The utilization of leftover as acid catalyst to catalyse the transesterification and esterification reactions

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Abstract. Biodiesel (Fatty Acid Methyl Ester, FAME) is a green and renewable energy. It is carbon neutral and produces less air pollutants in combustion. In my project, the selected feedstock of biodiesel production is grease trap oil (GTO). It is extracted from restaurants, and needs pre-treatment. The triglycerides and free fatty acid (FFA) are the main components of GTO. Both triglycerides and free fatty acid can be converted to biodiesel (Fatty Acid Methyl Ester) by transesterification and esterification, through reaction with alcohol (methanol) and catalyst. In the processes, acidic catalyst is chosen to speed up the reactions. The catalyst used in the study, a heterogeneous solid acid is applied. It is waste cooked rice (WCR) collected from leftover. The WCR powder is pyrolysed in 400°C furnace 15 hours and blown with nitrogen gas (incomplete carbonization). The WCR black powder is then mixed with concentrated sulphuric acid and heat in 160°C furnace 15 hours and continuous blown with nitrogen gas (sulphonation). This heterogeneous solid acid is used in the both transesterification and esterification to produce FAME. Moreover, in the optimal reaction conditions, this catalyst offers a stable catalytic effect. After 20 times usage in optimal reaction condition, the catalytic activity remains unchanged.

1. Introduction

Hong Kong is one of the most modern cities in the earth. It suffers from a lot of problems as same as other modern cities. Waste, air pollution, energy exhaustion and global warming are some of the important problems.

In Hong Kong, the year 2014, domestic solid waste is generated 6418 tonnes per day and disposed to landfill site finally [1]. There, the food waste is the major part and wasted cooked rice is one of the components.

Air Pollution in Hong Kong is worse year by year and the major source of the pollutants was derived from motor vehicles, marine vessels and power plants. They induce a problem which is the street–level pollution and region smog [2]. The first source of the pollutants is mainly caused by diesel vehicles, truck, buses and light buses. The other source is power plant. Subsequently, these pollutants are transformed to smog. It is happened under sun light. The pollutants include hydrocarbons, carbon monoxide, sulphur oxides, nitrogen compounds and Ozone. Especially in street level these pollutants are emitted from vehicle engines mainly [3].
The last and the most important problem is the global warming. It is proved that the carbon dioxide concentration level increased is one of the important factors to induce the global warming [4]. The byproduct of fuel combustion is carbon dioxide which emits into atmosphere and increases the carbon dioxide level. The usage of biofuel (biodiesel) is one of the ways to reduce the carbon dioxide emission because the carbon dioxide emitted from combustion of biodiesel is carbon neutral.

Biodiesel is derived from renewable biological materials such as plant. They pass through chemical and biological process to transform to biofuel. It is another form of indirectly utilized the solar energy. Moreover, the biofuel is as same as solar battery to store the solar energy and uses any time. It is because plant absorbs sunlight, carbon dioxide and water to process the photosynthesis and the result is sunlight energy is captured. Nowadays, the sources of biofuel mainly are derived from oil extracted from plant and non-edible oil especially the wasted cooked oil due to not induce a competition in food, land and other human resources.

Biodiesel is Fatty Acid Methyl Ester (FAME) which is monoalkyl ester of long chain fatty acid. It can be produced by transesterification reaction and esterification reaction. The transesterification reaction is the reaction of triglyceride TG and alcohol (methanol is the most common) to produce FAME and glycerol. TG is the combination of glycerol and three long chain fatty acids FAs. The esterification reaction is that carboxylic acid (Fatty Acids FAs) reacts with alcohol to produce FAME and water.

The chains of these fatty acids in triglyceride include saturated and unsaturated. The fatty acid chain without carbon-carbon double bonds is called saturated and then the present of carbon-carbon double is called unsaturated. The fat is saturated TG with higher viscosity and unsaturated TG is oil with lower melting point and is in liquid form in room temperature.

