



Application of heterogeneous catalysts for transesterification of refined palm oil in ultrasound-assisted reactor

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ABSTRACT

This research investigated the application of commercial heterogeneous catalysts i.e., calcium oxide (CaO) and potassium phosphate (K₃PO₄) for biodiesel production in an ultrasound-assisted reactor (US). For comparison, the results from the use of homogeneous catalysts i.e., sodium hydroxide (NaOH) and sulfuric acid (H₂SO₄) as well as from the use of conventional mechanical stirred reactor (MS) were also studied. High methyl ester yields were achieved in the US reactor for both CaO (90%) and K₃PO₄ (80%). The mixing characteristics generated from US and MS reactors resulted in the different performance (activation and deactivation) of CaO and K₃PO₄ catalyzed transesterification. The major overcome of using US reactor for heterogeneously catalyzed transesterification was found in the catalyst reusability test. Methyl ester yield of CaO catalyst gradually reduced when applying US reactor compared to MS reactor, particularly in the last cycle. The dissolution effect was more severe when employing K₃PO₄ catalyst in the MS reactor due to the mechanical stress and the mixing characteristic effects. Therefore, the use of US reactor did not only provide the high methyl ester yield in a short reaction time but also showed the hindrance of dissolution compared to the MS reactor. It can be concluded that the heterogeneously catalyzed transesterification in US reactor was not only favorable in the activation but also diminishable in the deactivation of solid catalysts.

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1. Introduction

Nowadays, the energy demand continuously increases because of the population growth. Therefore, to meet the energy demand, the development of modern and highly efficient technologies is necessary. Moreover, the lack of fossil fuels such as oil and petroleum causes the requirement of renewable and sustainable fuels. Biodiesel, one of the clean renewable fuels, becomes more attractive. It is possibly derived from many types of feedstocks such as edible oils [1–4], non-edible oils [5–9], waste oils [10–12], etc. Generally, fats or oils are reacted with a low molecular weight alcohol to form biodiesel and glycerol with or without presence of catalyst.

However, transesterification of triglycerides (TGs) involves three reversible consecutive steps which limit biodiesel yield [13]. Moreover, a problem on solubilization of methanol and oil also hinders the rate of reaction. Therefore, there are a large number of researches proposing efficient reactors to solve the problems as mentioned above. Ultrasound-assisted reactor (US) is one of the interesting technologies. A recent review summarized that this type of reactor provided a good efficiency for biodiesel production in terms of processing time reduction, sustainable raw materials usage and safer operation [14]. The ultrasound irradiation affects the variations of pressure in the liquid medium. It induces

the generation of microbubbles by cavitation in the reactor to form the emulsion phase. When the microbubbles were collapsed at the reactants boundary, the interfacial area for reaction was largely increased [15,16]. Vichare et al. [17] reported that the mixing time characteristic of sonochemical reactor could be correlated in a way similar to that of the case of jet mixing in tanks. They also found that the acoustic wavelengths are much larger than that in the blade or stirred reactor. Eventually, this enhanced mass transfer between two phases and accelerated the rate of reaction [18]. By applying this technique, high yield of biodiesel was achieved in a short reaction time. Under this operation, transesterification can be carried out at low temperature [3,19,20] and less amount of catalyst and methanol are required which are considered as advantages of this reactor [21–23]. Many researchers have proposed using homogeneous catalysts in an US reactor such as sodium hydroxide and potassium hydroxide [24–29]. However, the high cost of wastewater treatment and the environmental concern are crucial problems for using homogeneous catalyst. Heterogeneous catalyst would be a good choice for biodiesel production. It does not only solve the wastewater problem but also obtains the easy handling and separation [30,31]. Moreover, it is appropriate for utilization in the industrial scale.

By employing heterogeneous catalyst with an US reactor, there are some aspects to be of concern for realizing the advantages of using this catalyst. For example, durability, mechanical stability and deactivation of catalyst have to be concerned. Since those parameters probably affect the possibility for applying the catalysts in the long term

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operation under the violently mixing condition. Motabadi et al. [30,31] investigated the alkaline earth metal oxide catalyzed transesterification of palm oil using US reactor at the temperature of 65 °C. The severe activity drop for the catalyst reusability was also observed. It was found that 95% of biodiesel yield was achieved within 60 min. While the reaction required 2–4 h in a conventional batch type reactor at the same temperature. However, the deactivation of the catalysts in this study seems to be a main drawback. Furthermore, the synthesized nano-catalyst derived from hydrotalcite was applied in the US reactor by Deng et al. [32]. Methyl ester yield of 95.2% was obtained within 1.5 h at a temperature of 45 °C. Catalyst was reused three times and the yield decreased from 95.2 to 80.7% because the viscous liquid was absorbed on the catalyst surface. It was removed by washing with ethanol before being reused for transesterification of *Jatropha* oil. However, the catalyst was reused only eight times since its structure was collapsed under the turbulent mixing operation. The adsorption of organic species on the catalyst surface was more likely a crucial cause for catalyst deactivation in biodiesel production using solid catalyst [32]. Furthermore, using US reactor was less likely to affect the catalyst stability such as particle size of catalyst and removal of the active species [32]. Unfortunately, the effect of mixing characteristics (US and MS) on the activation and deactivation of heterogeneous catalyzed biodiesel synthesis process has not been investigated.

