for the esterification reaction. Therefore, the developed catalyst could be effectively used for the esterification of FFA in plant oil.

ABSTRAK

Biodiesel adalah bahan api alternatif yang dijanjikan boleh diperbaharui kepada tenaga fosil. Untuk pengeluaran biodiesel daripada bahan yang utama minyak tidak boleh dimakan seperti minyak *Jatropha curcas*, satu langkah rawatan awal adalah penting, yang merupakan pengesteran asid lemak bebas dalam stok utama untuk mengelakkan pembentukan sabun dan mengurangkan pemangkin penyahaktifan. FFA yang digunakan dalam eksperimen ini telah didapati daripada dua kaedah iaitu saponifikasi, di mana minyak (minyak *Jatropha*) ditukarkan kepada sabun dan juga pengeksidan, di mana garam kalium asid lemak bebas telah ditukarkan kepada FFA dengan menggunakan asid haidroklorik (HCL). Dalam kajian ini, Kalsium Ferit (CaFe_2O_4) pemangkin telah disediakan untuk pengesteran FFA. Kerana kemampuannya sebagai pemangkin yang berkesan dan tanpa mengubah struktur kristal, Kalsium Ferit boleh menghasilkan penukaran yang tinggi dalam pengesteran FFA kepada biodisel. Kalsium pemangkin Ferit telah disintesis melalui kaedah Pechini. Proses Pechini itu baru digunakan dalam bidang ini pengeluaran pemangkin. Ia adalah satu proses serbuk sintesis yang melibatkan pembentukan prekursor polimer (resin), menggunakan asid sitrik dan etilena glikol. Nisbah molar asid sitrik monohydrate kepada etilena glikol digunakan dalam eksperimen ini ialah 60:40. Ciri-ciri pengkalsinan daripada serbuk pelopor Kalsium Ferit dikaji di lingkungan suhu 450- 1200 °C dalam udara atmosfera. Pencirian sampel serbuk telah dilakukan dengan menggunakan beberapa proses termasuk Sinar-X (XRD), termogravimetri (TGA) dan Brunauer Emmett Teller (BET) penganalisis. Kesan suhu tindakbalas, metanol / FFA nisbah molar, kepekatan pemangkin pada penukaran FFA juga telah dikaji. Berdasarkan keputusan kajian ini, etanol kepada nisbah FFA daripada 30:1, berat 10% daripada pemangkin, tindak balas masa 6 jam dan suhu 70 °C telah didapati sebagai optimum untuk aktiviti pengesteran. Oleh itu, pemangkin yang telah dibangunkan boleh digunakan dengan berkesan untuk pengesteran FFA dalam minyak tumbuhan.

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LIST OF SYMBOLS

K_1	constant of eq.(1)
K_2	constant of eq.(2)
K_3	constant of eq.(3)
K_{-3}	constant of eq.(3)
K_4	constant of eq.(4)
K_5	constant of eq.(5)
r	rate constant of eq.(6)

LIST OF ABBREVIATIONS

FFA	Free fatty acid
FAEE	Fatty Acids Ethyl Ester
TGA	Thermogravimetric
BET	Brunauer–Emmett–Teller analysis
XRD	X-Ray diffraction
SEM	Scanning Electron Microscopy
CaFe_2O_4	Calcium Ferrite Oxide
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	Calcium Nitrate
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Iron Nitrate
$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$	Nitric Acid
$\text{C}_2\text{H}_6\text{O}_2$	Ethylene Glycol
$\text{C}_2\text{H}_6\text{O}$	Ethanol

1 INTRODUCTION

Since the beginning of the 18th century and early 19th century, energy has become an important source of human needs. This is to maintain stability and economic growth while improving the standard of living. The most of global vital energy production comes from fossil energy. However, this kind of sources has been decreases. Now-a-days petroleum based fuel is used in the world in great quantity but this has the limited reserve so the price is going high. By using the energy-saving, it helps to save the natural resources such as natural gas, oil and water. In addition, it also helps to reduce utility bills. Some of the energy used is a renewable energy. These include solar, wind, geothermal and hydropower. Among this renewable energy source biodiesel is one of the prominent one which is widely used in the world, because this can be converted form wide range of renewable sources (vegetable oil, animal fat, cooked oil etc) and this can used directly in automobile diesel engine without any modification also it can be used varies ratio with diesel.