- Transesterification reaction

\[
\begin{align*}
\text{RCOOR'} + R''\text{OH} & \xrightleftharpoons[H^+/\text{OH}^-]{} \text{RCOOR''} + R'\text{OH} \\
\text{TG} & \text{ alcohol} & \text{FAME} & \text{Glycerol}
\end{align*}
\]

- Esterification reaction

\[
\begin{align*}
\text{R'COOH} + \text{CH}_3\text{OH} & \xrightleftharpoons[H^+]{} \text{R'COOCH}_3 + \text{H}_2\text{O} \\
\text{FA} & \text{ alcohol} & \text{FAME} & \text{Water}
\end{align*}
\]

In order to shift the equilibrium to the right hand side to increase the yield, an excess amount of alcohol is added. For transesterification, methanol, and ethanol are suggested choices of alcohol [5]. The lowest priced methanol is the best choice for production.

The waste cooking oil is selected as feedstock of the FAME production according to statistic of Environmental Protection Department [1]. 2027 metric tonnes of waste oil are collected and needed to be treated and grease trap oil is included. Thus grease trap oil is selected as feedstock to produce biodiesel in my project. The grease trap oil must be under a pretreatment to be separated from the grease trap waste water. The collected grease trap oil includes a lot of mixture. There are mainly triglyceride, diglyceride, monoglyceride, fatty acid and a little amount of soapy water.

2. Literature review

In the production of biodiesel, a lot of processes can be applied. As early as year 1900 in Paris Exhibition, a peanut oil was directly used in engine for several hours by renowned scientist Sir Rudolf Diesel. It shows that the vegetable oil is an old diesel fuel used in diesel engine. Moreover, it was used as emergency fuel as in World War II. The vegetable oils used in the compression ignition engines, its exhaust emission are almost free from sulphur oxide [6]. But the usage of vegetable oil in engine induces several problems. At first, the physical properties of the vegetable oil are related high viscosity and with low volatility. They cause the damages of engine system. The vegetable oil will
block the fuel pipe and injectors, carbon deposit on the piston rings, and fouling on the piston head [7-10].

2.1. Catalyst
A catalyst has an important role to speed up the chemical reaction in biodiesel [11]. Nowadays, catalysts can be considered in transesterification and esterification to produce biodiesel is a lot. Generally, they include biotechnology methods (enzyme), base and acid catalyst to speed up the reaction.

2.1.1. Biocatalyst. Biotechnology is a technology to produce biodiesel by using enzyme as catalyst and lipases are generally used in biodiesel production passing through the process of esterification and transesterification [12, 13]. In biodiesel production of usage of enzyme as catalyst can be divided into several types. They are mobilized lipases; immobilized lipases and whole-cell biocatalyst. Although the development of immobilized lipases, whole-cell biocatalyst, new lipase, new fermentation optimization to increase the yield and reduce the cost [14, 15]. But their cost and reaction time is still relative higher and longer [16]. Moreover, If a short chain alcohols (e.g. methanol and ethanol applied in the biodiesel production, these short chain alcohol will cause denature in enzyme. In addition, glycerol is by-product of transesterification reaction; it can also induce a serious negative effect on the enzyme [17-19].

2.1.2. Chemical catalysts. Chemical catalysts can be divided into two main categories, which are base catalysts and acid catalysts. As early as 1984, Freeman et al studied the catalysts both acid and alkaline in the biodiesel production and concluded that the reaction time of alkaline catalyst is more rapid than the acid catalyst. The reaction conditions are NaOH in 1%, methanol to soybean oil molar ratio 6:1, temperature 60°C and in one hour. The FAME yield is 95%. In usage of 1% sulphuric acid catalyst, the yield of FAME is above 90%. But it needed 60 hours at 65°C and molar ratio of methanol to oil is 30:1 [20, 21].

2.1.3. Alkaline Catalyst. In base catalysts, they consist of homogenous and heterogeneous catalysts. The common homogenous catalysts contain potassium hydroxide, potassium methoxide, sodium hydroxide and sodium methoxide. They are the widely to be selected in transesterification reaction.

