# Parametric Study on the Transesterification Reaction by Using CaO/Silica Catalyst

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Recently, the application of heterogeneous catalyst has attracted considerable interest in biodiesel production compared to homogenous catalyst because of its reusability in successive reactions runs and easier to separate from the reaction mixture. Thus, attempts have been directed to develop supported catalyst to improve the efficiency and recovering ability of the prepared catalyst. In this study, a renewable low cost heterogeneous hybrid catalyst through utilization of waste material; rice husk and eggshell was synthesized via wet impregnation method. The performance of CaO impregnated with silica was tested for its catalytic activity via transesterification of waste cooking oil. The effect of silica content, catalyst loading, methanol to oil molar ratio, reaction time and reaction temperature on biodiesel yield were investigated. The result show that the calcium oxide (CaO) supported with silica is more effective for the production of biodiesel compared to CaO individually. Furthermore, it was determined that the transesterification conditions of 3 wt % catalyst loading. 15:1 methanol to oil molar ratio, 90 min reaction time and 60 ºC reaction temperatures resulted in biodiesel yield of 90 %.

## 1. Introduction

With the increasing fuel demand, many countries have invested heavily in the search for renewable energy sources to supply or replace fossil fuels. As an alternative solution, biodiesel has become an attractive option since it has low emissions. It is mainly produced via transesterification of vegetable oil, whereby a triglyceride reacts with an alcohol in the presence of a catalyst, producing a mixture of fatty acid methyl esters (FAME) and glycerol (Schuchardta et al., 1998).

Transesterification is catalyzed by either homogenous or heterogeneous catalyst. Although homogenous catalyst usually exhibit high catalytic activity and their processes are relatively fast, they possess several disadvantages, such as the production of large amount of waste water, occurrence of saponification and the difficulty for removal of the catalyst after reaction (Farooq et al., 2013). To circumvent these issues, researchers have focused on using heterogeneous catalyst to synthesize biodiesel since they can be reused repeatedly without any major loss in their catalytic activity, as well as less environmental pollution (Martino et al., 2008).

Presently, various heterogeneous catalysts have been synthesized including supported catalysts (Umdu et al., 2009), alkali earth oxides (Ilgen and Nilgu, 2009) and hydrotalcites catalyst (Liu et al., 2008). As a typical solid base catalyst, CaO has provided great potentials in the biodiesel production due to its long catalyst life, high activity and requires only moderate reaction conditions (Math et al., 2010). Recently, researchers have utilized waste eggshells as cheap resources of CaO for application as low cost heterogonous catalyst. However, the partial dissolution of $Ca^{2+}$ ions from the CaO surface often occurs during the transesterification process, thus resulting in a decreased catalytic activity (Chen et al., 2015). In order to address these problems, CaO have been incorporated on high surface area materials such as alumina (Umdu et al., 2009), zeolite (Wu et al., 2013) and silica (Chen et al., 2015; Samart et al., 2010) to enhance the stability of CaO.

Among these catalyst supports, mesoporous silica has attracted much attention due to its many excellent properties such as good thermal stability, high surface area and unique large pore structure characteristic (Melero et al., 2012). There are several studies available in the production of CaO impregnated with silica catalyst by using sodium silicate (Chen et al., 2015), tetraethyl orthosilicate (Mohadesi et al., 2014) and pluronic

P123 (Samart et al., 2010) as sources of silica. However, there has been no work done on the utilization of silica supported-CaO catalyst from rise husk for biodiesel synthesis.

Therefore, in this study, it is aimed to synthesize and characterize a new low cost, highly efficient supported base catalyst through utilization of the two waste materials, which are rice husk ash and egg shell for transesterification of palm oil to yield fuel grade biodiesel. As can be highlighted, this study is focusing on the utilization of waste materials for synthesizing of valuable hybrid catalyst using a simple and green approach. The findings of this study offers a more economic solution for biodiesel production and in the same time could reduce waste disposal problems.

## 2. Materials and method

### 2.1 Materials

The waste cooking oil was obtained from a local restaurant in Arked Meranti, UTM, Johor whereby this oil was used for the transesterification reaction without further treatment and purification. For catalyst production, chicken eggshell was collected from local restaurants and raw rice husk was purchased from Qhadijah Natural Farm, which was located at Parit Buntar, Perak. Other chemicals used in this study were hydrochloric acid and methanol, are reagent grade purchased from Sigma.

### 2.2 Catalyst preparation

The waste egg shells were cleaned to remove sand and flesh adhering to the shells by rinsing with distilled water several times. Then, the shells were dried in an oven at 60 ºC for 24 h. After being dried, the shells were crushed and ground to fine powder. The dried crushed shells were then calcined in a furnace at 900 ºC for 6 h in order to obtain CaO catalyst.