This research explored the effect of US irradiation on the catalytic activity and the catalyst stability of calcium oxide (CaO) and potassium phosphate (K_3PO_4) catalyst for transesterification of refined palm oil. The results have been compared to those of the conventional mixing (mechanical stirred reactor, MS) to gain more understanding about the effect of mixing characteristics on the catalytic activity and catalyst stability of heterogeneous catalyst. Moreover, the reusability and deactivation of catalyst were also considered in order to facilitate the use of heterogeneous catalyst for biodiesel production using US reactor compared to MS reactor. It should be noted that although there are some issues related to food security and sustainability using the edible grade oil, refined palm oil was used in this research for the preliminary study reason and for comparison to other available reports. Calcium oxide (CaO) and potassium phosphate (K_3PO_4) catalysts were used since they showed many advantages such as low cost, mild reaction conditions and availability.

2. Experimental

2.1. Materials

Refined palm oil as a commercial edible grade was purchased from local department store in Thailand. Methanol employed in the reactions was purchased from Qréc with 99.5% purity. All experiments were carried out using commercially available catalysts. Sodium hydroxide (NaOH) as purchased from Loba Chemie was ground and dissolved in methanol before use. Sulfuric acid (H_2SO_4 , 99.5%) was purchased from Qréc. Calcium oxide (CaO) was obtained from Riedel-deHaën. The decomposition temperature of uncalcined CaO catalyst was performed to investigate the optimum calcination temperature of CaO catalyst (data not shown). It was found that the weight loss of uncalcined CaO catalyst appeared from 350 to 550 °C due to the decomposition of $Ca(OH)_2$. Therefore, this CaO was calcined in a muffle furnace at 550 °C for 5 h and kept in a desiccator before transesterification. Moreover, potassium phosphate (K_3PO_4) in a granular form of 2–5 mm was provided from Sigma-Aldrich and used as received. Methyl heptadecanoate and heptane (internal standard and a solvent for GC analysis) was high purity chemicals from Sigma Aldrich and used as obtained.

2.2. Catalyst characterization

Surface area and pore volume of solid catalysts were analyzed by BET method. Catalyst samples were degassed at 300 °C and 10^{-3} mmHg for

3 h. Adsorption measurements were carried out using UHP N_2 adsorption at –196 °C in a Micromeritics ASAP 2020 automated system. All particle size measurements were performed using a Malvern Zetasizer. The sample was dispersed in the distilled water and placed in the ultrasonic bath for more dispersion before analysis. X-ray powder diffraction (XRD) patterns was measured on a Bruker D8 Advance Diffractometer at 40 kv, 40 mA with Cu-K α radiation ($\lambda = 1.54056$ nm). Data were collected over a 2θ range from 20 to 60° with a step size of 0.02 at a scanning speed of 0.5/min. Fourier transform infrared (FTIR) spectrum was performed on a Nicolet 6700 FT-IR spectrometer over a scanning range from 400 to 4000 cm^{-1} . Thermogravimetric analysis (TGA) was conducted with a SDT analyzer Model Q 600 from TA Instrument, under flowing air in the temperature range of 25–900 °C. CO_2 temperature program desorption (CO_2 -TPD) was carried out to determine the basicity of CaO and K_3PO_4 using a Micromeritics ChemiSorb 2750. For CO_2 -TPD, a 0.2 g of catalyst sample was heated to 550 °C in 20 mL/min of helium gas for 1 h in order to remove adsorbed impurities. After that, the sample was cooled to room temperature and saturated with 20 mL/min of pure CO_2 for 1 h. Physisorbed CO_2 was eliminated by flushing with a 20 mL/min of helium at room temperature for 1 h, and increase to 100 °C with a rate of 10 °C/min, then held for 4 h. The temperature was ramped up at a rate of 10 °C/min to 550 °C using TPD as a detector [33].

The methyl esters yield was analyzed according to EN 14103 using a Shimadzu gas chromatography Model GC-14B, equipped with a ZB5-HT capillary column (0.25 mm \times 30 m). Helium was used as a carrier gas. The oven temperature ramp program was started from 150 °C and held for 5 min, 170 °C with a rate of 10 °C/min and held for 5 min, 220 °C with a rate of 3 °C/min. Temperatures of the injector and detector were 250 °C.