In the homogenous alkaline catalysts such as potassium hydroxide (KOH) and is one of the common catalysts to be investigated. In the reaction of transesterification, KOH It is used to convert the karanja oil into biodiesel (FAME) and the optimum reaction condition includes the usage of KOH in 1%, methanol to oil molar ratio 6:1, temperature 65°C and in two hours. The FAME yield is 97% approximately [11]. Moreover, another scientist Karmee develops a better method, which is a usage of a co-solvent tetrahydrofuran (THF). It can increase the yield of FAME from 92 to 95% (feedstock is crude pongamis pinnata) and the reaction requirements are KOH 1%, methanol to oil ratio 10:1, temperature 60°C and 1.5 hours [22]. In the usage of KOH as catalyst, when lower amount of KOH and extra amount of methanol were chosen, it caused the soap formation and yield reducing. In there, the feedstock is carinata oil and the reaction conditions are in KOH 1.4%, methanol to oil ratio 4.6:1, temperature 20-45°C and 0.5 hours [23].

Potassium methoxide (CH₃OK) is an alkaline catalyst. It can be applied in organic chemistry such as process of transesterification. But it is lesser applied in biodiesel production. In the investigation, the performance of CH₃OK and KOH were compared. The reaction used CH₃OK as catalyst the yield is 99.2%. The reaction conditions are 0.455% of CH₃OK, methanol to vegetable oil 8.5:1 and the reaction time is one hour. In the catalyst of KOH, the yield is 98.1%. The reaction conditions are 0.382% KOH, methanol to vegetable oil ratio 11.3 :1 and in three hours [24].

Sodium Hydroxide (NaOH) is the more recommended than KOH and CH₃OK. It is because the NaOH is cheaper in price, easier in separation of product and with lesser emulsification happened within the transesterification reaction. The yield of FAME is as high as 85.5% that the catalyst is 3%
NaOH, temperature 55°C, methanol 35% and reaction time is 1.5 hours [25, 26]. In other research, the yield of biodiesel can be more than 97% when the NaOH in 1%, methanol to sunflower oil 6:1, temperature 65°C and reaction time is 60 mins [27]. In the feedstocks of crude palm oil and coconut oil, the investigation shows that although the oils containing Free Fatty Acid (FFA) in little amount, the yield can be dropped to 80% of palm oil and 55% of coconut oil. The reaction conditions are 1% NaOH, methanol 28%. It shows that the FFA is an important role to affect transesterification reaction yield. In the research of Crude Jatropha Curcas Seed Oil (JCJO) Berchmans found that a higher FFA content (15%) in CJCO sample, the yield is only 55% when directly use alkaline catalyst. But used two step reaction to treat the FFA, the yield of 90% is obtained. The 1.4% of NaOH is applied [28].

Sodium methoxide (CH$_3$ONa) is less recommended to apply in the commercial biodiesel production. It is because the price of the CH$_3$ONa is high, although the performance is higher than the catalyst of sodium hydroxide. The advantages of the CH$_3$ONa consist of does not form water in FAME production compared with the application of NaOH and KOH. Moreover, it is more effective than the usage NaOH in the production and it just only requires the 50% of amount of NaOH [29].

In the comparison of these four alkaline catalysts (potassium hydroxide, sodium hydroxide, potassium methoxide, and sodium methoxide), Singh finds the performance of methoxide catalysts are better than the hydroxide and with the better yield. In the reaction, it is not only to form lesser water but also elevated the conversion equilibrium. In the investigation, the most optimal combination is potassium methoxide as catalyst at 0.2 mol/mol (1.59%wt), reaction temperature 50°C, and methanol-to-oil molar ratio 4.5:1, which can obtain the max. yield as high as 95.8% and with min. soap formation 0.75% [30].

