

BIODIESEL PRODUCTION USING CAO IMPREGNATED WITH SILICA AS CATALYST

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ABSTRACT

Currently, biodiesel is produced by performing a transesterification reaction with homogeneous base catalysts such as KOH or NaOH dissolved in methanol. This production process can provide high FAME yields under mild conditions. However, the homogeneous catalytic process suffers some drawbacks of an inevitable production of wastewater from washing process of catalyst residues and unreusability of the catalysts. Thus, in this study, it is proposed to synthesize and characterize a renewable low cost heterogeneous hybrid catalyst through utilization of waste material; rice husk ash (RHA) and egg shell (ES) for transesterification reaction. The hybrid RHA-ES was synthesized via a wet impregnation method. Then, the synthesized hybrid catalyst was characterized using BET and SEM analysis. The effectiveness of the hybrid catalyst will be tested on biodiesel yield. From BET results, surface area of hybrid catalyst was found to have higher surface area than CaO catalyst. It could be due to the strong interaction of the CaO with silica support, which reduced the surface diffusion of Ca, inhibited sintering and stabilized the surface of CaO [Omar and Amin, 2011]. Furthermore, this result was supported by SEM image, whereby the significant agglomeration of the silica particles with a heterogeneous distribution was observed on the surface of CaO catalysts. In the transesterification study, 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. Therefore, it can be concluded that the hybrid RHA-ES catalyst derived from waste materials can be an excellent catalyst in biodiesel production.

Keywords: CaO; Hybrid Catalyst; Rice Husk; Egg Shell; Transesterification; Biodiesel

1. Introduction

Alternative fuels for diesel engines have gain importance because of diminishing petroleum reserves and the environmental consequences of exhaust gases from petroleum fueled engines (Xie et al., 2007). In this respect, biodiesel is an emerging alternative to diesel fuel derived from renewable and locally available resources which is biodegradable, nontoxic and environmentally friendly. It is mainly produced via transesterification of vegetable oil, which is a renewable and sustainable source (Kansedo et al., 2009). In the transesterification reaction, a triglyceride reacts with an alcohol in the presence of a catalyst, producing a mixture of fatty acids alkyl esters and glycerol (Schuchardta et al., 1998). Currently, biodiesel is produced by performing a transesterification reaction with homogeneous base catalysts such as KOH or NaOH dissolved in methanol. However, the major disadvantage of homogeneous catalysts is that they cannot be reused or regenerated, because the catalyst is consumed in the reaction. Moreover the separation of catalyst from products is difficult and requires more equipment which results in higher production costs (Freedman et al., 1984).

Based on these drawbacks, the use of heterogeneous catalysts could be an attractive solution. Heterogeneous catalysts can be separated more easily from reaction products and undesired saponification reactions can be avoided (Martino et al., 2008). Biodiesel synthesis using solid catalysts could also lead to cheaper production costs because of reuse of the catalyst and the possibility for carrying out both transesterification and esterification simultaneously (Dora et al.,

2005). A large variety of different heterogeneous catalysts have been investigated including supported catalysts (Umdu et al., 2009), alkali earth oxides (Ilgen and Nilgu, 2009) and hydrotalcites catalyst (Liu et al., 2008). Among them CaO has been received much interest due to its long catalyst life, high activity and requires only moderate reaction conditions (Math et al., 2010).

Incorporating CaO on high surface area materials such as silica (Samart et al., 2010), alumina (Umdu et al., 2009), and zeolite (Wu et al., 2013) was found be able to accelerate the catalytic activity of CaO and thus improved the biodiesel yield. 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, which reduce mass transfer limitations and allow high concentration of active sites per mass of material (Melero et al., 2012). However, there is no work has been reported on utilization of silica supported-CaO catalyst from rice husk ash (RHA) for biodiesel synthesis. Rice husk, a waste product of the processing of grain, is normally been used in power generation through combustion and its burning generates another residue, the rice husk ash (RHA). The presence of high amount of SiO₂ prompts its potential applicability as a low-cost catalyst support.