Biodiesel is the mixture of monoalkyl esters formed by a catalyzed reaction of the triglycerides found in the vegetable oils or animal fats with a simple monohydric alcohol. According to reaction stoichiometry, three moles of alcohol are needed for one mole of triacylglycerol to produce methyl esters. In practice, at least 1.6 times more alcohol is needed for a complete reaction because of that transesterification is a reversible reaction. Methanol and NaOH are commonly used in biodiesel production because of their low cost and high reactivity. The transesterification reaction requires approximately 1 hour at 60 °C. Typically, refined vegetables are used as feedstock for this reaction because excess free fatty acids result in soap formation by reacting with the catalyst (NaOH) and also, transesterification of free fatty acids is very slow. In fact, crude oils, fats or fryer grease has high free fatty acid content. Therefore, this types of acidic feedstock needs to be pre-treated with alkali soaps or acids to remove excess free fatty acids. Similarly, water has the same effect as free fatty acids since it reacts with triacylglycerol to form fatty acids (Emin .S. UMDU ,2008).

There are several types of vegetables oil which suitable to use in production of biodiesel. For example Palm oil, *Jatropha curcus*, and some of selected species of forest seed. Nowadays, there are more than 95% of biodiesel in the world is produced from edible oil. Edible oil is easily to get in largely scale from the agricultural industry. The competition for edible oil

sources as a food with fuel however makes edible oil not a good choice for feedstock of biodiesel production (H.C.Ong et al., 2011). Other reason why edible oil is not suitable as biodiesel is it will cause the global imbalanced, the decreasing of food sources and the capacities for commercial plant growth. Thus, there is a solution to overcome this kind of problem by switching to non-edible oil like Jatropha oil. This kind of plant is unreliable for human nutrition due to contain of toxic compound such as protein curcin and purgative agents. Other than that, by using non-edible oil is less cost in production of biodiesel. (I.B.Bankovic`-Ilic` et al., 2012)

A catalyst is needed for accomplish the synthesizing of biodiesel. There are homogenous acid catalysts such as sulphuric and hydrochloric acids, and homogeneous alkaline catalyst such as potassium hydroxide used in biodiesel synthesis. However, for those types of catalyst, there are disadvantages which constrained more time to produce biodiesel and also corrosive in nature. For other types of catalyst called alkaline catalysts, it will rise up the pH for the biodiesel which need to rinse with water in order to remove the excess catalyst in wastewater generation and as a result the ethyl esters is lost and caused loss of yield. Therefore, to solve these problems, research about heterogeneous catalyst has been introduced where can easily separated. This kind of catalyst also gives a high conversion and yield without any hesitate (YC Sharma, B Singh, J Korstad et al., 2009)

1.1 Motivation and statement of problem

Solid acid (heterogeneous) catalysts have a particular advantage in esterification and transesterification reactions which encourage the use of high acid value oil to be used as feedstock for synthesis of biodiesel. There are lots of solid acid catalysts such as resins, tungstated and sulfated zirconia, polyaniline sulfate, heteropolyacid, metal complexes, sulfated tin oxide, zeolite, acidic ionic liquid, and others have been known as potential heterogeneous catalysts. The activity of the catalyst differs a little for the resulting in moderate to high conversion and yield. The recycle behavior of the solid catalyst is controlled by their deactivation, poisoning, and the issue of leaching in the reaction medium. (YC Sharma, B Singh, J Korstad et al., 2010). Solid acid catalysts have been used in different industrial applications.

The solid acid catalysts vary in acidity, surface area, mechanical resistance, thermal and hydrothermal stability, and cost of production. Researchers had been done their big effort in

order to investigate the use of heterogeneous catalysts instead of use homogeneous catalysts in the production of biodiesel. There are several reason for the development of heterogeneous catalysts include high yield percentage of biodiesel and easier in catalyst separation process, high purity by products, low cost of separation and less energy consumption.

In order to make an improvement on catalyst which tested on esterification of FFA, calcium ferrite has been chosen as a solid catalyst to be produced. Calcium ferrite has the catalytic effectiveness of it is due to the ability of the metallic ions to migrate between the sublattices without changing the crystal structure (I.M Atadashi et al., 2013). This property makes the catalyst efficient for many organic transformation reactions and has a potential to be used for the esterification or tranesterification of a variety of feedstock acids and ester, e.g. for the production of biodiesel. Solid catalysts have been quite successful with high conversion and yield of biodiesel obtained. Details about the catalyst preparation are mentioned in research methodology. This project actually to find the excellent catalyst characteristic which can be optimized the operating condition such as temperature and pressure. The results of the process will be examined in the activity of the catalyst for the esterification of the *Jatropha* oil.

