CONTINUOUS TRANSESTERIFICATION FOR TUBULAR REACTOR

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ABSTRACT

Biodiesel production has been use for transportation to replace the petro diesel in Europe country since end of twenty century due to the gasoline and petroleum limitation. Biodiesel are produce from the waste cooking oil through the process of transesterification reaction and assisted by microwave. Transesterification is the most comment process for produce the biodiesel whereby microwave assisted to change the triglyceride(vegetable oil) to biofuel by adding the activated cement clinker (catalyst) and methanol in the condition 60°C with 6 minutes reaction time.The heterogeneous base catalystactivated cement clinker is chosen to use with several advantage such as reusable, environmental friendly and low costs. The microwave assisted in transesterification can reduce the reaction time and also increase the product yield. The catalyst made from cement clinker is activated by potassium hydroxide solution which characterized by several type of test such as Thermogravimetric Analysis, Brunauer-Emmett-Teller test, X-ray Diffraction test and Gas Pyrometer test. The parameter was determiningfor produce the biodiesel by using the activated cement clinker catalyst with the weight ratio(2, 3, 4, 5 and 6% wt.). The result was analysed by using gas chromatography (GCMS) showed that 5% wt. of activated cement clinker use are the optimum amount which having 92.85% conversion and 85.26% yield. For the conventional method by using activated cement clinker and pure calcium oxide obtained 92.63% and 85.37% yield respectively. Based on the yield result, transesterification assisted by microwave method is the best method for the reaction compare with conventional method.

Keywords: Transesterification, Thermogravimetric, Brunauer-Emmett-Teller.

ABSTRAK

Pengeluaran biodiesel telah digunakan untuk pengangkutan untuk menggantikan diesel petroleum di Eropah negara sejak akhir abad ke dua puluh kerana petrol dan petroleum yang terhad. Biodiesel adalah hasil daripada sisa minyak masak melalui proses reaksi transesterification dan dibantu oleh ketuhar gelombang mikro. Transesterification adalah proses komen yang paling untuk menghasilkan biodiesel di mana gelombang mikro dibantu untuk mengubah trigliserida (minyak sayur) dengan biobahan api dengan menambah klinker simen diaktifkan (pemangkin) dan metanol dalam keadaan 60 ° C dengan 6 minit masa tindak balas. Yang heterogen asas pemangkin simen klinker diaktifkan dipilih untuk digunakan dengan beberapa kelebihan seperti yang boleh digunakan semula, kos rendah dan mesra alam sekitar. Ketuhar gelombang mikro akan membantu dalam transesterification boleh mengurangkan masa tindak balas dan juga meningkatkan hasil produk. Pemangkin diperbuat daripada simen klinker diaktifkan dengan larutan kalium hidroksida yang terdiri daripada beberapa jenis ujian seperti Analisis Termogravimetri, ujian Brunauer-Emmett-Teller, sinar-X dan ujian Belauan ujian Gas pengukur api. Parameter ini menentukan untuk menghasilkan biodiesel dengan menggunakan diaktifkan pemangkin simen klinker dengan nisbah berat (2, 3, 4, 5 dan 6% berat.). Hasilnya telah dianalisis dengan menggunakan kromatografi gas (GCMS) menunjukkan bahawa 5% berat. diaktifkan penggunaan simen klinker adalah jumlah yang optimum yang mempunyai 92,85% penukaran dan hasil 85,26%. Untuk kaedah konvensional dengan menggunakan diaktifkan klinker simen dan kalsium tulen oksida diperolehi hasil 92,63% dan 85,37% masing-masing. Berdasarkan keputusan hasil, transesterification dibantu oleh kaedah gelombang mikro adalah kaedah terbaik bagi tindak balas bandingkan dengan kaedah konvensional.

Kata Kunci: *Transesterification, Termogravimetri, Brunauer-Emmett-Teller.*

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1 INTRODUCTION

1.1 Motivation and statement of problem

Increasingdevelop industrialization and motorization from 20 Century until today fossil fuels required up to 80% of the primary energy consumed in our planet(Poonam and Anoop , 2011).In this 80% of energy consumption, 58% alone is consumed by the transport sector (Gaurav and Sharma, 2014). This is the main causes of crisis of the energy sources. So that, limited sources of petroleum and gasoline are directly proportional increase due to the demand increase(Soo, 2011). Because of the limited resources, scientist are try to find a new source which having a same properties as petroleum and gasoline. The type of fuel produces from animal or plant oil and known as Biodiesel.

For Long-chain of fatty acid and mono-alkyl ester actually is defined as biodiesel from the renewable feedstock (F.Manzano-Agugliaro et al., 2012).Vegetable oil and animal fat contain mono-alkyl ester which defined as biodiesel component(Zuraida and Hameed, 2011). The environmental friendly for the biodiesel also as the biggest advantage compare with the gasoline and petroleum. Biodiesel are similar with petroleum diesel which are contains regulated pollutants. On the other hand, biodiesel probably has better efficiency than gasoline(Gaurav and Sharma, 2014). Compare the costs of combustible vegetable oil are higher than the fossil fuel process diesel. So this is the most disadvantages for the biodiesel production.So that, low price raw material like waste cooking oil and non-edible oils such as *Jatropha* are chosen for the transesterification process(Borges and Diaz, 2012).