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 is rice husk ash and egg shell for transesterification of palm oil to yield fuel grade biodiesel.

2. Materials and Method

2.1 Materials

The virgin cooking palm oil was purchased from local market and 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 obtained commercially from MD Interactive Sdn Bhd.

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°C for 24 hours. After being dried, the shells were crushed and ground to fine powder. The dried crushed shells were then calcined in a furnace at 900°C for 6 hours 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°C overnight. The cleaned rice husks were converted into rice husk ash by heat-treating at 700°C for 6 hours, whereby the ash was brownish in color. Subsequently, the ash was boiled in 3N hydrochloric acid for 1 hour to get impurity free ash. The ash was then filtered, washed and dried in an oven. Finally, the ash was calcined at 700°C for 6 hours.

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 hours at 80°C. Subsequently, the mixture was filtered and dried in an oven. The dried mass was then calcined in a furnace at temperature of 800°C for 3 hours. The calcined mass obtained was referred as hybrid catalyst.

2.3 Catalyst characterization

The BET surface area, total pore volume and pore size distribution of the catalyst were determined with AUTOSORB-1C, Chemisorption-Physisorption analyzer. Surface area was calculated by using BET equation from the adsorption branch of the isotherm in a relative pressure range from 0 to 1. The total pore volume of the catalyst was examined by N₂ physisorption method while the pore size distribution was determined from absorption branch by the Non-Local-Density-

Functional-Theory (NLDFT) method. The surface morphology of the catalysts were investigated by using a JEOL JSM–6390LV scanning electron microscope, with the accelerating voltage of 50 kV. All specimens were coated with gold and then observed.

2.4 Transesterification reaction and biodiesel yield

The transesterification was carried out in a batch reactor. A 50 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 influence of silica content on the biodiesel yield was investigated by varying the silica content from 3 to 10 wt%, whereby the catalyst dosage, methanol to oil molar ratio, reaction time and temperature was fixed at 3 wt%, 15:1, 2 hours and 60°C, respectively. The yield of biodiesel is determined according to Equation 1.

$$\text{Yield (\%)} = (\text{Weight of biodiesel} / \text{Weight of oil}) \times 100 \quad (\text{Equation 1})$$

3. Results and discussion

3.1 BET analysis

Table 1 The physical properties of CaO, silica and hybrid catalyst

| Catalyst | BET area (m ² /g) | Total pore volume (cm ³ /g) | Average pore diameter (nm) |
|-----------------|------------------------------|--|----------------------------|
| CaO | 6.83 | 0.0319 | 7.86 |
| Silica | 132.83 | 0.3644 | 15.89 |
| Hybrid catalyst | 12.29 | 0.0429 | 11.76 |