2.3. Experimental setup

All experiments were performed in a 125 mL 3-neck round bottom flask immersed into an ultrasonic cleaning bath of 40 kHz Crest Ultrasonic Cleaner with a power of 160 W. Since the sound wave propagates through the liquid medium and the attenuation of sound wave increases with the increasing of the distance from transducer [15]. In other words, the ultrasonic activity is more pronounced at the zone nearby the irradiating surface and suddenly decreases as far away from the source both in axial and radial directions [34]. Then, the position of the flask was fixed at the center of the ultrasonic cleaning bath for all experiments. While using MS reactor, the experiments were performed with the stirrer speed of 800 rpm. The reaction temperature was controlled at 65 °C by circulating hot water through the bath for all experiments. The 3-neck round bottom flask was equipped with a condenser circulated with cold water from an ice bath, a thermometer and a sampling valve as illustrated in Fig. 1.

Refined palm oil was reacted with methanol in a molar ratio of 1:6. Catalyst loadings were 3, 5, and 1 wt.% of oil for solid catalysts, H_2SO_4 , and NaOH, respectively. Two milliliters of sample was taken out of the reactor within the intervals of time period and quenched in an ice bath to stop the reaction. The sample was centrifuged to remove the solid catalyst and kept in the refrigerator before analysis by GC.

2.4. Reusability of catalysts

In the case of catalyst reusability studies, the reaction condition was the same as previously described. Refined palm oil was also reacted with methanol in a molar ratio of 1:6. Solid catalyst loading was 3 wt.% of oil without any pretreatment. The reaction mixture was carefully removed from 3-neck round bottom flask by syringe and the spent catalyst was recovered. Then, fresh refined palm oil and fresh methanol were filled in the reactor. The reaction time for each cycle was set up for 1 h. The catalyst was recovered and used for three times. Then, reaction mixture of each cycle was analyzed.

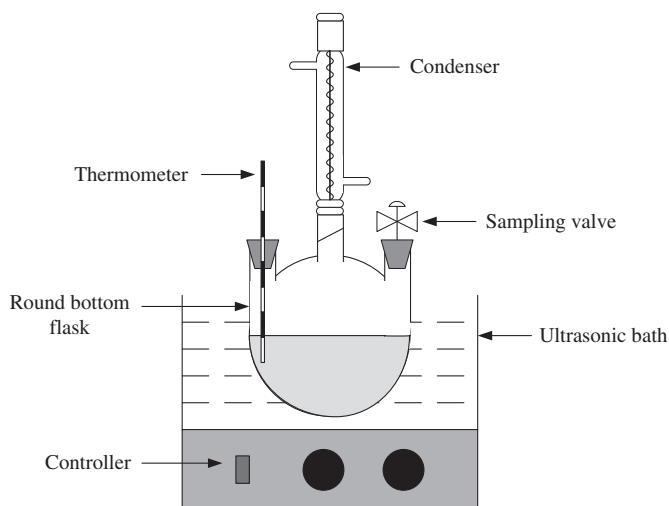


Fig. 1. Setup of an ultrasonic wave assisted reactor.

2.5. Deactivation of catalysts and dissolution studies

The fresh and used catalysts were analyzed by TGA, FTIR and Zetasizer to investigate the cause of catalyst deactivation. Moreover, dissolution of catalyst into the reaction mixture was carried out to investigate the possibility of catalyst reusability. First, solid catalyst was mixed with methanol and heated at the reaction temperature for 1 h. After that the catalyst was filtered out and the remaining methanol was then reacted with oil for 2 h at 65 °C. Lastly, the product mixture was then analyzed by gas chromatography.

3. Results and discussion

3.1. Catalyst characterization

Table 1 shows the properties of fresh solid catalysts used for transesterification of refined palm oil. The BET surface area of CaO was higher than that of K_3PO_4 as well as the pore volume because the particle size of CaO was smaller than that of K_3PO_4 . However, K_3PO_4 was found to have a more basic site (348 $\mu\text{mole/g}$) than CaO (only 46 $\mu\text{mole/g}$). This work was in good agreement with the previous study the BET surface area of CaO was 13 m^2/g [35]. Moreover, the particle size of commercial CaO as reported was more than 100 nm [36] while the pore volume as reported was 0.02 cm^3/g [37].

XRD patterns of calcined and uncalcined CaO are also shown in Fig. 2. For uncalcined CaO, many peaks of calcium hydroxide ($\text{Ca}(\text{OH})_2$) were observed at $2\theta = 28.8^\circ$, 34.1° , 47.1° and 50.8° . However, those peaks disappeared after calcination process. The remaining peaks observed at $2\theta = 32.3^\circ$, 37.4° and 53.9° were characterized as calcium oxide. Those observed peaks were corresponding with other works [38,39]. It was noted that there was no peak of calcium carbonate (CaCO_3) which was not an active phase for transesterification of triglycerides [40].

Table 1
Properties of fresh solid catalysts.