Biodiesel production is the process to produce the biodiesel by using Transesterification and esterification reaction(Lopez et al., 2008).Transesterification is the most comment process whereby microwave assisted to change the triglycerides (vegetable oil) to biofuel by adding the catalyst and methanol in the condition 60°C- 65°C. In the process of transesterification, triglyceride will react will convert to diglycerides. After that, diglycerides convert to monoglycerides and finally become glycerol. Each of the converting process will produce a methyl ester (Kumar et al., 2011).

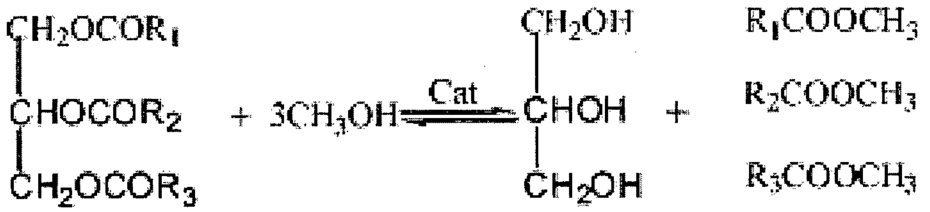


Figure 1: Transesterification by triglycerides react with methanol (Xie et al., 2006).

The catalysts in thetransesterification process are usuallyhadthree types which are homogeneous, heterogeneous and enzymatic catalyst. First type is homogeneous alkaline catalysts, example of catalyst such as NaOH or KOH, and acid catalysts such as H_2SO_4 or HCl(Su., 2013).Homogeneous catalysts are having better reaction efficiency compare with heterogeneous catalysts(Zhao et al., 2013).However,the separation process for the biodiesel and the catalyst are very costly anda large amount of water is required to transfer the catalysts from the organic phase to a water phase after the reaction(Konwar et al., 2014). Therefore, it is considerably more costly to separate the catalyst from the produced solution (Liu et al., 2008). Moreover, the process wastewater is environmentally toxic because of its high basicity caused by the homogeneous alkalinecatalyst(Ilgen., 2011). Furthermore, the separation of the homogeneous base catalysts following the reaction is the key problem and the water-bath process might initiate the emulsification or saponification reaction(Ming et al., 2011).

For the enzymatic catalyst, have several of enzymes can be used as catalyst in transesterification such as *pseudomonas*cepacia, *candidaantarctica* and *Baciliussubtilis encapsulated*(Lam et al., 2010).The advantage of enzymatic catalysis is enables byproduct separation conveniently at moderate temperature which also can produces high purity of biodiesel (Li et al., 2012),transesterification can be implemented at low temperature, even lower than the reaction for using a homogeneous base catalyst process; But for the disadvantages arethe reaction rate are very slow even slower than the transesterification process by using heterogeneous catalyst for conventional heating and having very high costs for lipases limits its industrial application(Poonam and Anoop , 2011).So enzymatic are still no very suitable used for industrial purposes.

Heterogeneous catalyst also a common catalyst used in transesterification process. There are several advantages for using the heterogeneous base catalyst compare with the homogeneous base catalyst for biodiesel production. Heterogeneous base catalysts are reusable, noncorrosive(Dehkordi and Ghasemi, 2012), show greater tolerance to water and free fatty acids (FFAs) in feedstock, improve the purity and yield of the biodiesel, purification process are simple due to remove the glycerol and are easy to separate from the biodiesel product. Therefore, many heterogeneous base catalysts for the transesterification of oils have been applied in industry propose(Ming et al., 2011).

For heterogeneous base catalyst; one of the most common catalysts is CaO for the transesterification of vegetable oil. A lot of advantage for solid base catalystCaO in producing the biodiesel, such as higher activity, mild reaction conditions, and reusable and low cost(Liu et al., 2008). The activated calcium oxide produce from cement clinker is use for the transesterification due to low cost and easily to obtain in Malaysia(Jolius et al., 2013). Calcium oxide (CaO) having a lot of industrial applications. The use of CaO as a heterogeneous catalyst hasbeen around for many years.Peterson and Scarrahreported on the transesterification of rapeseed oil using CaO in 1984. Thefindings proved CaO as a good potential solid catalyst in transesterifyingtriglycerides to methyl esters. Since then, many researchers havereported on the use of CaO as a heterogeneous based catalyst in process of transesterification to producebiodiesel. Unlike many other solid catalysts, CaO could be preparedwithout very complicated method.

Several amounts of researchers has been investigated, theimportant variables that will affect the transesterificationreaction, the reaction temperature, the amount of catalyst(2, 3,4,5 and 6% wt. of the oil), the ratio of alcohol to vegetableoil(1:4, 1:6, 1:8, and 1:10for the weight of oil), the mixing intensity and the reaction time (30,60, 90 and120min). Besides that, number of the catalyst reusable also need to test and analysis the remaining catalyst. In the investigation, the experiment needed the equipment such as S-type microwave, centrifuge, and gas chromatography help to complete the task.

1.2 Objectives

The following are the objectives of this research:

- Catalyst study for making activated cement clinker
- Reaction study for producing the biodiesel from waste cooking oil via microwave assistedtransesterification and conventional method using a limestone-based heterogeneous catalyst.

1.3 Scope of this research

The following are the scopes of this research:

i) To prepare and characterize the catalyst

ii) To perform microwave assisted of waste cooking oil

iii) To purify methyl ester and compare with the literature

iv) To study effect of catalyst loading and also compare with the conventional method of transesterification by using activated cement clinker with pure calcium oxide.

1.4 Main contribution of this work

Thesis research presented the production of biodiesel from waste cooking oil. Biodiesel is well known as one of the main sources for replacing the petrol diesel. A lot of countries are using biodiesel such as Europe country and India. Biodiesel has same identity as petrol diesel.In addition, biodiesel are environmentally friendly which can protect the earth away from air pollution.