The purpose of this research is to prepare and also to analyze the activity of calcium ferrite catalyst. The thermogravimetric(TGA) analysis will used in order to analyze the mass loss and possible energy transition, calcium iron citrate complex which is the thermal decomposition of the organic precursor (R.A Candeia et al., 2004). In addition, the typical characterization techniques are the Surfer Analyzer BET pore size distribution and surface area, which are established by adsorption and desorption of nitrogen. For the crystalline phase and cell volume measurements, X-ray diffraction (XRD) will introduce, as an external standard (R.A Candeia et al., 2004).

1.2 Objectives

The following are the objectives of this research:

- To prepare and characterize calcium ferrite catalyst and to study the kinetics of esterification of free fatty acid (FFA) of Jatropha oil with low molecular weight alcohol.

1.3 Scope of this research

The following are the scope of this research:

- i) The catalyst will be prepared by using modified Pechini Method.
- ii) For the catalyst will be characterized by using TGA, BET and XRD.
- iii) FFA will be prepared from Jatropha oil by using saponification followed by neutralization reactions.
- iv) The effect of different parameters, such as temperature, reaction time, ethanol/FFA ratio and catalyst concentrations on esterification reaction will be studied.
- v) The kinetic data will be treated in a suitable model.

1.4 Main contribution of this work

The following are the contributions

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a description of the FFA from Jatropha oil. General descriptions on the solid catalyst, as well as the comparison between other catalysts in industries are presented. This chapter also provides a brief discussion of the method used in preparation of the catalyst which is Pechini method. A summary of the previous experimental work on other method of preparation catalyst is also presented. A brief discussion on the experiment of analyzing of FFA contains is also provided.

Chapter 3 gives a complete reviews on chemicals used in the procedures on how to the catalyst be prepared and being characterized by using the equipment such as TGA and BET. After get the catalyst characterization result, the catalyst will be next analyst its activity on the esterification of FFA. The analyzing steps consist of measuring of the percentage of ethyl-ester

content from the esterification process. The result will further discuss in the next chapter which is chapter 4.

Chapter 4 includes the results and discussion based on the effectiveness of catalyst followed by several parameters such as calcined temperature, catalyst concentration, ethanol to FFA molar ratio and reaction time. A brief for calculation on percentage conversion of FFA to ethyl-ester is also presented. The data tabulated and graph is shown inside this chapter.

Chapter 5 will touch about a few recommendations which can be made based on the findings of this study and also the conclusion.

2 LITERATURE REVIEW

2.1 Overview

This paper presents the kinetic study of esterification of FFA over calcium ferrite. The method to prepare the catalyst is using modified Pechini method. Commonly, the sulphuric acid as homogeneous catalyst is used in esterification of FFA. However, the process become complex because neutralization is present. Thus, heterogeneous catalyst study has been introduced due to easier in separation process. The catalyst with high contains of acid and low solubility need to synthesize. In this experiment, calcium ferrite has been introduced. After test the catalyst in esterification process then it will show the percentage conversion for FFA contains.

2.2 Introduction

This paper presents a preparation of heterogeneous catalyst which calcium ferrite by using Pechini process, characterization of the catalyst and also the esterification of FFA form Jatropha oil.

2.3 FFA from Jatropha oil

M. Mofijur et al . , 2012 stated that Jatropha curcas is one of the suitable feedstocks of biodiesel which comes from non-edible oil type and not affected food price and spur the food versus fuel dispute. This kind of plant also can be eco-friendly and promoted many social and economically benefits for Malaysia and can overcome the crisis of energy demand in this country. In addition, for FFA contains Jatropha curcas crude oil (JCCO), Oleic acid consists of high percentage for the composition of FFA in JCCO (G. Corro et al., 2013). It can be refer in the table below for the FFA composition of JCCO.