For silica preparation, dry raw rice husks were sieved to eliminate residual rice and clay particles and then washed with distilled water. After through washing, rice husks were filtered and dried in an oven at 60 ºC overnight. The cleaned rice husks were converted into rice husk ash by heat–treating at 700 ºC for 6 h, whereby the ash was brownish in color. Subsequently, the ash was boiled in 100 mL of 3N of hydrochloric acid (HCl) from concentrated HCl for 1 h to get impurity free ash. The ash was then filtered, washed and dried in an oven. Finally, the ash was calcined at 700 ºC for 6 h.

The hybrid catalyst of CaO and silica was prepared using wet impregnation method. A sample of approximately 5 g of CaO was added to 100 mL water to prepare aqueous solution. Then, this solution was added to an amount of silica and mixed vigorously under total reflux for 4 h at 80 ºC. Subsequently, the mixture was filtered and dried in an oven. The dried mass was then calcined in a furnace at temperature of 800 ºC for 3 h. The calcined mass obtained was referred as silica impregnated calcium oxide catalyst.

### 2.3 Transesterification process

The transesterification was carried out in a batch reactor. A 40 mL of oil was stirred in a 500 mL round-bottom flask equipped with a reflux condenser. A mixture of methanol and catalyst at a designated amount was added to the oil and the transesterification was conducted for the required reaction times. Upon the reaction completion, phase separation was carried out in a separatory funnel at room temperature. The reaction parameters involved were the weight ratio of silica over CaO (0–10 wt%), the catalyst dosage (2–10 wt%), molar ratio of methanol to oil (5:1–25:1), the reaction time (30–150 minutes) and the reaction temperature (40–80ºC). The yield of biodiesel is determined according to Eq(1).

$$\text{Yield of biodiesel } (\%) = \frac{\text{Weight of biodiesel}}{\text{Weight of oil}} \times 100 \qquad (1)$$

## 3. Results and discussion

### 3.1 Effect of silica content

The influence of the amount of silica on the activity of CaO catalyst was tested at reaction time and temperature of 2 h and 60 °C with molar ratio of methanol to oil at 20:1. Figure 1 shows the yield of methyl ester using different content of silica.
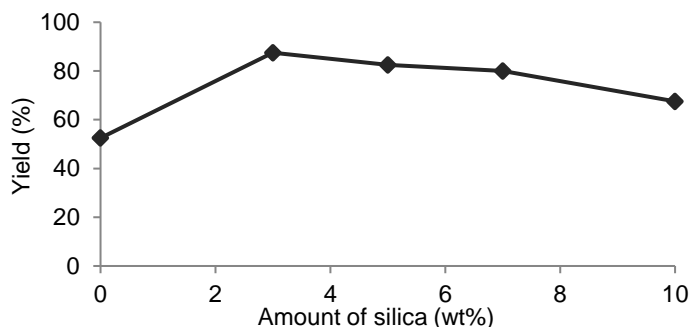
*Figure 1: Effect of silica content on biodiesel yield.*

From the result, it was found that the CaO supported with silica had a higher yield of methyl ester than CaO individually. This might be due to the solid state reaction between silica compound and the surface of CaO in the activation process, whereby the silica could have inserted in the vacant sites of CaO. Furthermore, it was noted that the introduction of silica in the CaO catalyst is able to improve the surface area due to increasing total pore volume, which in turn providing the opportunity to increase the number of active sites that interact with the reactants and consequently facilitates the biodiesel formation. However, the further increase in the amount of silica leads to low yield of methyl ester. The reduction of the product is caused by covering the active sites on CaO surface by excess silica, resulting in a lowered catalytic activity. Therefore, the optimum amount of silica is 3 % by weight of CaO catalyst.

### 3.2 Effect of catalyst dosage

The dosage of catalyst is an important factor of the biodiesel yield. In this study, the catalytic activities of CaO impregnated with 3 wt% silica were investigated with catalyst content varying from 1 to 5 wt% (weight to oil) at 60°C with molar ratio of methanol to oil at 20:1 for 2 h and the results were presented in Figure 2.
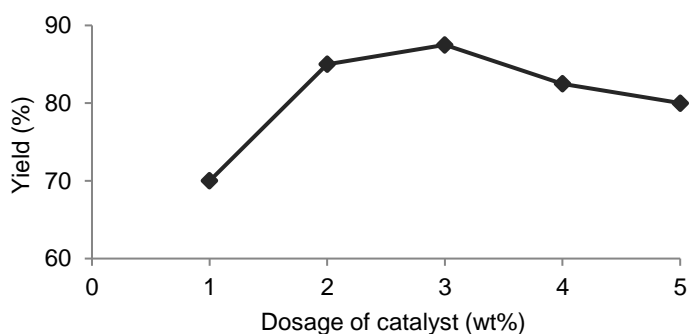