1.5 Organisation of this thesis

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

Chapter 2 briefly describe the different between esterification and transesterification process in biodiesel production. The catalyst characterization is presented. A comparison of various extraction technique and different oil type in transesterification were discussed. Besides, catalyst selection for the previous experiment work on the transesterification process was reviewed.

Chapter 3 presentedthe materialsused and methodology done for the research. It covers the procedures from oil preparation, catalyst activation characterization, biodiesel separation and final product properties determination.

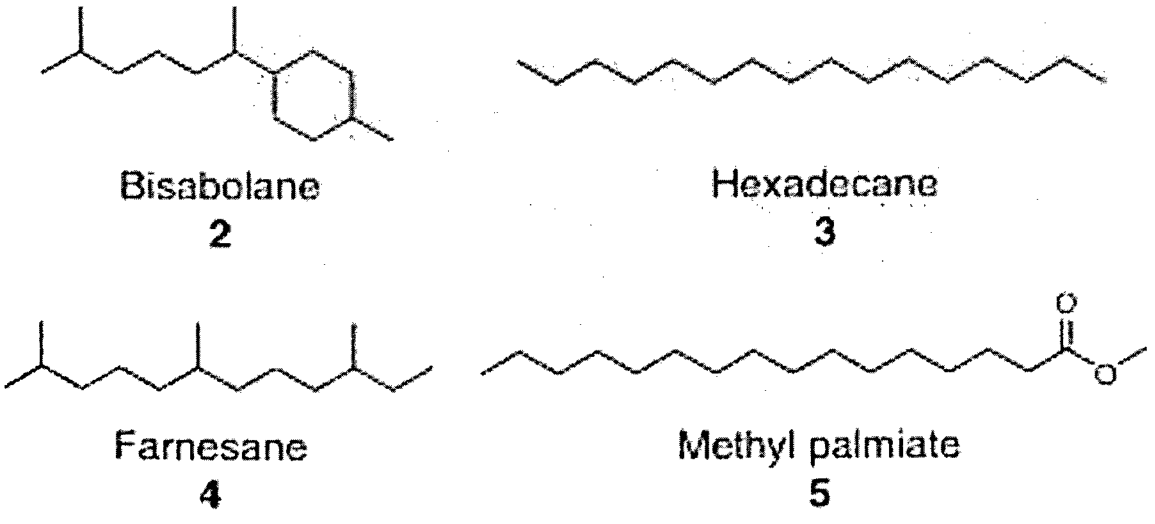
Chapter 4 are discussed on the results obtained from the experiment work.The various catalysts catalyst characterization method, i.e.,Thermogravimetric analysis (TGA), Gas Pynometer, Scanning Electron Microscope (SEM), Brunauer-Emmett-Teller analysis (BET), X-ray diffraction (XRD) and Energy-Dispersive X-ray spectroscopy (EDX) were discussed.The finding obtained from the reaction study for different catalyst weight loading measured by using the gas chromatography.

Chapter 5summarized the overall motivation methodology and finding of the thesis and the outlines of the future work.

2 LITERATURE REVIEW

2.1 Overview

Biodiesel mainly contain of long-chain fatty acid methyl ester (FAME). There are various types of FAME, as shown in Figure 2-1. Biodiesel is produced, through the chemical reactions transesterification and esterification. The reaction involved in transesterification and esterification is shown in Fig. 1 (Ghoreishi and Moein. , 2013). Transesterificationisa bypass process which from triglyceride (from plant or animal oil) reacts with three alcohol (normally use methanol) to produce fatty acid methyl ester (FAME) and glycerol directly. But the biodiesel cannot directly produce from the plant or animal oil through the esterification. In the esterification process, triglyceride needed to transformed into free fatty acid and then react with alcohol molecule (normally use methanol) to produce FAME and water. This process involves reaction between vegetable or animal fat and oils with the short –chain alcohols(F.Manzano-Agugliaro et al., 2012).In this work, productions of biodiesel were performed using transesterification method since the purpose of transesterification reaction to changing or reduce the oil viscosity become identical with the petro diesel. This chapter discussed on the various catalyst characterization techniques. Besides, the comparison of different extraction methods at different operating conditions and different types of catalyst were presented.



Bisabolane
2

Hexadecane
3

Farnesane
4

Methyl palmiate
5

Figure 2-1: Example for fatty acid methyl ester(F.Manzano-Agugliaro et al., 2012).