Heterogeneous base catalysts is the kind of alkaline catalyst is very effective. The heterogeneous catalyst means the catalyst composes unrelated or different part of body it also means with different phase. Such as usage the homogeneous base catalyst, a separation of the liquid state of FAME and the liquid catalyst can be needed. In the other hand, the Heterogeneous base catalysts are in solid state, they can be more simply to be separated from product. Moreover, these catalysts can be reused many time any just a simple filtration to be applied. The most common solid base catalysts include alkaline earth metal oxide, Zeolite, KNO$_3$ loaded on Al$_2$O$_3$, KNO$_3$/Al$_2$O$_3$, BaO, SrO, CaO, MgO etc. [31, 32].

In other investigation shows the usage of CaO (8%) as catalyst can obtain FAME above 95% [33]. The reaction conditions are molar ratio of methanol to oil 12:1, temperature 65°C and 2.03% water content in methanol. Moreover, the catalyst activities can maintain after repeat usage in 20 cycles productions.

At the same period, another investigation found that the catalysts of CaTiO$_3$, CaMnO$_3$, Ca$_2$Fe$_2$O$_5$, CaZrO$_3$, and CaO–CeO$_2$ shown high activities to give high yield of about 90% and the reaction conditions are at 60°C, molar ratio of methanol to oil 6:1, and reaction time is 10 hours. In the investigation, the catalyst of CaZrO$_3$ and CaO–CeO$_2$ show high durability and suitable to be used in biodiesel production processes as heterogeneous base catalysts [34].

### 2.1.4. Acid Catalyst

The homogenous acid catalysts can also be used in the FAME production. They have their advantages in the production of FAME but they also include disadvantages when used in the FAME production.

In the above explanation, the limitation of basic catalyst is that they have high catalytic power in biodiesel production and show high yield, but the feedstock content must be controlled in low concentration of water and free fatty acid FFA. Otherwise, the basic catalysts are consumed and also the saponification will be induced. Moreover, the best feed stock of biodiesel is grease trap oil, which always contains water and FFA and in related high concentration.

According to the characteristic of grease trap oil with high water content and high concentration of FFA, acid catalysts are the best selection in biodiesel production. Because the esterification process it is not only to consume the FFA but also produce FAME from FFA. Thus a two steps biodiesel production is induced. At the first an esterification is initial to produce FAME and consume FFA then
a basic catalyst is applied in this feedstock which without FFA or FFA in low concentration to process transesterification [28, 35-37].

The most common homogeneous acid catalyst is sulphuric acid [38-40]. In the usage of sulphuric acid catalyst, this can get the yield as high as 99%. The reaction conditions are 1 mol % of sulphuric acid, molar ration 30:1, temperature 65°C and 50 hours. If the butanol (in 117°C) and ethanol (in 78°C) are instead the reaction time can be reduced to 3 hours and 18 hours respectively [38]. In the other research of usage crude palm oil to produce FAME, the reaction conditions are varies in 70, 80, 95°C but the sulphuric acid concentration, molar ratio of oil to alcohol are kept constant. Then the experiment can conclude the reaction rate be increased by temperature increased. The 99.7% yield is controlled by 5% sulphuric acid and oil to butanol molar ratio 40:1 when the temperature is kept in 95°C and the react time can be reduced to 9 hours [41].

Finally, the usage of the homogeneous acid catalysts will induce some problems [42, 43]. They include:

- higher amount of alcohol be used;
- consume more energy by needed higher reaction temperature;
- lower reaction rate; corrosive problem in reactor; and
- environmental problem in waste acid treatment before disposal.

In heterogeneous acid catalysts, they not only have the advantages of homogeneous acids type catalysts, but also have less disadvantages of homogeneous acid catalyst in biodiesel productions.

In some researches, the heterogeneous acid catalysts are investigated e.g. sulphated zirconia (SO\textsubscript{4}/ZrO\textsubscript{2}), sulphated tin oxide (SO\textsubscript{4}/SnO\textsubscript{2}) and sulphated titanium oxide (SO\textsubscript{4}/TiO\textsubscript{2}). All of them have good catalytic activities performances in the processes of esterification and transesterification simultaneously. In addition, the stability of them is also high. Unfortunately, they are not chosen in the production of biodiesel in industries. The reasons are the high catalyst costs and hard to be recycle by their small size. Thus they are difficultly to be separated by simple filtration [44-46].