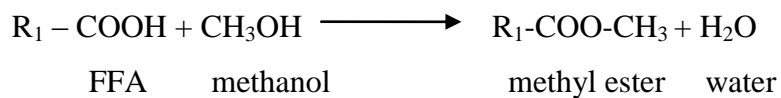
Table 2-1: FFA composition of JCCO (G. Corro et al., 2013)

Free Fatty Acid	wt %
Oleic acid	8.12
Linoleic acid	6.33
Palmitic acid	2.73
Linolenic acid	0.15
Other acids	0.72
Total FFA content	18.05

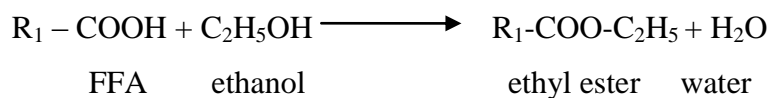
2.4 Esterification reaction

Esterification, as it applies to biodiesel production, is the chemical reaction by which a fatty acid, typically a free fatty acid in a degraded or second-use oil, reacts with an alcohol to produce an alkyl ester and water. The process differs from the transesterification reaction in that the reaction is occurring directly between the alcohol and the fatty acid molecule. The intermediate steps of cleaving the fatty acid chains from the glycerin backbone are not present. For this reason, no glycerin is produced during the esterification reaction.

The following formula shows the basic esterification reaction with methanol. A fatty acid molecule reacts with a methanol molecule to form a methyl ester plus a water molecule:



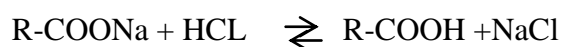
The above formula was adopted from Deshmane (2006) and represents the basic chemical reaction for all industrial esterification reactions using methanol as the alcohol. In this paper, alcohol is placed with ethanol ($\text{C}_2\text{H}_5\text{OH}$) and the formula for all reaction in the experimental section of this thesis as below:



2.5 Need for Esterification

As previously discussed, the esterification reaction of free fatty acids directly into ethyl esters is a favored method of pre-treating degraded oils with high free-fatty acid concentrations in vegetables oil like jatropha curcas oil. Alternative methods involve the saponification where oil is converting to soap. Saponification of oils is conducted by reacting NaOH solution with oil to form glycerol and fatty acids. This reversible reaction needs higher stoichiometric molar ratio of NaOH/oil for complete or great conversion of FFA and so triglyceride. Unconsumed NaOH was then acidified using HCL in acidification process. In

acidification step the sodium salts of free fatty acids are converted to FFA by following reaction:



HCl solution with a FFA/HCl molar ratio of 1/1.5 is added to the soap solution to convert the soap into FFA. Its FFA content was determined by a standard titrimetric method. In order to get high conversion of FFA into ethyl ester in biodiesel production, one modified heterogeneous catalyst has been synthesized from this study.

2.6 Comparison between Homogeneous and Heterogeneous Catalyst

2.6.1 Basic Catalyst for Transesterification and Esterification

There have two types of basic catalyst mainly homogeneous basic catalyst and heterogeneous basic catalyst. The examples of homogeneous alkali catalyst are included sodium hydroxide, potassium hydroxide and sodium methoxide (Leung and Guo, 2006). The examples of heterogeneous alkaline catalyst are basic Mg–Al–CO₃ hydrotalcite catalyst (Barakos et al., 2007), CaO, MgO and CaO/Al₂O₃ (Umdu et al., 2009).

2.6.1.1 Advantages of Homogeneous Basic Catalyst

Homogeneous basic catalyst is mainly used in biodiesel production via transesterification due to several advantages possessed by this catalyst. High yield of biodiesel (> 96%) can achieve under these optimum condition of reaction temperature of 70°C, reaction time of 1 h, catalyst concentration 1 wt% and molar ratio of methanol to oil of 6:1 (Agarwal et al., 2011). This result also have agreement with other researchers that homogeneous basic catalyst can produce biodiesel from neat oil with high yield in low temperature and pressure, short reaction time, low catalyst concentration and low molar ratio of methanol to oil (Ejikeme et al., 2009; Leung and Guo, 2006).

2.6.1.2 Disadvantages of Homogeneous Basic Catalyst

This process required anhydrous condition (Demirbas, 2006) and low content of FFA (Leung and Guo, 2006; Donato et al., 2008; Demirbas, 2006). This is due to presence of water will decrease the yield of the alkyl ester (Demirbas, 2006) while presence of FFA will react with the base catalyst and form saponification product and tend to emulsify the biodiesel and glycerol, resulting difficulty of separating these two products (Leung and Guo, 2006; Donato et al., 2008; Melero, Iglesias and Morales, 2009), consume catalyst and reduce effectiveness of catalyst (Demirbas, 2006; Leung and Guo, 2006).