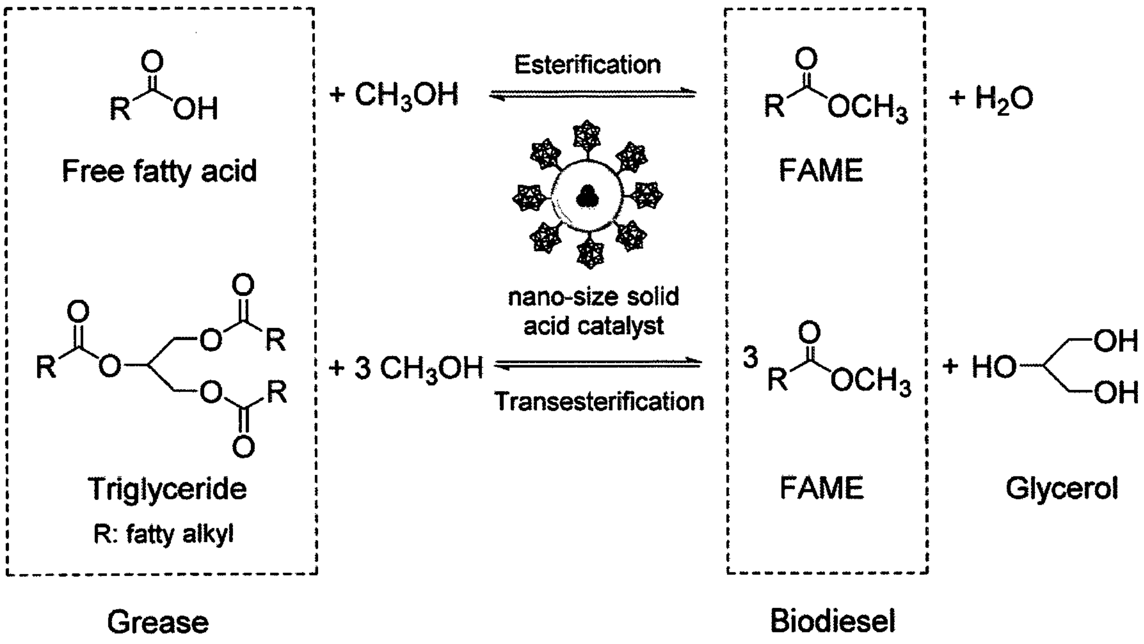


Figure 2-2: Reaction mechanisms for the esterification and transesterification(Ghoreishi and Moein. , 2013).

2.2 Catalyst characterization method

2.2.1 Gas pycnometer

The gas pycnometer is non-destructive techniques to the sample testing for density measurements. The gas pycnometer has a high precision of measurementwhereaccuracy of an order of 5×10^{-5}. Ordinary, the density of the sample are measured by using Archimedes technique. This technique is very sensitive to several parameters (i.e., bubble surface tension, chemical changes, and calibration of the fluid dencity), so attentionis must when doing the measurement(Westwood and Kabadi, 2003).However, the accuracy is limited to0.02 g/cm^3. To improve the accuracy of the gas pycnometer technique, it has been developed in glove box.The determinations of the sample by measuring the variations of helium gas pressure in a calibrated volume were performed by using thepycnometer. Boyle and Marriott law were employed(Ast et al. , 2007).Helium gas is used as medium in the gas pycnometer to calculate the volume of the sample. From the volume of sample, the density of sample can be defined.

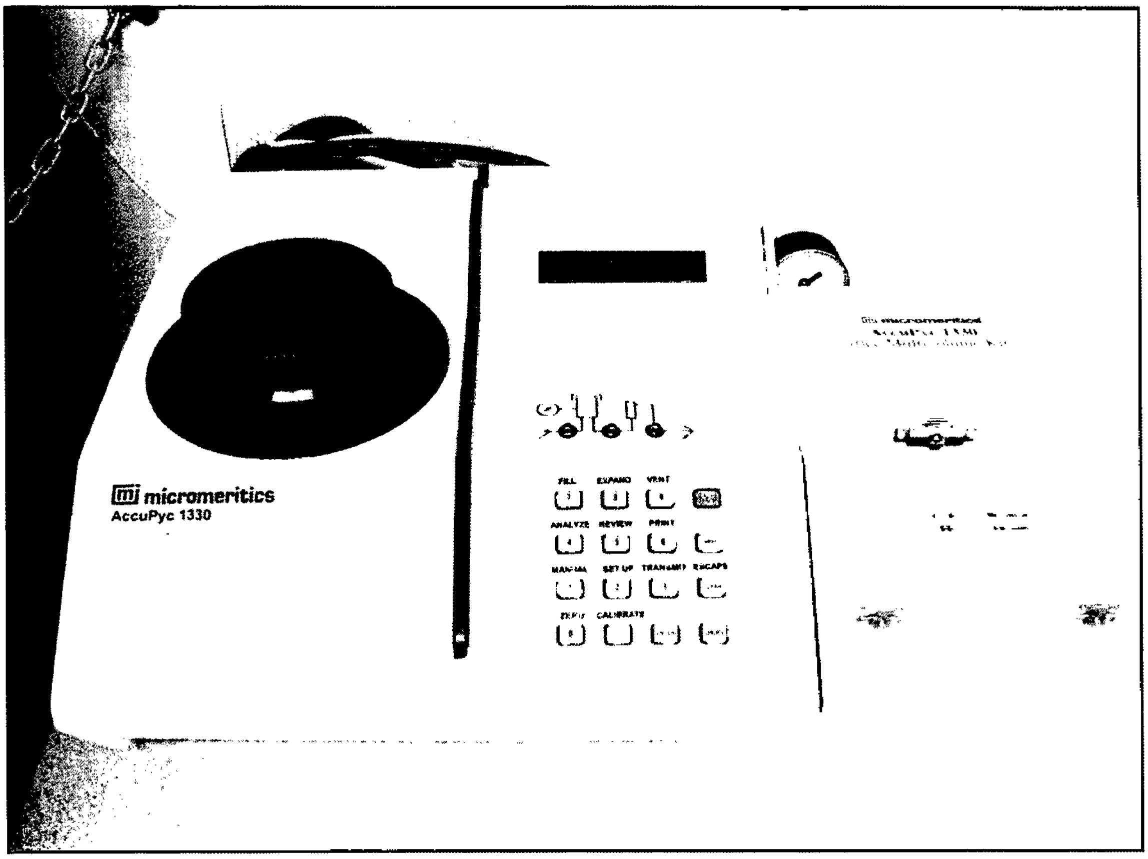


Figure 2-3: Gas Pycnometer for the density analyst of the catalyst

2.2.2 Thermogravimetric analysis

Thermogravimetric analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. An alternate definition: TGA is a technique in which, above heating a material, its weight increases or decreases. A simple TGA Concept to remember: TGA measures a sample's weight as it is heated or cooled in a furnace(Thermogravimetric Analysis (TGA), 2010).A TGA consists of a sample pan that is supported by a precision balance. During the experiment, the pan resides are heated or cooled inside the finance. The mass of the sample is monitored during the experiment. A sample environment is controlled by a sample purge gas. The gases flow over the sample and exeunt through exhaust which maybe in inert or reactive gases (Jeske et al., 2012).