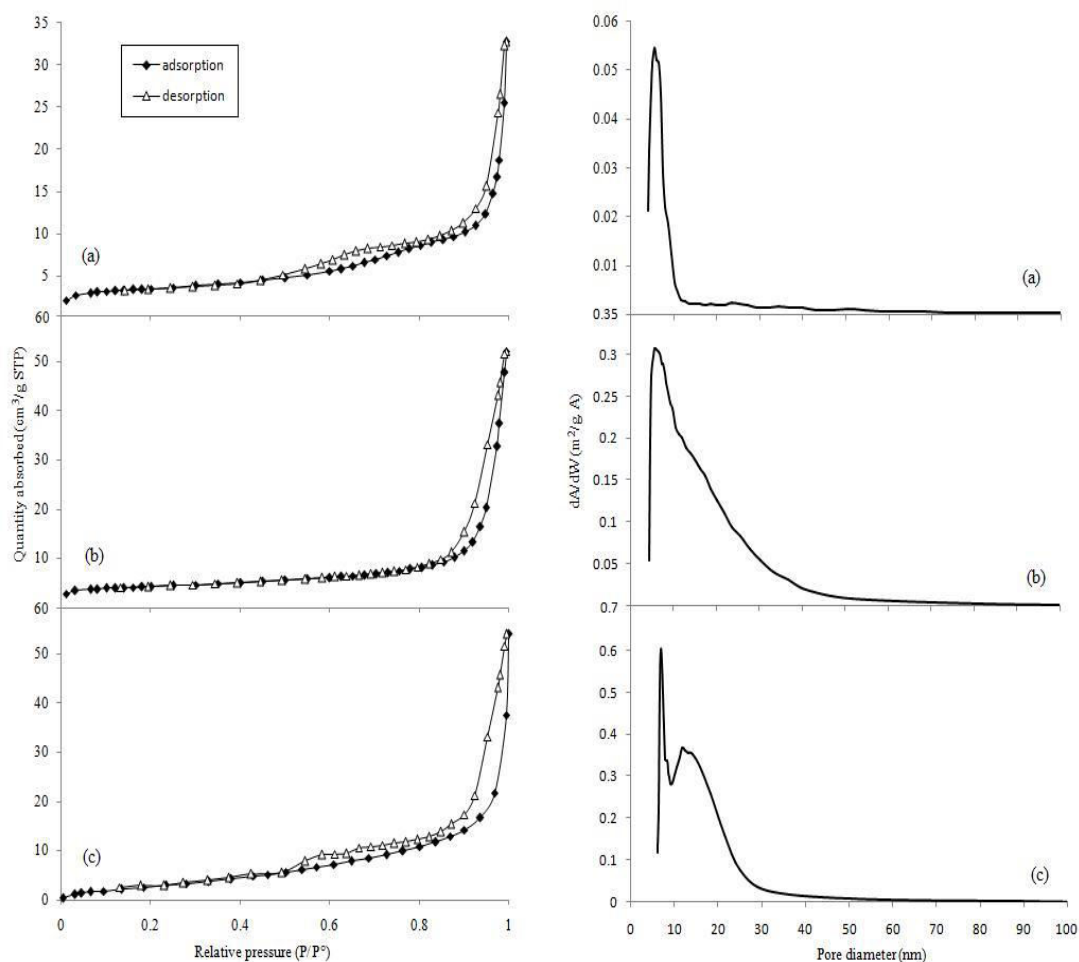


Fig. 1. N₂ adsorption–desorption isotherm and pore size distribution of the (a) CaO, (b) silica and (c) CaO impregnated with 3% silica; hybrid catalyst

The BET surface area, total pore volume and pore diameter of CaO, silica and hybrid catalyst were measured and summarized in Table 1. The BET surface area of CaO catalyst derived from waste egg shell was found to be 6.83 m²/g. Upon impregnation with silica, which has high surface area of 132.83 m²/g, there was an increment of the surface area to 12.29 m²/g. The increasing surface area of the catalyst might be due to the strong interaction of the CaO with silica support, which reduced the surface diffusion of Ca, inhibited sintering and stabilized the surface of CaO (Omar and Amin, 2011). Thus, it can be expected that the hybrid catalyst would lead to improve the activity of catalyst in transesterification process by increasing the accessibility of the active sites and provide enough attachment area as reported by Istadi et al. (2015).

The porosity of the catalyst was examined by N₂ physisorption method while the pore size distribution was determined from absorption branch by the NLDFT model. Nitrogen adsorption–desorption isotherms and the corresponding pore size distribution plots of all catalysts are shown in Fig. 1. All isotherm curves showed a type IV profile and type H3 hysteresis loops, except silica, whereby there was no hysteresis loop in the first capillary condensation. The first step of capillary condensation, in a relative pressure of 0.5, was attributed to the nitrogen condensation that took place in the internal mesopores and secondly at a higher partial pressure ($P/P^0 = 0.8$), which was attributed to the presence of interparticle porosity. Furthermore, it could be observed that the pore size of the CaO catalyst was in the range of 3–10 nm and can be classified as mesopores. Upon introduction of silica into CaO and following calcination, the catalyst particles exhibited bimodal pore size distribution that consisted of a primary pore at 7 nm and secondary pore at 13 nm.