In other research, various heterogeneous solid acids are investigated in production of FAME converted from canola oil which with 10% content of FFA. In there, a technology of immobilization of Keggin-type heteropolyacid (HPA) on different support e.g. hydrous zirconia, silica, alumina, and activated carbon is investigated. The hydrous Zirconia support induces to the best catalytic performance [47].

Finally, the interested catalysts are introduced. These novel strong solid acids are developed by Takagaki. They select a carbon material (D-glucose) as catalyst resource. At first, the glucose is under incomplete carbonization to break down some their bonds and then deals with sulphonation to bind with SO\(_2\)H group then a novel strong solid acid is formed. In the incomplete carbonation the glucose is pyrolyzed at 400°C in 15 hours and blown with nitrogen continuously. The polycyclic aromatic carbon is obtained. In the sulphonation, the polycyclic aromatic carbon is heat concentrated sulphuric acid in 150°C, 15 hours and under nitrogen. The new solid acid is formed [48].

The D-glucose derived catalyst is compared with other catalysts, which including sulphate zirconia, amberlyst-15 and niobic acid. The D-glucose derived catalyst shows the best result. They also concluded that the glucose derived catalyst is very suitable to replace sulphuric acid and other acid catalysts as a green catalyst to produce biodiesel from waste oil with high acid value [49].

A further study of that type of acid catalyst is set up to focus on the carbohydrate compounds. The D-glucose, sucrose, cellulose and starch are converted to heterogeneous solid acid catalyst by passing through incomplete carbonization and sulphonation. In the investigation, all of them can act as acid catalysts to produce biodiesel and the starch is the most high efficiency, high recyclable and environmental friendly catalyst to produce biodiesel from waste oil and with High acid value [50].

From the above references, the biodiesel production should select the waste cooking oil (grease trap oil) as feedstock. Moreover, the catalyst should consider the carbohydrates derived substances. Waste cooked rice (WCR) is a good direction to be investigated to act as a heterogeneous solid acid in the production of biodiesel.
3. Experimental

3.1. Materials
The sulphuric acid was purchased from Riedel-DeHaen, (Extra Pure). The Oleic acid and Methanol were purchased from Sigma-Aldrich (analytical standard). The peanut oil was purchased from Knife Pure Peanut oil. The grease trap oil was collected from Chinese restaurant and was heated to 60°C and the top brown oil was separated easily. After the pretreatment, the grease trap oil contained mainly triglyceride, 38.7% free fatty acid and 0.08% of water. The waste cooked rice was collected from leftover of high school after lunch and treated with washing and drying in oven.

3.2. Catalyst preparation
At first, the treated dry waste cooked rice (WCR) was grinded in powder form and put 20 g of rice powder into the reactor to pyrolyze in temperature 400°C for 15 hours and well mixing. Nitrogen was blown into the reactor continually within the reaction period. In the end of the reaction some rice compound bonding were broken and the rice powder was changed to black color and in lump form. After cooling, the incomplete carbonization of product was grinded in powder by mortar and pestle. The black grinded powder was put into the reactor again and mixed with concentrated sulphuric acid heating to 160°C for 15 hours. Simultaneously, nitrogen was continually blown into the reactor until the end of the reaction. At the end, the product of mixture was cooled to 30°C and diluted with 800 ml DI water. In there, the black precipitate was settled into the bottom and the upper liquid was removed. These black precipitate was washed with > 80°C DI water continually until the pH of the washed DI water changed to neutral. Finally, the wet black precipitate was dry in oven at 65°C oven and the heterogeneous solid acid catalyst was formed.