*Figure 2: Effect of catalyst loading on biodiesel yield.*

From Figure 2, it is observed that the increase in catalyst dosage from 1 to 3 wt% resulted in corresponding increase in methyl ester yield from 70 to 87.5%. As reported by Leung and Guo (2006), low loading of catalyst (2 wt%) is insufficient to drive the reaction for completion and the yield of biodiesel was only less than 75% after 2 hours. Increase in the yield of methyl ester with increase in amount of catalyst was attributed to the sufficient number of active sites available for the transesterification reaction of oil. An addition of 4 wt% of catalyst content however had deterioration effect for methyl ester yield as a decrease was observed from 87.5 to 82.5%. Then, the yield of the methyl ester decreased slowly from 82.5 to 80% along with an increase in catalyst content from 4 to 5 wt%. An excessive amount of catalyst gave rise to the viscosity of the reaction mixture and led to the poor diffusion between reactants and catalyst, which in turn lowers the ester production yield (Jitputti et al., 2006; Maneerung et al., 2015). Moreover, at a higher catalyst loading, biodiesel products may get absorbed on the surface of the unused catalyst, thus reducing the methyl ester yield. Based on this result, 3 wt% of catalyst amount was selected as the optimum amount in this study.

### 3.3 Effect of molar ratio of methanol to oil

Stoichiometrically, the molar ratio of alcohol to triglyceride for the transesterification reaction is 3:1. Since the transesterification reaction is reversible, excess methanol can generally be used to convert the oils or fats

completely to esters. In this study, the reaction was carried out at 5:1, 10:1, 15:1, 20:1 and 25:1 molar ratios of methanol to oil with hybrid catalyst fixing at 3 wt%. The reaction time and temperature was also set at 2 hours and 60°C. The effect of methanol to oil molar ratio on the yield of biodiesel is illustrated in Figure 3.
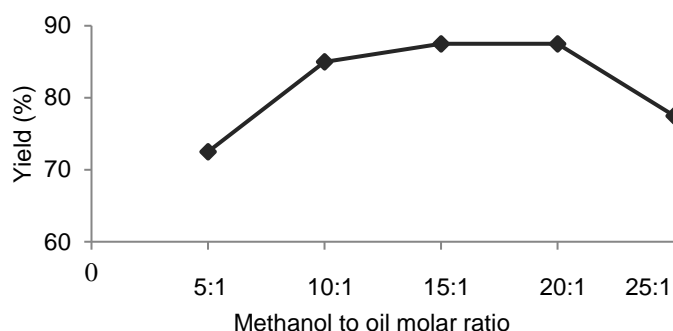


*Figure 3: Effect of methanol to oil molar ratio on biodiesel yield.*

As shown in Figure 3, the yield of biodiesel was around 72.5 % for molar ratio of 5:1, increased tremendously to around 85 % for methanol to oil molar ratio of 10:1 and further increased to 87.5 % for methanol to oil molar ratio of 15:1. Comparatively, methanol to oil molar ratio of 20:1 also provided high yield same as the yield at 15:1, thus this ratio could be avoided for the purpose of cost minimization. In agreement with the literature, the high amount of methanol was able to promote the formation of methoxy species on the catalyst surface, leading to a shift in the equilibrium in the forward direction and therefore increasing the rate of the transesterification reaction (Buasri et al., 2013). However, a further increase in the methanol to oil molar ratio to 25:1 had no significant influence on the biodiesel yield and the observed biodiesel yield at 25:1 was found to be lower as compared to the 20:1 molar ratio. The obtained result can be attributed to the fact that the glycerol would largely dissolve in excessive methanol and subsequently inhibited the reaction of methanol to the reactants and catalyst, resulted in a lower biodiesel yield (Obadiah et al., 2012; Viriya-empikul et al., 2010). Furthermore, the polar hydroxyl group in methanol acting as emulsifier and leads to the formation of gels, resulting in difficulty in the separation and purification of methyl ester (Ali et al., 2015). Thus, 15:1 was the ideal proportion in the transesterification reaction using CaO impregnated with 3 wt% silica catalyst.