2.2.3 X-ray diffraction

For the investigation of the structure of a substance by methods that make use of the spatial distribution and intensities of X-radiation scattered by the object under study. X-ray diffraction analysis investigates structure through the use of diffraction for neutron diffraction and electron diffraction analysis. X- Rays are diffracted when X- radiation interacts with the electrons of substances.The wavelengths of the X- ray's implant are direct affect to the diffraction pattern in the structure of the object. The order of atomic dimension is used to investigate the atomic structure which the radiation of wavelength is approximately 1 angstrom (Å). The methods of X-ray diffraction analysis are used in several type of analysis study, for example, metals, alloys, minerals, inorganic and organic compounds, polymers, amorphous materials, liquids, gases, and the molecules of proteins and nucleic acids. X-ray diffraction analysis has been used most successfully to establish the atomic structure of crystalline substances because crystals have a rigid periodicity of structure and constitute naturally produced diffraction gratings for X-rays.(X-ray diffraction analysis , 2012)

2.2.4 Brunauer-Emmet-Teller (BET)

BET analysis provides accurate specific surface area evaluation of materials using a fully automated analyser to measured relative pressure by nitrogen multilayer adsorption. BET analysis is used to determine the total specific surface area in m^2/g yielding important information in studying the effects of surface porosity and particle size in many applications by the technique of encompasses external area and pore area evaluations (Zhu et al., 2013). That is having rapid single point and multipoint specific BET surface area determinations.Full BET surface area characterisation of disperse, nonporous or macroporous materials pore diameter >50nm (type II isotherms) and mesoporous materials with pore diameter between 2 nm and 50 nm (type IV isotherms)(Yang and Qiu. , 2011). For BET surface area characterisation comparison of microporous materials is smaller than macroporous and mesoporous (<2 nm, type I isotherms) (Gauden et al., 2010).

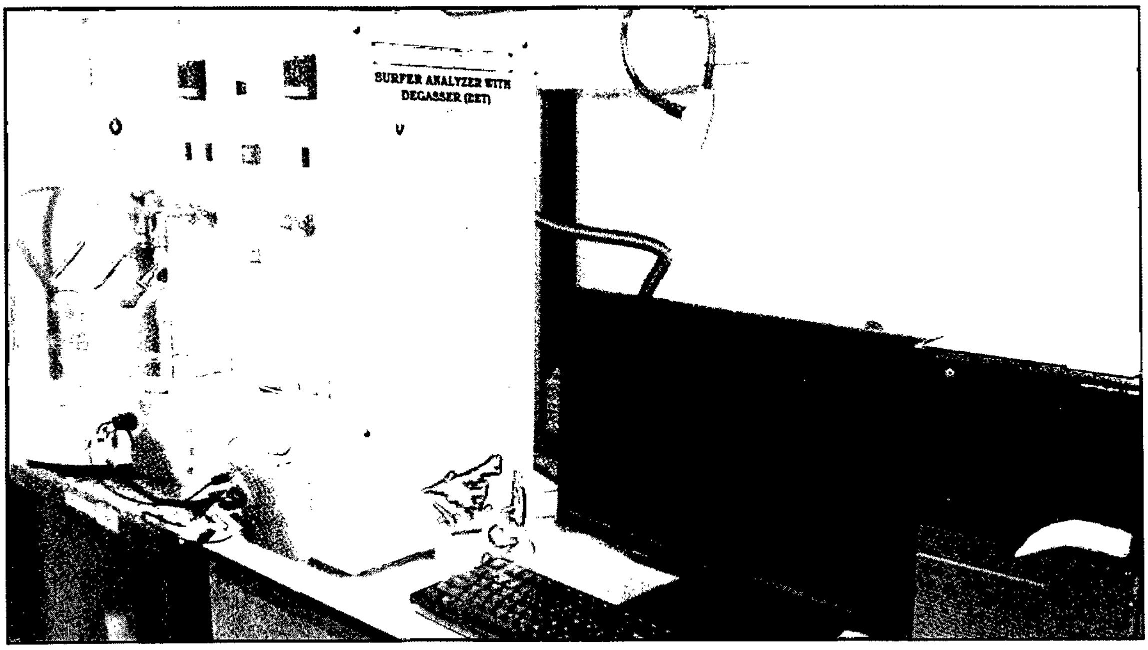


Figure 2-4: BET machine in lab

2.2.5 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a surface scanning instrument used to study the microstructure and morphology of the heterogeneous activated cement clinker catalysts were observed using Philips XL30S model(Y.H. Taufiq-Yap et al., 2011). The sample, i.e., activated cement clinker was poured into a carbon tape placed on aluminium stub as the base for electron reflection. Before the observation and analyses, the sample was vacuumed for 5-10 minutes were made at different magnification.The energy dispersive X-ray detector (EDX) mounted on the microscope use for analyse the element of the compositionmicroscope.