The total pore volume and average pore diameter of CaO and silica were 0.0319 cm³/g, 7.86 nm, 0.3644 cm³/g and 15.89 nm, respectively, while for CaO impregnated with 3% silica these

parameters were $0.0429 \text{ cm}^3/\text{g}$ and 11.76 nm , respectively. In comparison, the pore diameter of the catalysts are somewhat larger than the reactant molecules, whereby the dimensions of triglyceride, methyl oleate and glycerin are approximately 5.8 nm , 2.5 nm and 0.6 nm , respectively (Granados et al., 2007; Jacobson et al., 2008; Wu et al., 2014). It has been reported that the larger average pore diameter and larger interconnected pores of catalyst would minimize diffusion limitations of reactant molecules. Therefore, the reactant molecules can easily infiltrate into the interior of the catalyst and most of the active site will be utilized during the transesterification reaction (Omar and Amin, 2011; Wu et al., 2014).

3.2 Scanning electron microscopy

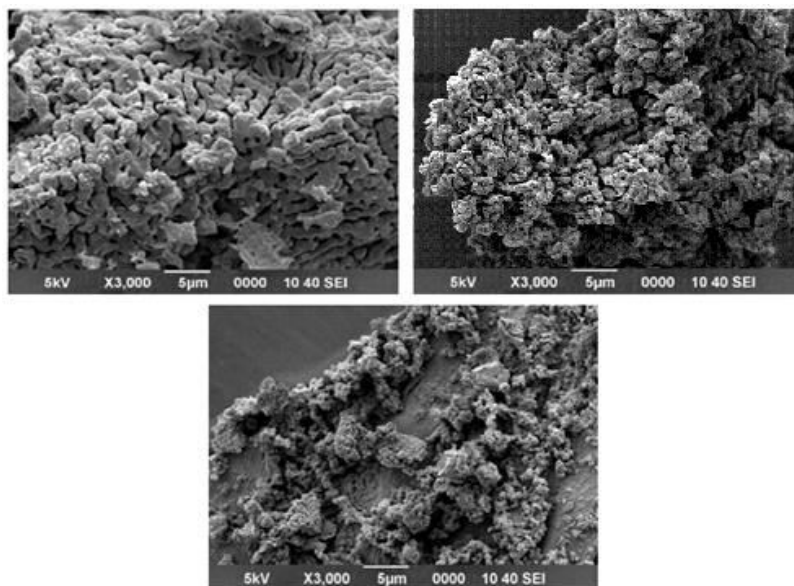


Fig. 2 SEM photographs of (a) CaO, (b) silica and (c) CaO impregnated with 3% silica; hybrid catalyst

The morphology of the CaO, silica and hybrid catalyst samples was studied by SEM and the monograph of each catalyst is demonstrated in Fig. 2. It was observed that the CaO catalyst was comprised of rod-like particles and some of them were bonded together as aggregates, while the particles of the silica have a spherical and porous structure. In the case of hybrid catalyst, the image showed the significant agglomeration of the silica particles with a heterogeneous distribution on the surface of CaO catalysts. Furthermore, the pores among these agglomerates were relatively large and therefore, the surface of the catalyst can fully contact with oil ester and methanol where they undergo transesterification reaction to produce biodiesel, resulting in better catalytic activity.

3.3 Effect of silica on the yield of the transesterification

The influence of the amount of silica on the activity of CaO catalyst was tested at reaction time and temperature and time of 2 hours and 60°C , respectively with molar ratio of methanol to oil at 15:1. Fig. 3 shows the yield of methyl ester using different content of silica.