Catalysts	Properties			
	Surface area (m^2/g)	Pore volume (cm^3/g)	Particle size (μm)	Basic site ($\mu\text{mole/g}$)
CaO	13.66	0.0520	0.150	46
K_3PO_4	1.97	0.0078	3,000	348

3.2. Transesterification of refined palm oil

3.2.1. Effect of different catalysts on methyl ester yield

The effect of various homogeneous and heterogeneous catalysts for transesterification of refined palm oil in US reactor on the methyl ester yield is shown in Fig. 3. Homogeneous base catalyst, NaOH, provided the highest methyl ester yield of nearly 100% within 2 h of reaction time. It was reported earlier by Rashid et al. [41] that the methyl ester yield was 97% at the similar conditions. In case of homogeneous acid catalyst, H_2SO_4 , biodiesel yield was rather low (only 15%) because the acid catalyzed transesterification required a high reaction temperature. Goff et al. [42] also proposed that the operation temperature above 100 °C can achieve high yield of 99% with H_2SO_4 loading of 0.5 wt.% of oil. Moreover, it also required more reaction time (8 h). The previous work [43] reported that the homogeneous acid catalyzed transesterification is 4000 times slower than that of the homogeneous base catalyst.

For heterogeneous base catalyst, CaO was a good catalyst for transesterification of refined palm oil since a quite high methyl ester yield was obtained under the similar conditions. The methyl ester yield was about 90% within 2 h of reaction time. Although K_3PO_4 has more basic site than that of CaO catalyst, the methyl ester yield was only 80%. This might be due to its less surface area. Viola et al. [44] also reported that the reaction rate was mainly dependent on the active granules surface of K_3PO_4 .

3.2.2. Effect of mixing types on methyl ester yield

The previous section revealed that CaO and K_3PO_4 could catalyze transesterification of refined palm oil in the US reactor. Therefore, it should be interesting to compare the reaction performance from different mixing types. Fig. 4 shows the methyl ester yields achieved in MS and US reactors for biodiesel production using heterogeneous catalysts. For CaO catalyst, the yield of methyl ester at 2 h was nearly the same for both types of mixing. However, it can be noticed that at the initial reaction period (0–1 h), the US reactor provided higher methyl ester yield than the MS reactor. It was due to the external mass transfer barrier between oil and methanol phase was eliminated. Since ultrasound irradiation enhances the mixing efficiency in a liquid medium by formation and destruction of microbubbles to form emulsion phase, resulting in the better mixing of the reactants [14]. However, K_3PO_4 catalyst exhibited the remarkably different results. It was found that the MS reactor provided higher methyl ester yield than the US reactor. It might be due to the effect of mixing characteristics on the kinetic mechanism of base catalyzed transesterification of oil which is related to the reactant adsorption step on the catalyst surface [11]. For MS reactor, the methanol phase was more potential to adsorb on the K_3PO_4 surface due to the hydrophilic properties [45].

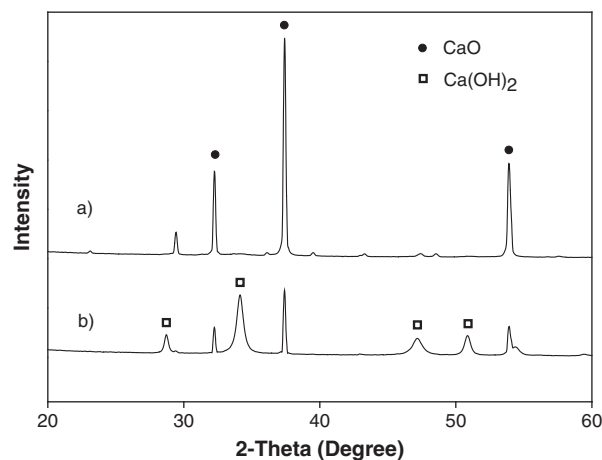


Fig. 2. XRD patterns of a) calcined and b) uncalcined CaO.

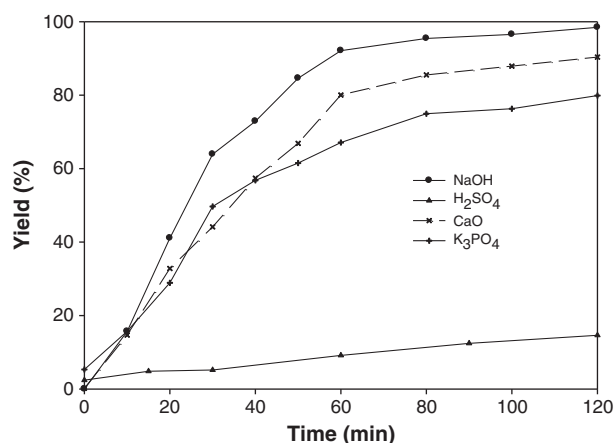


Fig. 3. Effect of different catalysts on methyl ester yield (US reactor).