2.2.6 Dispersive X-ray Spectroscopy (EDX)

Energy dispersive X-ray spectroscopy (EDX) is a non-destructive technique for catalyst of chemical characterization using scanning electron microscopy (SEM). The electron beam of uniform energy will simulated the atom in the sample.The atom will generates X-rays with specific energies for each element such that the energy of the emitted radiation to provides analysis information about the substances composition of the sample.(Nikolaos Scoutaris et al., 2014). Although ED-EPMA (or SEM–EDX) is very powerful, it has limited capabilities for performing molecular speciation of particles and probing semi volatile particles under non-destructive conditions due to the electron beam used and/or high vacuum maintained in the sample chamber. Finally, the elemental analysis is not sufficient to fully characterize the chemical structure of single particle internally composed of several species. Alternatively, vibrational spectroscopic techniques are powerful for functional group identification and molecular speciation of organic and inorganic chemical compounds including hydrated species under ambient conditions.(Elżbieta A. Stefaniak et al., 2009). Automated SEM/EDX can provide quantitative information on the elemental composition of a large number of particles and has been used successfully to characterize a range of atmospheric aerosol samples. (S. Sobanska et al., 2014).

2.2.7 Moisture analyser

Moisture analyser is used to determine the moisture content in the particle. (activated cement clinker) Masato Kouzureported that the conversion of the transesterificationis affected by the high moisture content of the particle (Masato et al., 2008). Thereby, this analysis is important to study the effect of themoisture content of the activated cement clinker in the transesterification process.

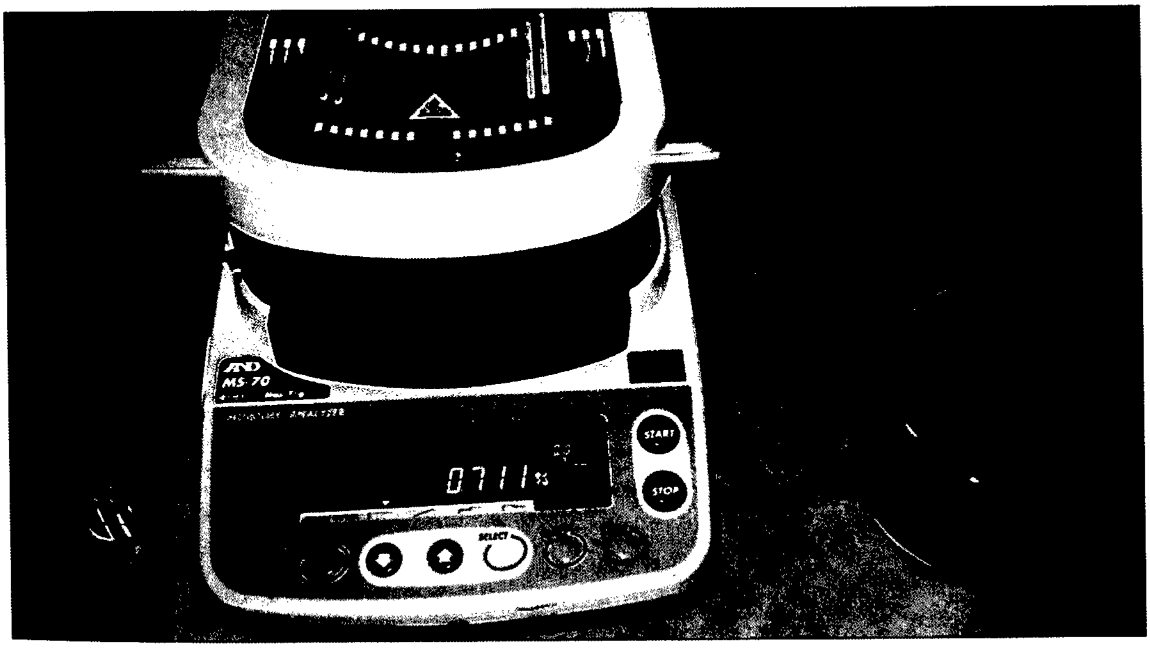


Figure 2-5: Moisture Analyzer in laboratory

2.3 *Transesterification process method*

Several type of extraction method can be used for transesterification such as microwave assisted, in situ method, conventional heating, ultrasound method, supercritical method, and enzymatic process. The comparison between the different extraction methods for the transesterification was presented in Table 2-1.

Table 2-1:Comparison between method, type of oil, type of catalyst and the yield for the transesterification.

(Barnwal and Sharma , 2005)	Supercritical method	Vegetable oil		98%
(Canakci, 2007)	Microwave assisted	Soybean oil	KOH or NaOH	90.54%
(Chen et al., 2012)	Microwave assisted	Waste vegetable oil	CH_3ONa	96.6%
(Dmyryshyn et al., 2004)	Conventional method	Canola oil and green seed canola oil	KOH	87%
(Encinar et al., 2012)	Microwave assisted	Soybean oil	KOH	96.5%-98.2%
(Kanitkar et al., 2011)	Microwave assisted	Soybean and Rice bran oil	NaOH	98.64% and 98.82%
(Kumar et al., 2011)	Microwave assisted	Pongamiapinnata seed oil	KOH	97%
(Rashid and Anwar, 2008)	Conventional method	Rapeseed oil	KOH, NaOH, CH_3ONa and CH_3OK	92.7%
(Liao and Chung, 2011)	Microwave assisted	Jatrophaoil	H_2SO_4	99.36%
(Nautiyal et al., 2014)	Enzymatic process	-	Chlorella, Spirulina and pond water algae	74.6% and 79.5%
Ghoreishi and Moein (2013)	Supercritical method	Vegetable oil	-	95.27%
(Thanh et al., 2010)	Ultrasound method	Waste vegetable oil	KOH	97.5%
(Vujicic et al., 2010)	Conventional Method	Sunflower oil	Activated CaO	91%
Liu et al. (2008)	Conventional Method	Soybean oil	Activated CaO	95%
(Yan et al., 2009)	Conventional Method	Soybean oil	CaO modified with lanthanum	94.3%
(Vicente et al., 2004)	Conventional Method	Sun flower oil	NaOH, KOH, CH_3ONa and CH_3OK	99%
(Saka and Kusdiana, 2001)	Supercritical Method	Rapeseed oil	-	95%
(Lersathapornsuk et al., 2008)	Microwave assisted	Waste frying palm oil	NaOH	97%