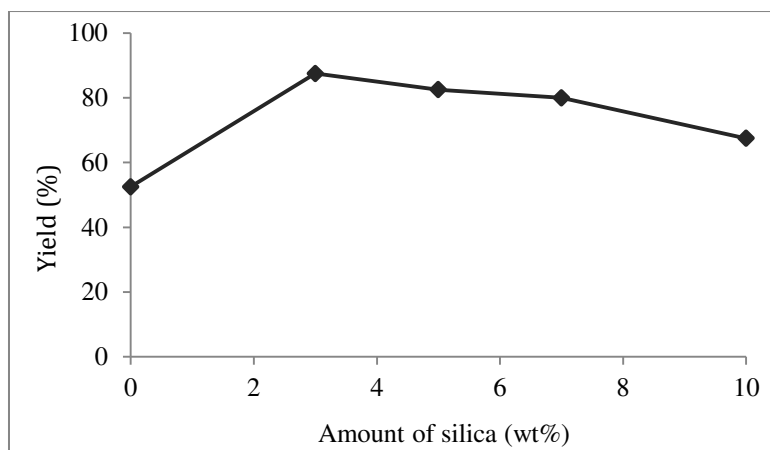


Fig. 3 Effect of silica content on biodiesel yield

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.

3.2.2. 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 hours and the results were presented in Figure 6.

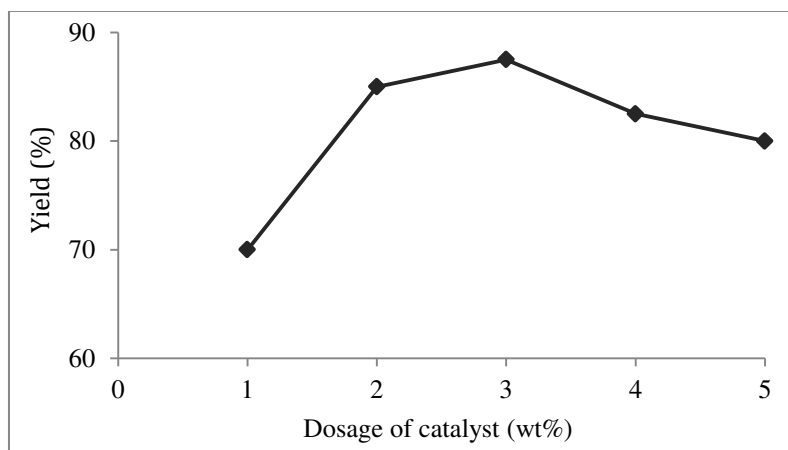


Figure 6: Effect of hybrid catalyst loading on biodiesel yield

From Figure 6, 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.

3.2.3. 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, respectively. The effect of methanol to oil molar ratio on the yield of biodiesel was illustrated in Figure 7.

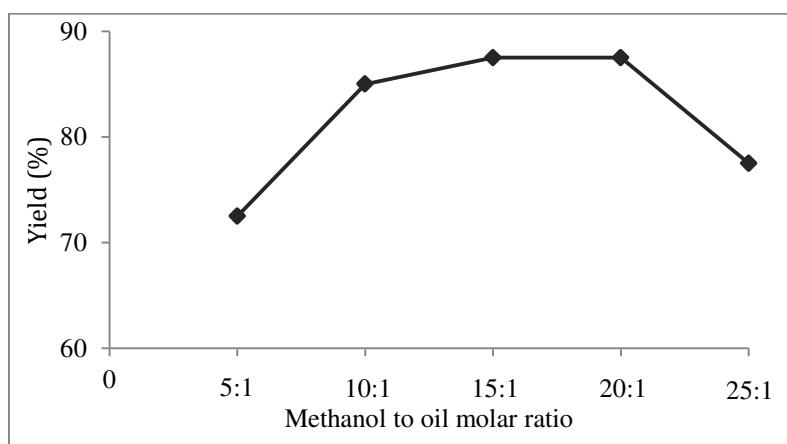


Figure 7: Effect of methanol to oil molar ratio on biodiesel yield

As shown in Figure 7, 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; Viriya-empikul *et al.*, 2010). 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 produces a stable emulsion, resulting in difficulty in the separation and purification of methyl ester (Lee *et al.*, 2015). Thus, 15:1 was the ideal proportion in the transesterification reaction using CaO impregnated with 3 wt% silica catalyst.

3.2.4. 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 minutes, whereby the catalyst dosage, methanol to oil molar ratio and reaction temperature was fixed at 3 wt%, 15:1 and 60°C, respectively. The result obtained from the effect of reaction time of biodiesel yield is illustrated in Figure 8.