3.3. Catalyst activity performance
At the first, the WCR derived catalyst activity was investigated in esterification reaction. The WCR derived catalyst was used to catalyze the reaction of oleic acid and methanol. Before the reaction the WCR derived catalyst was dried in oven 100°C for one hour to remove the moisture on the catalyst surface. All of them were transferred to reactor. The 10% weight of catalyst, methanol, oleic acid (molar ratio 20:1) were transferred in to reactor form 8 hours and the temperature was 80°C. In each hour, 400 µL sample was withdrawn and put into centrifuge (Microcentrifuge) for 10 min at 10000 rpm. At the same time, the vacuum was applied and kept in 70°C. After removed the catalyst, each sample FAME yield was determined from GC.

A similar investigation was applied to investigate the esterification and transesterification. The different was the oleic acid changed with neat peanut oil and mixed with 38.7% oleic acid.

3.4. Optimum parameters of biodiesel production reaction
Attempt was made to optimize parameters such as the reaction temperature, catalyst concentration and molar ratio of methanol to oil in the biodiesel productions. Each parameter was tested in turns, with the other variables controlled at constant values. For example, in investigation of the effect of reaction temperature, different reaction temperatures were tested respectively. While the other parameters such as methanol to oil molar ratio, catalyst concentration etc. were kept constant. Thus the relationship between the reaction temperature and the production yield becomes clear.

3.5. Production yield of FAME converted by grease trap oil
After the optimum reaction parameters of the WCR derived catalyst were obtained, the yield of biodiesel was investigated according the optimum parameters. In the investigation the feedstock was the grease trap oil collected from Chinese restaurant. In there the esterification and transesterification were conducted simultaneously. The samples were withdrawn from each hour to investigate the FAME yield percentage. It was used to consider the reaction rate.
3.6. Stability of WCR derived catalyst

Finally, the stability of the RCW derived catalyst was investigated. The experiment was based on the section 3.5. But the FAME yield percentage was only considered at the end of reaction. Each reaction time was set to five hours. The catalyst was reused 20 cycles under same reaction condition. In there, the catalyst will be recovered by dry at 100°C oven two hours between each experiment. It is because a little amount of catalyst will be lost at each cycle of recovering, thus a suitable amount of catalyst were added to fulfill the catalyst in 10wt % weight in each cycle.

4. Results and discussion

4.1. Catalytic activity of waste cooked rice (WCR) derived catalyst

A number of solid acid catalysts derived from carbohydrate had been investigated by other researchers [50]. They included starch, cellulose, sucrose and D-glucose, and etc. They were converted to solid acid catalysts, and their usage in biodiesel production was compared. They were processed through incomplete carbonization, and pyrolysis in 400°C, 15 hours and blown with nitrogen, in order to achieve dehydration and dissociation of bonds in –C–O–C–. During the reaction, polycyclic aromatic carbon ring was form. This polycyclic aromatic carbon ring (semi-product) takes part in the subsequent sulphonation, in which the semi-product was mixed with concentrated sulphuric acid, heated to 150°C for 15 hours, and blown with nitrogen simultaneously. The SO₃H group, derived from the concentrated sulphuric acid, can bind into the polycyclic aromatic carbon ring to form heterogeneous solid acid catalyst. It had been reported that starch (polysaccharide), among the different substances tested, shows an excellent catalyst performance. Inspired by this information, waste cooked rice (WCR) is selected as the feed stock, and it is to be treated with similar reactions. The waste cooked rice indeed also shows high catalyst activity performance. The high catalyst activity performance can be attributed to similarity between rice and starch; rice contains approximately 89-94% endosperm, which comprises a lot of polygonal starch granules and some protein body.

![Figure 1. Yield of Biodiesel (FAME) produced form Oleic acid (FFA) and catalyzed by waste cooked rice (WCR) derived catalyst. Reaction condition: 80°C; molar ratio of methanol to oil 20: 1; catalyst 10wt%.](image)

In figure 1 the yield of biodiesel (FAME) is 70.5% in 5 hours. The waste cooked rice (WCR) derived catalyst shows a high reaction rate. WCR derived catalyst is demonstrated capable of catalyzing the esterification between oleic acid and methanol. The role of the oleic acid is to substitute
the FFA in grease trap oil (GTO).