2.6.1.3 Advantages of Heterogeneous Basic Catalysts

Heterogeneous basic catalyst was developed to overcome the limitation of homogeneous basic catalyst which mainly is separation of catalyst from reaction mixture, generation of waste water during washing stages (Sharma et al., 2010) and reusability of catalyst (Shahid and Jamal, 2011). Besides, the heterogeneous catalyst also preferred due to reusability of catalyst for continuous process. The biodiesel obtained from heterogeneous catalyst were better than those biodiesel synthesized from homogeneous catalyst in term of physical properties of pour and cloud point (Agarwal, 2011).

2.6.1.4 Disadvantages of Heterogeneous Basic Catalysts

However, the heterogeneous base catalyst only can use to covert neat vegetable oil into biodiesel due to it will react with FFA and moisture to form soap and caused deactivation of catalyst respectively (Kouzu et al., 2007). Besides, the catalyst have low stability that the reusability of the catalyst drop after 3 cycles resulted low yield of biodiesel production (Agarwal et al., 2011). In addition, longer reaction duration and higher reaction temperature were needed to improve the yield of biodiesel production (Sharma et al., 2010).

2.6.2 Acidic Catalyst for Transesterification and Esterification

Similar to basic catalyst, acidic catalyst composed of homogeneous catalyt and heterogeneous catalyst. Sulfuric acid, methanesulfonic acid, phosphoric acid and trichloroacetic acid

(Melero, Iglesias and Morales, 2009; Warabi, Kusdiana and Saka, 2004) are the types of homogeneous acidic catalyst while alkyl sulfonic compounds (Melero, Iglesias and Morales, 2009; Warabi, Kusdiana and Saka, 2004), sulfated zirconia (Garcia et al., 2007), and Zirconia supported tungsten oxide (WO_3/ZrO_2) (Ramu et al., 2004).

2.6.2.1 Advantages of Homogeneous Acidic Catalyst

Warabi et al. (2004) concluded that sulfuric acid and methanesulfonic acid were the best catalyst with nearly 90% conversion from triglycerides to biodiesel among phosphoric acid and trichloroacetic acid. Besides, those homogeneous acid catalyst can convert feedstock with high FFA into biodiesel with yield that higher than 90%. This is because homogeneous acidic catalyst can catalyze esterification and transesterification simultaneously to convert the FFA and triglycerides respectively into fatty acid methyl ester without any soap formation.

2.6.2.2 Disadvantages of Homogeneous Acidic Catalyst

However, the disadvantages by using homogeneous catalyst are formation of acidic effluent, no reusable catalyst and high cost of equipment. In addition, it has low catalytic activity that it need long reaction time and high mole ratio of methanol to feedstock (Wang et al., 2006). There have research shown that the usage of sulfuric acid will lead to biodiesel with high sulfur content which cannot fulfill the specification (Melero, Iglesias and Morales, 2009).

2.6.2.3 Advantages of Heterogeneous Acidic Catalyst

Heterogeneous acid catalyst can replace homogeneous acid catalyst to eliminate the problem of equipment corrosion and the treatment of water effluent produced after the process. Besides, heterogeneous acid catalysts can remove easily from the reaction medium through filtration and the catalyst can be recycled for reuse in the new process, thus, no loss of catalyst (Melero, Iglesias and Morales, 2009; Shu et al., 2010). In addition, heterogeneous acid

catalyst has higher stability that able to have high tolerance of free fatty acid without catalyst deactivation (Lotero et al., 2005).

2.6.2.4 Disadvantages of Heterogeneous Acidis Catalysts

However, heterogeneous catalyzed reaction has low catalytic activity (Lotero et al., 2005). Some other group of author also stated that heterogeneous catalyzed reaction requires extreme reaction conditions in order to increase the yield of biodiesel and to shorten the reaction time (Rattanaphra et al., 2012). In addition, high temperature and pressure is needed and higher methanol to oil ratio is needed as well (Melero, Iglesias and Morales, 2009).