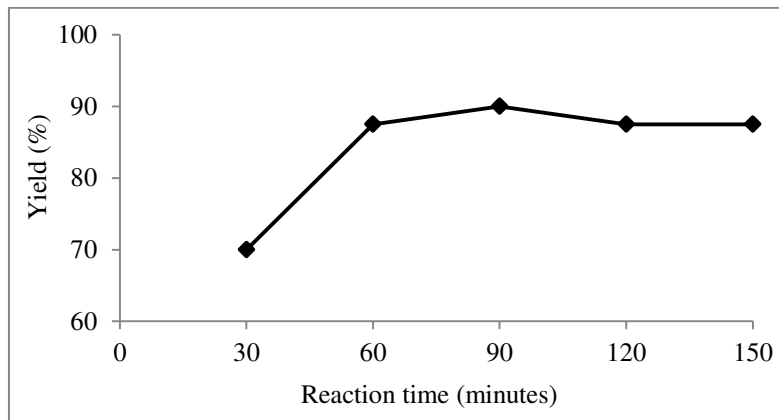


Figure 8: Effect of reaction time on biodiesel yield

The results showed that the yield of methyl ester increased along with the increase of reaction time from 30 to 150 minutes. According to Tang *et al.* (2013), the reaction is slow at the initial stages of the transesterification reaction due to the difficulty of mixing and dispersion of alcohol into oil. 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 minutes, and from 60 to 90 minutes 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 minutes is sufficient to cross the energy barrier by the reactant in order or transform the triglycerides and methanol to methyl ester.

3.2.5. 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 50 to 70°C. The dependence of reaction temperature on the biodiesel yield has been shown in Figure 9.

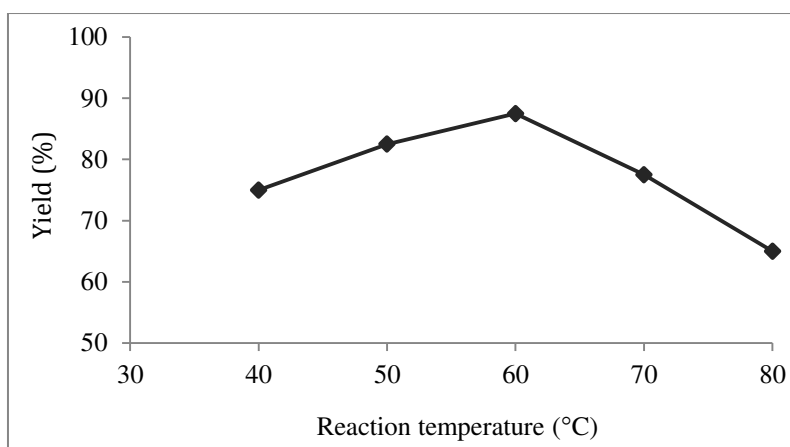


Figure 9: Effect of reaction temperature on biodiesel yield

As illustrated in Figure 9, the reaction rate was slow at low temperature for the CaO impregnated catalyst, whereby the biodiesel yield was only 75% after 90 minutes of reaction at 50°C. Subsequently, an increase in temperature from 55 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; Li *et al.*, 2015; Pukale *et al.*, 2015; Shahrake *et al.*, 2015). Nevertheless, the yield of methyl ester is drastically decreased to 77.5 and 65% at higher reaction temperature of 70 and 80°C, respectively. 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 (Boro *et al.*, 2014; 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. Conclusion

In this study, the CaO supported with silica catalyst was successfully synthesized from waste egg shell and rice. 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 hours, which is higher than the biodiesel yield over CaO individually. This is probably due to the higher surface area of hybrid catalyst compared to CaO catalyst and therefore facilitates the biodiesel formation. Furthermore, the yield of biodiesel was also affected by different silica content. The yield at low silica content in CaO catalyst is higher because the excess silica tended to cover the active sites on CaO surface. As a conclusion, this hybrid RHA-ES catalyst is promising to be an ideal candidate as a catalyst in the transesterification reaction of oil to produce biodiesel.

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