Therefore, there should be more active sites for the surface reaction, and thus higher yield can be acquired. On the other hand, for US reactor, the production of oil and methanol microbubbles from US irradiation due to the cavitation phenomena was occurred rapidly with less mixing time as proposed by the work [17]. This phenomenon takes place before the adsorption of emulsion phase reactants on the catalyst surface. Thus, the emulsion phase might hinder some K₃PO₄ active sites, resulting in the lower of methyl ester yield. However, the

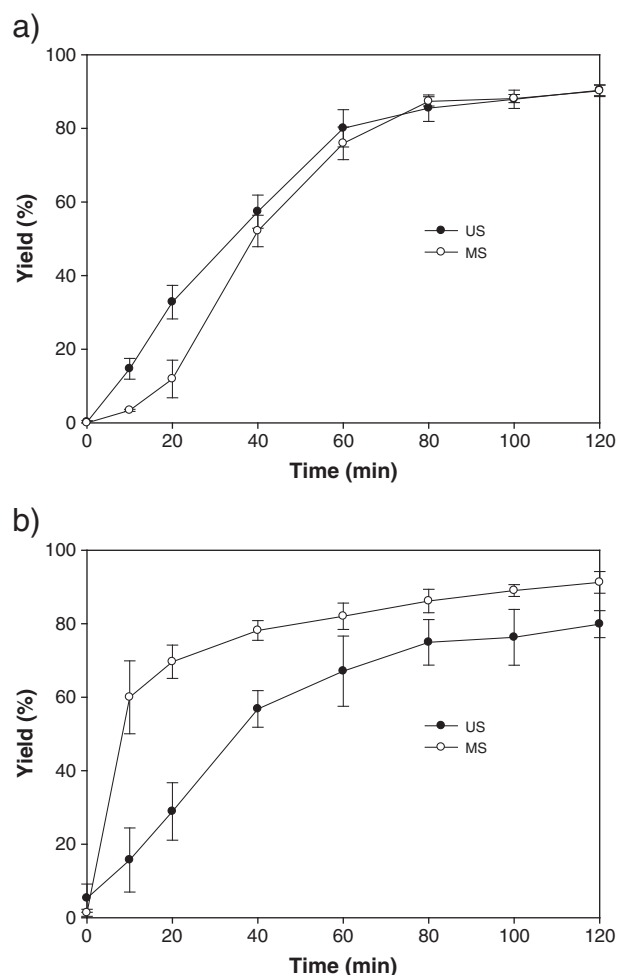


Fig. 4. Effect of types of mixing on methyl ester yield using solid catalysts: a) CaO and b) K₃PO₄.

total surface area and the difference in the surface texture properties of CaO and K₃PO₄ catalysts associated to the various catalytic activities. The effect of mixing characteristics on the adsorption of the reactant (from MS) or emulsion phase (from US) as discussed before was less likely significant for CaO catalyst.

3.3. Reusability and deactivation of catalysts

3.3.1. Reusability of catalyst in US and MS reactors

In this study, the catalyst was instantly reused in three consecutive cycles without any pretreatment step. For CaO catalyst, the methyl ester yield from both the US and MS reactors decreased in the subsequent cycles as shown in Fig. 5. It was significantly found that methyl ester yield from the last cycle using the MS reactor dramatically reduced compared to the US reactor. Under US irradiation, the microbubbles of reaction products especially glycerol have more chance to adsorb on the CaO surface and thus generate the glyceroxides species as the alternative active sites. Kouzu et al. [35,46] and Granados et al. [47] reported that the glyceroxides species was more active for transesterification than that of CaO itself. However, the CaO surface did not only adsorb glycerol but also adsorbed the other reaction mixtures, leading to deactivation of CaO catalyst. This phenomenon should be called counter balancing effect with the summation of positive effect (generated glyceroxides species) and negative effect (deactivation of catalyst by adsorption of organics species). On the other hand, using MS reactor provided less chance to form glyceroxides species on the CaO surface. Thus, the deactivation of catalyst from organic adsorption was more pronounced as seen from the results of the last cycle.

As seen in Table 2, the size of CaO catalyst used in each cycle was higher in the later cycle. In general, a smaller particle size refers to a larger surface area which provides higher chance of reaction. Therefore, the obtained methyl ester yield decreased in the subsequent cycle which was related to the particle size of CaO catalyst. However, the particle size of CaO in the US reactor used in each reuse cycle was larger than that of MS reactor. This was because of a larger amount of calcium glyceroxides produced in US reactor. Kouzu et al. [48] mentioned that the slight amount of soluble substance from calcium glyceroxides leached into the product mixture. This incident would cause the agglomeration of catalyst since some part of the soluble substance was crystallized under the reacting condition and formed into fine particles functioning as a binder to agglomerate the catalyst. Therefore, the particle size of CaO catalyst in US reactor was larger than that from MS reactor in every cycle. The generation of calcium glyceroxides was also occurred significantly hence, the methyl ester yield in the last cycle can be obtained almost 50% in the US reactor while there was almost no activity in the MS reactor from the full