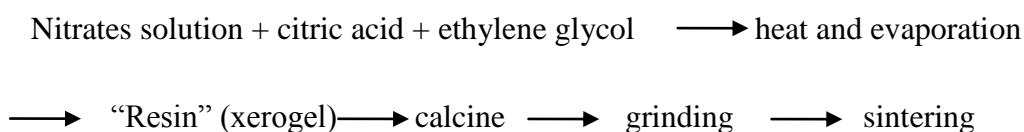
As conclusion, this study is about to determine the conversion of FFA when temperature, amount of alcohol, amount of catalyst and amount of initial FFA used are vary. The amount of catalyst used only affect the time of conversion. However, the final conversion is still the same between different amounts of catalyst used. When molar ratio was varied, the amount of alcohol affects the reaction. When the amount of alcohol is higher, the rate of reaction became slower but it reaches higher conversion of FFA. This reaction however, is hard to separate the catalyst from the product since it is miscible in the product. It has affected the yield gain and the purity of the product will become lower. Catalysis is a mechanism of regulating the rate and direction of a chemical reaction. It can be divided as homogeneous and heterogeneous catalysis. When the catalyst is the equal phase with the reactant, either gas or liquid phase, or no phase boundary exists is named homogeneous catalysis. On the other side, when a phase boundary disentangle the catalyst from reactants is called heterogeneous catalysis. Currently, researchers become more attracted to heterogeneous catalyst in promoting new methods for biodiesel productions due to can be done under comparably mild conditions. In addition, for separation catalyst from product, heterogeneous system is the best choice and accessible to separate rather than used homogeneous system. Therefore, the high demand of processes refers to the heterogeneous system (Ausadasuk, 2006).

2.7 Pechini method in preparation of calcium ferrite catalyst

According to J. Mater. Res., 1992, Pechini Method is The formation of a polyester between citric acid (CA) and ethylene glycol (EG) was found to be a decisive factor for the foaming of

resin intermediates in a Pechini-type powder process. This process was modified by changing the organic/mass ratio of CA/EG which results in ceramic powders with different morphologies. The most porous resin intermediate (with or without chelated cations) was prepared using a polymeric gel made of equimolar citric acid and ethylene glycol. It was also found that a premixing of organic components, prior to adding constituent nitrate solutions, makes the whole process more controllable.

In this powder-synthesis route, citric acid forms poly (basic acid) chelates with the metal cations. These chelates undergo polyesterification, when heated with poly(hydroxy alcohol), such as ethylene glycol, at a temperature of ~150°C to form a polymeric precursor resin. The cations are expected to be dispersed uniformly throughout the polymeric resin. Additional heating of the resin in air (at ~400°C) results in the removal of organics and the formation of a char with a controlled cation stoichiometry, with little cation segregation. Then, the char is heated to higher temperatures and oxidized to form the oxide ceramics, below is the figure and equation for the steps inside Pechini method:



([http://libattery.ustc.edu.cn/chinese/ppt/\(9\)%20Sol-gel%20and%20others.pdf](http://libattery.ustc.edu.cn/chinese/ppt/(9)%20Sol-gel%20and%20others.pdf)).

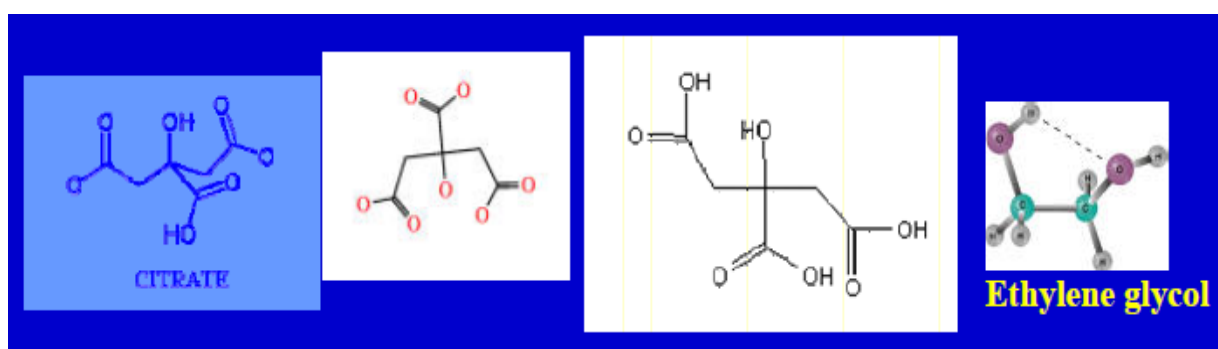
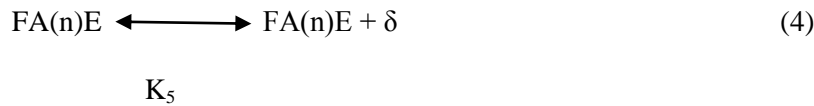
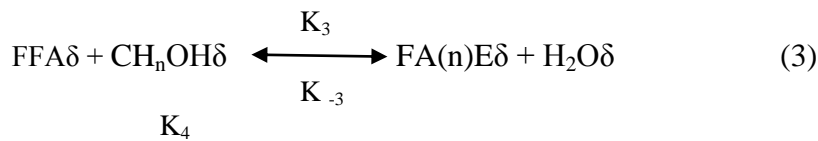
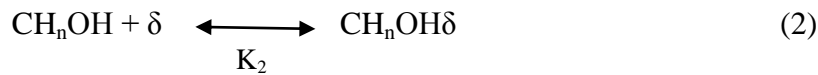