Table 2-2:Comparison between method, type of oil, type of catalyst and the yield for the transesterification (cont'd)

(Roces et al., 2009)	Conventional method	Jatrophaoil	NaOH, KOH	92.7 %
(Haas et al., 2004)	In Situ transesterification	Soybean oil	NaOH	88%
(Hass et al., 2007)	In Situ transesterification	Distillers gains	NaOH	91.1 %
(Khang et al., 2014)	In Situ transesterification	Coconut Oil	-	96.7 %
(Shuit et al., 2010)	In Situ transesterification	*Jatrophacurcas*	H_2SO_4	99%
(Biktashev et al., 2011)	Supercritical Method	Rapeseed Oil	-	96%
(Yusup and Khan, 2010)	Conventional	Vegetable Oil	KOH	98%
(Hsiao et al., 2010)	Microwave assisted + Ultrasonic	Soybean Oil	NaOH	97.7 %
(Galia et al., 2011)	Supercritical method	Rapeseed Oil	styrene-divinylbenzenemacroporous acid resins	96.4 %
(Zhang et al., 2010)	Microwave assisted	*Xanthocerassorbifolia* Bunge oil	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	96.22 %
(Zahir et al., 2011)	Microwave assisted	Safflower seed oil	NaOH	98.4 %
(Khemthong et al., 2012)	Microwave assisted	Palm oil	CaO	96.7 %
(Hsiao et al., 2011)	Microwave assisted	Soybean oil	CaO	96.6 %

Microwave irradiation is a well-established method of accelerating and enhancing rate of the chemical reactions. Because of microwave irradiation are delivers the energy directly to the reactant.So if with conventional heating, the heat transfer is less effective than the microwave irradiation. Hence, microwave irradiation can completed the reaction in a much shorter time(Lidstrom et al., 2001). Thus, in the reaction for production of biodiesel, microwave irradiation is one of the best methods to shorter the reaction time and also can obtain the higher yield of product.It enhances the speed of the reaction and makes the separation process easier in comparison with conventional heating. So, the microwave irradiationmethod is wide-ranging reviewed by scientist(Motasemi and Ani, 2012). Base on Table 2-1, the journal state that those experiments, the method of microwave irradiation having a higher yield compare with conventionalheating method. So for the Table 2-2 the optimum parameter for extractionusing microwave.

For supercritical fluid technology method, several advantages of this method such as, short reaction time (4-6 minutes), high yield (>95%), wide flexibility of the raw oil (certain amount of free fatty acid or water does not affect the yield and quality of the biodiesel product), simple separation and no catalyst are needed(Chen et al., 2011). But the reaction condition of the reaction is 350°C and (20-40)MPawhich are require high costs spend for the condition especially the pressure(Choi et al. , 2011). As one of the noble processes, catalyst-free transesterification utilizing supercritical methanol was studied by Saka and Kusdiana. By their process, rapeseed oil was converted into biodiesel for only 4 min at 350 °C under 30 MPa with a molar ratio of oil to methanol of 1:42.

Ultrasound method also call as ultrasonic technology can solve the problem related with the low rate of reaction for producing biodiesel in very effectively. Poor contact between the reactant due to the mutual immiscibility create a problem stems. The mass transfer rate for the between the reactant can be enhanced by the ultrasonic irradiation in the process which leading to significant improvement in the reaction rate(Baddy et al., 2014). The mass transfer rate can be enhanced by using ultrasonic irradiation between the reactant leading to major improvement in the rateof reaction(Badday et al., 2012). Application of ultrasound in biodiesel production process has been illustratedto increasing the reaction speed leading to great reduction in reaction time with some improvement in the production yield(Parag R. Gogate, 2008) and (Ji et al., 2006). The base-catalyst biodiesel production from the ultrasonic energy or two stages process which are investigated by(Deng et al., 2010) and (Hanh et al., 2008). However, for ultrasonic irradiation by using heterogeneous acidic catalyst still is immature research area that require more further investigation to prove the result and theory. As base catalyst are far more relatively active than solid acid catalyst, to speed up the reaction by means of ultrasound irradiation will offer more interesting opportunity toward a more productive and economical biodiesel product.