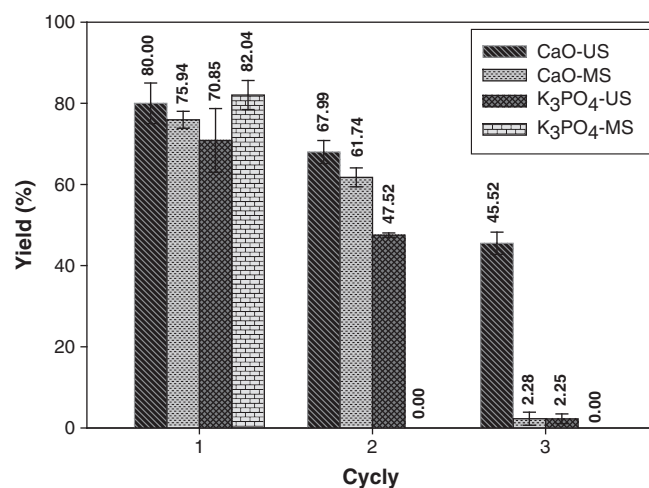


Fig. 5. Effect of reusability of CaO and K₃PO₄ on methyl ester yield at 1 h.

Table 2

Particle size of calcium oxide used in each cycle of reusability experiment.

Reactor	Particle size (μm)		
	Fresh	After 1st cycle	After 2nd cycle
Ultrasonic assisted	0.150	1.348	2.577
Mechanical stirred	0.150	0.192	1.718

coverage of reaction mixture on the CaO surface. This is because the mixing characteristics affected the size of reaction mixture, resulting in the different catalytic behavior.

In the case of K_3PO_4 (Fig. 5), the methyl ester yield decreased in the subsequent cycle of the spent catalyst when using the US reactor. It dramatically decreased to about 2% in the last cycle. However, the deactivation of this catalyst was more likely due to the dissolution of active species into the reaction mixture. Since the amount of catalyst remaining after each reaction cycle noticeably decreased. This result was corresponding with another research [49] reporting that K_3PO_4 showed high sensitivity to water and free fatty acids which caused the dissolution and agglomeration tendency. The soluble K_3PO_4 catalyst was more emphasized in the MS reactor. The catalyst from the first cycle was quite tiny. Then, the catalyst could not be able to reuse in the consecutive cycle. Kouzu et al. [50] reported that the K_3PO_4 catalyst catalyzed transesterification with homogeneous mechanism by partial dissolution of the catalyst. This result also confirmed the effect of mixing characteristics on the catalytic activity as well as those obtained from CaO catalyst. It was concluded that US reactor would diminish this dissolution for K_3PO_4 catalyzed transesterification of refined palm oil. Moreover, the catalyst deactivation has been investigated in the next section.

3.3.2. Deactivation of catalysts

As seen in Table 2, the size of CaO catalyst used in the subsequent cycles was increased. It might be because of the reaction mixture covering on the catalyst surface and/or the agglomeration of the catalyst. Therefore, the surface of fresh CaO and used CaO catalysts were analyzed by FTIR. It was found that there were many peaks including C=O stretching of ester ($1000\text{--}1320$, 1750 cm^{-1}), C–O and C–H stretching of CaO to calcium methoxide ($\text{Ca}(\text{OCH}_3)_2$) (1050 and $2800\text{--}3000\text{ cm}^{-1}$), $-\text{CH}_2$ vibration of Ca-glycerol complex ($700\text{--}1000$ and $1200\text{--}1350\text{ cm}^{-1}$) [37,19] in Fig. 6. Those products mentioned above did not only hinder the catalyst but also caused the agglomeration of the catalyst as observed by the increased catalyst size in the later cycle [48]. It was noticed that when applying the US reactor, calcium glycerol complex peak was noticeable compared to the MS reactor. This also confirmed that the high amount of calcium glyceroxides was produced from US reactor.

The covered surface by reaction mixture was also confirmed by TGA results shown in Fig. 7. The decomposition was divided into 3 periods. The weight loss was present in the first period, as referred to the decomposition of saturated fatty acid methyl esters ($100\text{--}230\text{ }^\circ\text{C}$) [51]. The second period was the decomposition of unsaturated fatty acid methyl esters, glycerol and triglycerides ($230\text{--}500\text{ }^\circ\text{C}$) [52,53]. Lastly, the weight loss from the third periods which occurred at high temperatures ($500\text{--}850\text{ }^\circ\text{C}$) was referred to the decomposition of carbon residuals [53]. Furthermore, the spent CaO catalysts also showed a significant loss in mass with temperature when compared to the fresh CaO. It was indicated that there were some organic compound of the reaction mixture deposited on the catalyst surface. The weight loss of the reused catalyst from the US reactor was lower than that from the MS reactor. This indicated that there were fewer organic compounds adsorbed on the catalyst surface since only microbubble of reactants was adsorbed on the CaO for US reactor. Whereas, more amount of organic compounds was adsorbed using MS reactor because of it could not generate the microbubbles of reactants as seen the dramatically decrease in the second period of TGA result (Fig. 7). This can be concluded that the US reactor could overcome to diminish the adsorption of organic