Figure 2-1: Illustration of the polymeric precursor resin by L.-W. Tai and P. A. Lessing (1992)

2.8 Reaction kinetic model

The kinetics of esterification was conducted based on the Langmuir-Heinshelwood (LH) mechanism. It mainly consisted of 5 elementary reactions (δ denoting an active site) (Chin. J. Chem. Eng., 2009):



The kinetic model was built on the following assumption:

- 1) The rate of the non-catalyzed reactions can be neglected compared to the catalyzed ones;
- 2) The sites at the catalyst surface are the same;
- 3) The surface reaction was the rate-control step;
- 4) The adsorption and desorption of reactants and products were fast and at equilibrium.

The rate equation in the rate-control step could be depicted as follows:

$$r = \frac{K_3 K_1 K_2 C_{\text{FFA}} C_{\text{FFA}} C_{\text{CH}_n\text{OH}} - K_{-3} K_4 K_5 C_{\text{FA}(n)\text{E}} C_{\text{H}_2\text{O}}}{(1 + K_1 C_{\text{FFA}} + K_2 C_{\text{CH}_n\text{OH}} + K_4 C_{\text{FA}(n)\text{E}} + K_5 C_{\text{H}_2\text{O}})} \quad (6)$$

where K_1 , K_2 , K_4 and K_5 represent the equilibrium constants of FFA, CH_nOH , $\text{FA}(n)\text{E}$ and H_2O , respectively, and K_3 and K_{-3} represent the rate constants (Chin. J. Chem. Eng., 2009),

$$K_1 C_{\text{FFA}} + K_2 C_{\text{CH}_n\text{OH}} + K_4 C_{\text{FA}(n)\text{E}} + K_5 C_{\text{H}_2\text{O}} \gg 1 \quad (7)$$

3 MATERIALS AND METHODS

3.1 Overview

This study gives a complete reviews on chemicals used in the procedures on how to the catalyst be prepared and being characterized by using the two equipments such as TGA and BET. After get the catalyst characterization result, the catalyst will be next analyst its activity on the esterification of FFA. The analyzing steps consist of measuring of the percentage of ethyl-estercontent from the esterification process.

3.2 Introduction

This paper presents a preparation of solid heterogeneous catalyst which calcium ferrite by using Pechini process, characterization of the catalyst and also the esterification of FFA form Jatropha oil.

3.3 The Sample Materials

This paper presents the chemical that has been purchased from The Fisher Scientific supplier by lab technical unit officer and also from supervisor to produce the calcium ferrite catalyst.

The materials that will be used to prepare the catalyst are as in the **Table 3.1** follow.

Table 3.1: Experimental materials

Name	Structure	Purity
Calcium Nitrate	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	99%
Iron Nitrate	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	99%
Citric Acid	$\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$	99%
Ethylene Glycol	$\text{C}_2\text{H}_6\text{O}_2$	99%
Ethanol	$\text{C}_2\text{H}_6\text{O}$	99%

3.4 Apparatus and Instruments

Table 3.2 shows experimental instruments and apparatus used in this experiment.

Table 3.2: Experimental instruments and apparatus

Apparatus	Model
Stirring Hot Plate	Favorit
Oven	Memmert
Centrifuge Spin Rotor	Eppendorf
Muffle Furnace	Carbolite
Agate Mortar and Pestle	MTI