In situ transesterification also as one of the alternative method to produced biodiesel. It differs from other process method especially for conventional heating in that the oil-bearing material contacts with acidified or alkalized alcohol directly instead of reacting with pre-extracted oil and alcohol. The catalysts are needed to activate this method of transesterification process. To increase the ability of the solvent to aces the oil by using acid or alkaline catalyst helping to break the cell wall of the seed. Many advantage s for this process by previous report review such as reduce the reaction time, reduce the reagents, solvents used, wastewater production and also significantly maximized ester yield. For Silver-Marinkov and Tomasevic(Marinkov and Tomasevic, 1998) studies that the in situ transesterification process by using homogeneous acid catalyst sulphuric acid in 0.75% wt of oil which having 98% of oil conversion, but the reaction time is too slows which is 4 hour. For Haas (Hass et al., 2007) studies that the same process but using base homogenous catalyst which is sodium hydroxide in 0.4% wt of oil which having 91.1% of oil conversion and the reaction time is 1 hour and 12 minutes.

The enzymatic transesterification can be a solution for solvent- free system. For biodiesel production, enzymes can be used as the catalyst. However, to make enzymatic transesterification competitive on industrial scale there are several issues that have to be addressed: solvent engineering, lipases immobilization, selection of acyl acceptor, and selection of the reactor system. Kumari et al. reported that 94% biodiesel yield from Jatropha oil was recovered as temperature increased up to 55°C,using 50μ of immobilized E. aerogenes lipases with 1:4 oil to methanol molar ratio at 55°C for 48 hours. Immobilized lipase in this study was stabile which indicates that the process was efficient. In the other hand, Sotoft et al. reported that Enzymes were more expensive and slower reacting than traditional chemical catalyst, but give much easier and simpler biodiesel purification.

Table 2-3: The optimum parameter for extractionusing microwave for transesterification process

Type of oil	**catalyst**	**Parameter**	**Optimum condition**	**References**
Cottonseed oil	KOH	- Catalyst weight ratio (0.5%, 1% and 1.5%) - Reaction time (5, 6 and 7 minutes) - Reaction temperature (323, 328 and 333 Kelvin)	- Catalyst weight ratio 1.5% - Reaction time 7 minutes - 333K reaction temperature	(Azcan and Danisman, 2007)
Rapeseedoil	KOH and NaOH	- reaction temperature in (313K, 323K and 333K) - Reaction time in 1,3 and 5 minutes	- Catalyst weight ratio 1% - presence KOH of microwave	(Azcan and Danisman, 2008)
Waste cooking oil	$NaOCH_3$	- Methanol ratio 1:3, 1:4 and 1:6 - Catalyst weight ratio 0.5, 1.0 and 1.5% wt.	- methanol molar ratio 1:6 with the oil -Catalyst weight ratio 1%	(Azcan and Yilmaz, 2013)
Vegetable oil	$NaOCH_3$	- Reaction temperature 60°C, 70°C and 80°C - Catalyst weight ratio 0.5, 0.75 and 1.0 % wt.	- methanol molar ratio in between 4.05-5.57 - Catalyst weight ratio 1%	(Barnwal and Sharma , 2005)
Waste cooking oil	$NaOCH_3$, NaOH and KOH	- Catalyst weight ratio 0.5, 0.75 and1.0% wt. - Different type of catalyst tested NaOH, KOH and CH_3ONa	-0.75% of catalyst weight ratio -time for the reaction in between 1-3 minutes	(Chen et al., 2012)
Vegetable oil	KOH	- Catalyst weight ratio 0.5, 1.0 and 1.5% wt. - Reaction temperature 50°C to 115°C - Power 300W to 700W - Reaction time 2 to 50 minutes - Molar ratio of methanol 3:1, 6:1, 9:1 and 12:1	- 1.5% of catalyst weight ratio - reaction time in between 4 to 15 minutes - Microwave power 700W - Methanol molar ratio 9:1 - Temperature in between 65°C to 90°C	(Dmyryshyn et al., 2004)

Table 2-4:The optimum parameter for extractionusing microwave for transesterification process (cont'd).

Soybean oil	Nano CaO	- Molar ratio of methanol in 6:1, 7:1, 8:1, 9:1 and 10:1 to oil. -Reaction time in 15, 30, 45, 60 and 75 minutes - The reaction temperature are 323K, 328K, 333K, 338K and 343K - Catalyst weight ratio in 1%, 2%, 3%, 4% and 5% w/w.	-65°C for the reaction temperature -60 minutes for the reaction time - The methanol oil ratio is in 7:1 -3% of the catalyst weight ratio	(Hsiao et al., 2011
Jatrophacurcas oil	H_2SO_4	- Catalyst weight ratio 1%, 2%, 3% and 4% - Methanol molar ratio 16%, 24%, 32%, 40% vol%	- The methanol molar ratio is 1:9 to the oil - 1.2% of the catalyst weight ratio to the oil	(Liao and Chung, 2011)
Sunflower oil	BaO, SrO	-Methanol oil ratio in 6:1, 9:1, 12:1 and 15:1 -Catalyst weight ratio in 0.5%, 1.0%, 1.5% and 2.0% - The reaction time is in 1, 2, 3, 4 and 5 minutes - Different in power dissipation which are 20%, 40%, 60%, 80% and 100%	-The methanol oil ratio is in 9:1 - Catalyst weight ratio is 2% - the reaction time is 4 minutes - power dissipation is 40%	Prafulla et al, (2010)

2.4 Catalyst selection for the transesterification process

Transesterification is performed using homogeneous base catalyst and heterogeneous catalyst. Those homogeneous catalysts in conventional heating process have several advantages including high activity which can finish the reaction within 1 hour, and the reaction condition also moderate which in 65°C and 1 atm. However, these homogeneous base catalysts are corrosive and unable straight forward to remove all the homogeneous catalyst from the reaction. On the whole, doing the washing glycerol process is generating the large amount of waste washing water, and a long time is