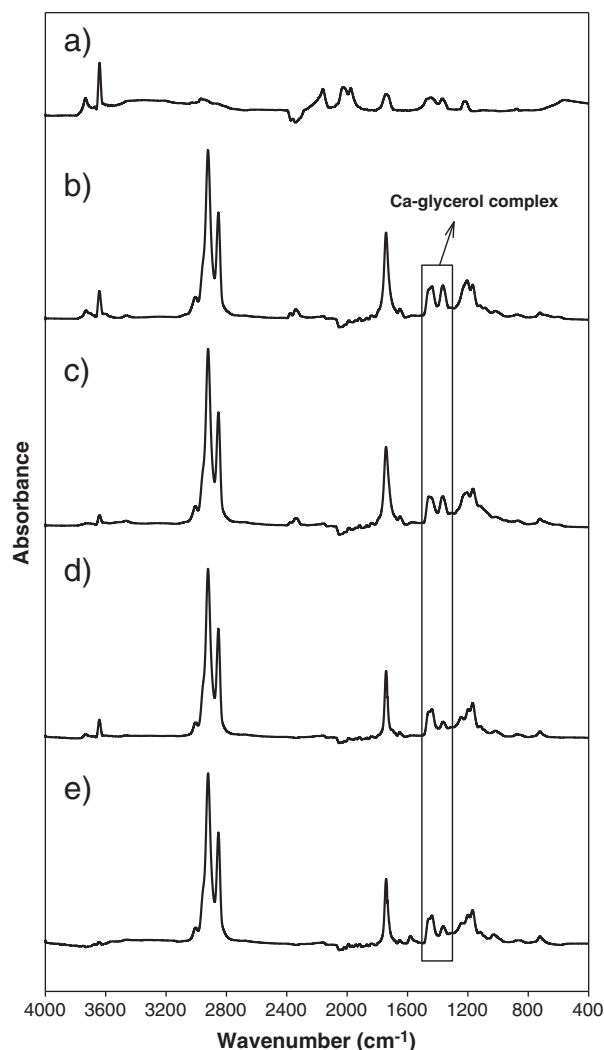


Fig. 6. FTIR spectra of CaO after the reusability test: a) fresh catalyst, b) after 1st cycle (US), c) after 2nd cycle (US), d) after 1st cycle (MS) and e) after 2nd cycle (MS).

compounds from the reaction mixture on the catalyst surface [54]. Then, the higher methyl ester yield can be obtained.

For K_3PO_4 catalyst, the methyl ester yield also decreased in the subsequent cycles. This can be explained using the same explanation as that for the CaO catalyst. There was the agglomeration of the

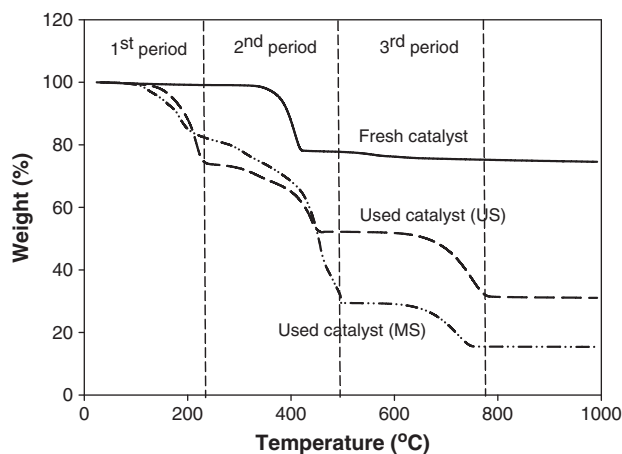


Fig. 7. TGA profiles of fresh and used CaO.

catalyst; the active species of catalyst were covered by the reaction mixture as confirmed by particle size (Table 2), FTIR spectra (Fig. 8) and TGA profiles (Fig. 9). However, the weight loss obtained from the TGA results for the spent K_3PO_4 catalyst in both US and MS reactors were not different. It can be implied that there was the adsorption of organic compounds from reaction mixture on the catalyst surface in both cases. Therefore, the main reason of the K_3PO_4 catalyst deactivation could be the dissolution effect.