![Graph of yield of biodiesel vs reaction time](image)

**Figure 2.** The yield of Biodiesel (FAME) from neat peanut oil and with 38.7wt% of oleic acid catalyzed by Waste cooked rice (WCR) derived catalyst. Reaction condition: 80°C; molar ratio of methanol to oil with oleic acid 20:1; catalyst 10wt%.

In figure 2 the neat peanut oil is mixed with 38.7% oleic acid, to simulate the composition of grease trap oil. WCR derived catalyst also shows good catalyst activity in transesterification. The FAME production yield can be as high as 68.1% in 80°C; molar ratio of methanol to oil is 20 : 1; catalyst 10 wt%. Comparing figure 1 and figure 2 the yield in figure is higher than the yield of figure 2. In figure 2, the WCR derived catalyst needs to catalyse two different type reactions (transesterification & esterification reaction) and thus the performance might be different. In addition, the transesterification reaction is believed to be more complicated than the esterification.

4.2. Optimum parameters of WCR derived catalyst in biodiesel production

In order to find out the optimum parameters to induce the best WCR derived catalyst activities. Several investigations about the parameters are carried out. The parameters include reaction temperature; molar ratio of methanol to neat peanut oil with 38.7% oleic acid; and catalyst concentration.

4.2.1. Reaction Temperature. Reaction temperature plays an important role in chemical reaction. In the investigation higher temperature increases both the reaction rate and product yield. In figure 3 the temperatures are set to 65°C, 80°C, and 95°C. The reaction conditions: Molar ratio of methanol to oil mixed with 38.7% oleic acid is 20:1, and catalyst concentration is 10wt%. The best result is obtained when reaction temperature is set at 95°C. The reaction rate is the fastest and the production yield is the highest (71.8%). When the reaction temperature is kept at 65°C, the reaction is the slowest and the product yield is the lowest (62.2%). At 80°C, the performance is intermediate. The reaction rate and yield are just marginally below those at 95°C reaction temperature. Thus the optimum reaction temperature is chosen as 80°C. Because it can save the energy to reduce the production cost.
Figure 3. The yield of Biodiesel (FAME) from neat peanut oil and with 38.7wt% of oleic acid catalyzed by Waste cooked rice (WCR) derived catalyst in different temperature. Reaction condition: Molar ratio of methanol to oil with oleic acid 20:1; catalyst 10wt%.

Figure 4. The yield of Biodiesel (FAME) from neat peanut oil and with 38.7wt% of oleic acid catalyzed in different weight % of Waste cooked rice (WCR) derived catalyst. Reaction condition: 80°C; Molar ratio of methanol to oil with oleic acid 20:1.

4.2.2. Catalyst Concentration. The catalyst loading is another important parameter. When the catalyst loading increases, the reaction rate and production yield are increased. Different catalyst loadings were tested in the investigation; these were 5 wt%, 10 wt% and 15 wt% respectively. The other parameters in the investigation consist of reaction temperature (80°C), the molar ratio of methanol to oil with 38.7 wt% oleic acid (20:1). Figure 4 shows, when catalyst concentration increases from 5 wt% to 10 wt%, the production yield is increased sharply from 65.8 to 71.1%. However, when the catalyst
concentration further increases to 15 wt%, the production yield becomes stationary, or increases slightly at best (Use data for 5 hours reaction time). From this test, the suitable catalyst concentration for conversion of biodiesel is chosen to be 10 wt%, as increasing the catalyst concentration above 10 wt% does not increase the yield much.