### 3.4 Effect of reaction time

The influence of reaction time on the biodiesel yield was also investigated by varying the reaction time from 30 to 150 min, whereby the catalyst dosage, methanol to oil molar ratio and reaction temperature was fixed at 3 wt%, 15:1 and 60 °C. The result obtained from the effect of reaction time of biodiesel yield is illustrated in Figure 4.
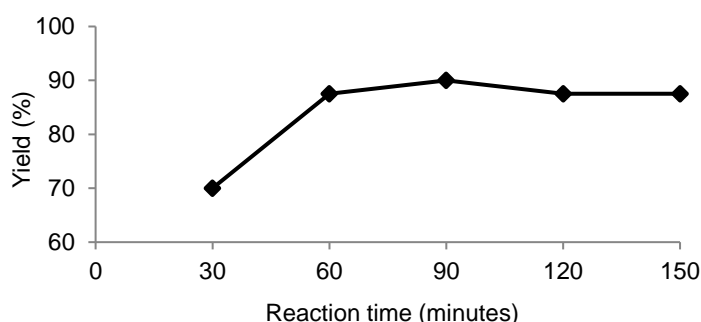


*Figure 4: Effect of reaction time on biodiesel yield.*

The results showed that the yield of methyl ester increased along with the increase of reaction time from 30 to 150 minutes. According to Garnica et al. (2009), the reaction is slow at the initial stages of the transesterification reaction due to the difficulty of mixing and dispersion of alcohol into oil, since the reactants initially form a two-phase liquid system. As a result, it can be seen that the yield of methyl ester for 30 minute of transesterification reaction was found to be 70 %. Subsequently, the yield of methyl ester was more than 85 % at 60 min, and from 60 to 90 min the biodiesel yield increases slightly from 87.5 to 90 %. Further increases in reaction time were

found to have no significant increase in biodiesel yield. Therefore, 90 min is sufficient to cross the energy barrier by the reactant in order or transform the triglycerides and methanol to methyl ester.

### 3.5 Effect of reaction temperature

Reaction temperature is also one of the factors affecting the transesterification reaction because the intrinsic rates constant are strong functions of temperature. In order to determine the optimum reaction temperature, transesterification reaction was carried out with 15:1 methanol to oil molar ratio in the presence of 3 wt% hybrid catalyst in 90 minutes reaction at different temperature from 40 to 80 °C. The dependence of reaction temperature on the biodiesel yield is shown in Figure 5.
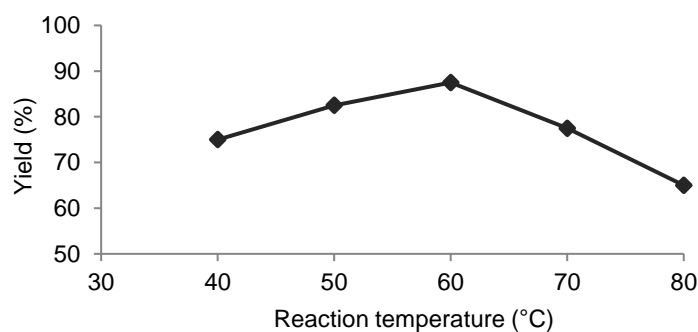


Figure 5: Effect of reaction temperature on biodiesel yield.

As illustrated in Figure 5, the reaction rate was slow at low temperature for the CaO impregnated catalyst, whereby the biodiesel yield was only 75 % after 90 min of reaction at 40 °C. Subsequently, an increase in temperature from 50 to 60 °C, a corresponding increase in the biodiesel yield from 82.5 to 90 % is obtained. At higher reaction temperature, it is expected that the kinetic energy of the reactants is sufficient to speed up the rate of mass transfer and overcome the diffusion resistance among the three phases of oil-methanol catalyst, which in turn led to increased methyl ester yield. Furthermore, the yield of methyl ester increases with raising the temperature can also be attributed to the enhanced miscibility of oil-methanol and viscosity of the oil decreases resulting into better contact of reactants (Boro et al., 2014). Alves et al. (2013) also reported that that the value of the solubility parameter of methanol decrease and become closer to that of vegetable oil if proper temperature is employed. Nevertheless, the yield of methyl ester is drastically decreased to 77.5 and 65 % at higher reaction temperature of 70 and 80 °C. This is probably due to the fact that the boiling point of methanol is around 65 °C and reaction above this temperature might cause the methanol to vaporize in gas phase leading to low catalytic activity. In addition, too high temperature would increase the risk of saponification (Li et al., 2015). Thus, the highest reaction temperature was limited to 60 °C for the transesterification of oil and methanol using CaO impregnated with silica catalyst.

## 4. Conclusions

In this study, the CaO supported with silica catalyst was succesfully synthesized from waste egg shell and rice husk. The hybrid catalyst showed high catalytic activities for the transesterification reaction. The biodiesel yield of transesterification reaction over the CaO supported by silica catalyst reaches to 87.5 % at 2 h, which is higher than the biodiesel yield over CaO individually. Furthermore, the yield of biodiesel was also affected by different silica content, catalyst loading, methanol to oil molar ratio, reaction time and reaction temperature. As a conclusion, this waste-derived catalyst showed a potential use for biodiesel production, which could not only eliminate the waste but display desirable catalytic performance in the transesterification reaction. These wastes could stand for abundant resources of low-cost catalysts which provides a simple and green method in order to produce biodiesel fuel.

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