As discussed before, the catalyst dissolution seems to be a serious problem when using K_3PO_4 catalyzed transesterification in both reactors. Therefore, the catalyst dissolution experiments were investigated for both catalysts. Based on the dissolution results, it was found that there was no dissolution from CaO catalyst into the reaction mixture in both US and MS reactors. This was corresponding with the results from Mootabadi et al. [30] which reported that only 0.04% weight loss of CaO was leached into biodiesel products for the stability testing in the US reactor. On the other hand, K_3PO_4 catalyst dissolution was occurred apparently. Since K_3PO_4 catalyst is a polar chemical, it could be better dissolved in methanol phase than oil phase. However, Guan et al. [45] reported that K_3PO_4 was relatively insoluble in methanol but rapidly dissolved in water.

Furthermore, it was noticed that K_3PO_4 was more significantly dissolved in the MS reactor (83.9%) than in the US reactor (23.8%). This also supported the hypothesis of the effect of mixing characteristics on the adsorption step of kinetic mechanism. The active species of K_3PO_4 catalyst obtained from the MS reactor should show the greater dissolution and dissolving in methanol because of the mixing characteristics as described in the previous section. Another possibility could be explained that the mixing characteristics were controlled by the stirrer speed for the MS reactor. However, the mechanical stress also promoted the negative effect on the granules of catalyst, then, the catalyst could break into the smaller pieces [44]. It could be attributed to the higher contact between the active sites and reaction mixture, especially methanol and easily to dissolve in the reaction mixture. On the other hand, ultrasound irradiation employed only the bubble collapse between the methanol and the oil phase to form emulsion phase as mentioned before. The catalyst seems not to be affected from the mechanical stress as found in the MS reactor. In this case, dissolution of active species was then lower in the US reactor. From the results, it was noted that US reactor has overcome to scale-up in the industrial process for the heterogeneous catalyzed transesterification of oil.

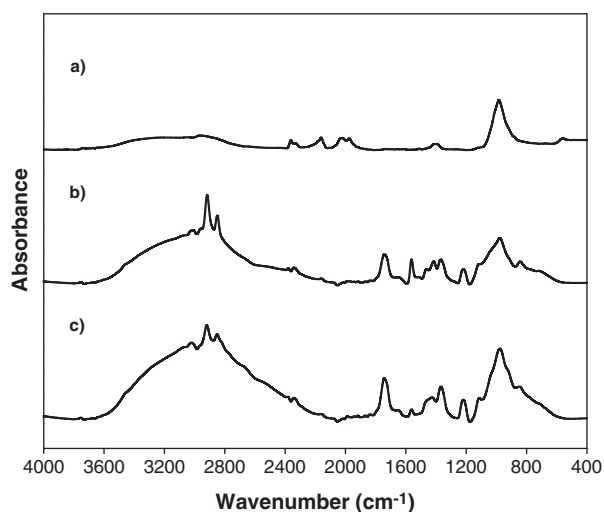


Fig. 8. FTIR spectra of K_3PO_4 after the reusability test: a) fresh catalyst, b) after 1st cycle and c) after 2nd cycle (US reactor).

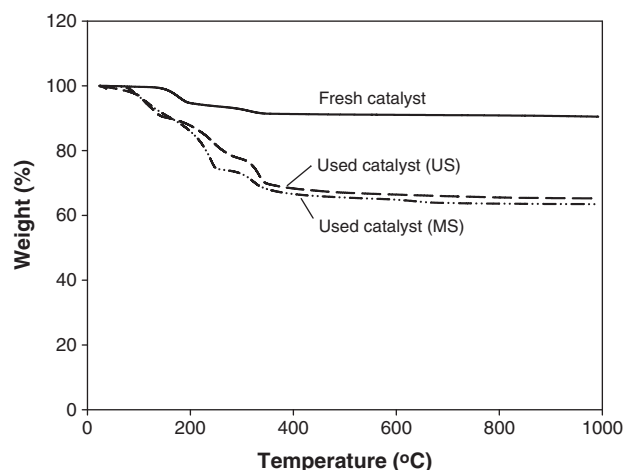


Fig. 9. TGA profiles of fresh and used K_3PO_4 .

4. Conclusions

This work investigated the possible use of commercial heterogeneous catalysts, CaO and K_3PO_4 , for biodiesel production in the US reactor. All results were compared with those from the MS reactor. The highest methyl ester yield of 90% from CaO catalyst was achieved in the US reactor at a methanol to oil molar ratio of 6 under the reaction temperature of 65 °C using catalyst loading of 3 wt.% of oil within 2 h of reaction time. CaO catalyst gained higher yield in the short reaction time in the US reactor as compared to the MS reactor. On the other hand, K_3PO_4 catalyst provided the higher yield in the MS reactor. For catalyst reusability test, using CaO catalyst, the methyl ester yield from the last cycle using US reactor was higher than that from MS reactor. Conversely, K_3PO_4 catalyst was observed a severe dissolution to the reaction mixture in MS reactor. It can be concluded that the activation and deactivation of solid catalyst were related to the different mixing characteristics. Moreover, US reactor promoted the heterogeneously catalyzed transesterification of refined palm oil by hindering the catalyst deactivation.

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