4.2.3. Molar ratio of methanol to peanut oil with 38.7wt% oleic acid. Theoretically, in the esterification reaction, one mole of oleic acid should react with one mole of methanol. In transesterification, one mole of triglyceride will react with three moles of methanol to produce biodiesel. In reality, the methanol should be increased to shift the equilibrium toward the right hand side to favour the product. Furthermore, the transesterification reaction is reversible. Thus in order to keep a high product yield, the methanol should largely increase. However, to keep the production cost low, usage of the methanol should be as less as possible. In the investigation of figure, different molar ratios of methanol to neat peanut oil with 38.7% oleic acid are set, specifically 5:1; 10:1; 15:1; 20:1; 25:1; and 30:1. The other parameters: reaction temperature 80°C; catalyst concentration10wt%; and the reaction time 5 hours. In figure 5 the yield increases together with the increase of methanol. But the optimum molar ratio of the methanol to oil is the 20:1. It is because the further increase the molar ration of methanol to oil 30:1, the yield is just slightly increased from 69.3% (20:1) to 71.9%. Thus the best molar ratio of methanol to oil in the conversion of FAME is 20:1.

![Figure 5](image)

**Figure 5.** The yield of FAME from neat peanut oil and with 38.7wt% of oleic acid in different molar ratio of methanol to neat peanut oil with oleic acid. Reaction condition 80°C; catalyst 10wt%; and 5 hours.

4.3. Biodiesel converted from GTO and catalyzed by WCR derived catalyst
In the above investigations, the optimum parameters are determined. When the feedstock is changed to cheap grease trap oil (GTO), these optimum parameters are still used. The first step is a pretreatment, in which the collected GTO is heated and impurities separated. In figure 6, the conversion of GTO to biodiesel, the reaction conditions are: temperature 80°C; WCR derived catalyst 10wt%; molar ratio methanol to FTO 20:1 and the reaction is 5 hours. The yield is 63.9% and it is similar to experimental yield 68.1%. The difference is 4.2%. The difference may be caused by the feedstock. In the experiment, the oil is the neat peanut oil and the oleic acid is analytical standard, thus the yield can be
as high as 68.1% in 5 hours. In practical investigation, the feedstock is changed to cheap GTO. Although the collected GTO is pretreated, it may contain vegetable oil, seed oil, or animal fat. The most important difference is that animal fat is always in solid form in room temperature due to their long saturated chains and the other oils such as vegetable oil and seed oil are in liquid form in room temperature, as their chains are relatively short and are unsaturated. The long saturated chain is more compacted and non-polar while the unsaturated chains are packed more loosely. These structures of animal fats are hard to be mixed to with polar methanol. Thus the production yield converted from GTO is lower than the neat peanut oil, may be the GTO contains animal fats.

![Figure 6. The Yield of Biodiesel (FAME) produced by grease trap oil (GTO). Reaction condition: 80°C; catalyst 10wt%; molar ratio methanol to GTO 20:1.](image)

4.4 Stability of WCR derived catalyst in biodiesel production

The other important factor in the production cost of biodiesel is the reusability and stability of the catalyst. The higher number of catalyst recycle and better catalyst activities stability will reduce the production cost and conserve our resources. Thus the same catalyst is repeatedly used in the biodiesel production to investigate the WCR derived catalyst stability. In figure 7, the yields of biodiesel in twenty cycles are similar and the reaction conditions are reaction temperature 80°C; catalyst concentration 10wt%; molar ratio of methanol to GTO 20:1 and reaction time is five hours. It means the stability of WCR derived catalyst is high and can maintain the catalyst activities within 20 cycles in the optimum reaction condition.
Figure 7. The stability test of the WCR derived catalyst in 20 cycles of biodiesel (FAME) productions. Reaction condition: 80°C; catalyst 10wt%, molar ratio 20:1; and 5 hrs.

5. Conclusion
A new catalyst is developed for biodiesel production from waste cooked rice (WCR). It is a heterogeneous solid catalyst, which can catalyse esterification and transesterification reactions at the same time. Moreover, the catalyst is a solid. It can be easily separated from the product and can be recycled. The WCR derived catalyst shows a good catalyst activity in the production of biodiesel (FAME) from cheap feedstock of grease trap oil (GTO) with 38.7% free fatty acid (FFA). It also shows a stable performance. The yield maintains similar, even when the catalyst has been reused 20 times. The WCR derived catalyst has great potential to be applied in industrial biodiesel production in the future.

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