RESEARCH ARTICLE

Transesterification of waste frying oil for synthesizing biodiesel by KOH supported on coconut shell activated carbon in packed bed reactor

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ABSTRACT: Heterogeneous catalysis of transesterification using potassium hydroxide supported on coconut shell activated carbon (KOH/AC) catalyst was used to produce biodiesel from waste frying oil (WFO) and methanol. The effects of reaction temperature, methanol to oil molar ratio, catalyst bed height, reaction time, and reusability of catalyst on the conversion to fatty acid methyl ester in a packed bed reactor were studied. The results showed that increasing reaction temperature, methanol/oil molar ratio, catalyst bed height, and reaction time can enhance the conversion of WFO. The optimum conditions were a reaction temperature of 60 °C, methanol/oil molar ratio 25:1, catalyst bed height 250 mm, and reaction time 2 h which yielded 86.3% of the conversion. KOH/AC could be used repeatedly for 4 times without activity loss and no activation treatment was required. The fuel properties of biodiesel were determined.

KEYWORDS: heterogeneous catalyst

INTRODUCTION

In recent times, renewable energy is considered to be a pivotal solution to combat global warming and to stabilize the climate, through the reduction of greenhouse gas emissions. Biodiesel or fatty acid methyl ester (FAME) is receiving increasing attention as an environmentally friendly and renewable alternative for the petroleum based diesel fuel[1]. It is biodegradable and non-toxic. It has a more favourable combustion emission profile, such as low emissions of particulate matter and unburned hydrocarbons. CO_2 produced by combustion of biodiesel can be recycled by photosynthesis, thereby minimizing the impact of biodiesel combustion on the greenhouse effect[2,3]. Biodiesel has a relatively high flash point which makes it less volatile and safer to transport or handle than petroleum diesel[4]. It provides lubricating properties that can reduce engine wear and extend engine life. Therefore, biodiesel fuel is considered the best choice in bioenergy and has led to its use in many countries, especially in environmentally sensitive areas[5].

In general, biodiesel is derived from a transester-ification reaction of triglycerides in vegetable oils or animal fats with alcohol (methanol or ethanol) under the presence of catalysts[6]. Transesterification of vegetable oil to biodiesel can be catalysed by bases, acids, and enzymes[7]. The commonly used homogeneous base catalysts are KOH, NaOH, and their alkoxides. Homogeneous acids catalysts, such as HCl and H_2SO_4 require a long reaction time. Therefore, homogeneous alkali-catalysed transesterification is much faster than acid-catalysed one[8,9]. However, a large amount of water is required to remove the residual catalyst from bulk biodiesel after reaction[10]. For this reason, heterogeneous catalysis is likely to be used replacing the conventional method in the near future[11]. It has a simpler separation process compared to homogeneous catalyst process[12].

Activated carbon (AC) has proved to be highly effective as a catalyst support in liquid and vapour phase reactions. The properties of AC make it advantageous for use as a catalyst support in transesterification reaction. It has a large surface area which allows the catalyst to disperse over it largely and effectively[13]. It can be produced from a variety of

raw materials. However, coconut and palm shells are mainly used as a raw material because it can be sought in the country [14]. These renewable agricultural wastes are cost-effective alternatives to more expensive and polluting precursors like coal for the production of AC [15].

The increasing production of waste cooking oil or waste frying oil (WFO) from household and industrial sources is a growing problem all around the world. This residue is regularly poured down the drain, resulting in problems for waste water treatment plants and energy loss, or is integrated into the food chain through animal feeding, thus becoming a potential cause of human health problems [16, 17]. The objective of this work was to optimize the process for biodiesel production from WFO using potassium hydroxide supported on coconut shell activated carbon (KOH/AC). The effects of reaction temperature, methanol to oil molar ratio, catalyst bed height, reaction time, and reusability of catalyst are systematically investigated.

MATERIALS AND METHODS

Materials

WFO was purchased from a local market without further treatment. The free fatty acid (FFA) and water content of the oil were measured to be 39.14 and 0.11 wt%, respectively. Non-oil components of the WFO were removed by separation. Filter paper was used to remove impurities from the oil feedstock before use. The AC used in this work was coconut shell-based, produced by chemical activation process. All other chemicals were analytical grade reagents (Merck, > 99% purity) and were used as received.

Catalyst preparation

The coconut shell was cleaned with water to remove fines and dirt, and dried at 100 °C for 12 h. The dried sample was crushed with a grinder and sieved to a particle size 1.8–2.8 mm. It was soaked in phosphoric acid (H_3PO_4) solution with an impregnation ratio of 1.7 for 24 h at ambient temperature [18]. After that, it was dried in oven at 100 °C for 12 h. The resulted sample was further activated in a horizontal automatic tubular furnace at 500 °C for 24 h under nitrogen atmosphere [19]. After cooling, the AC was washed successively several times with distilled water until the pH became neutral. The washed sample was dried at 110 °C for 12 h to obtain AC of coconut shell as the final product, cooled in a desiccator, and stored in glass containers.

A potassium containing solution was prepared by
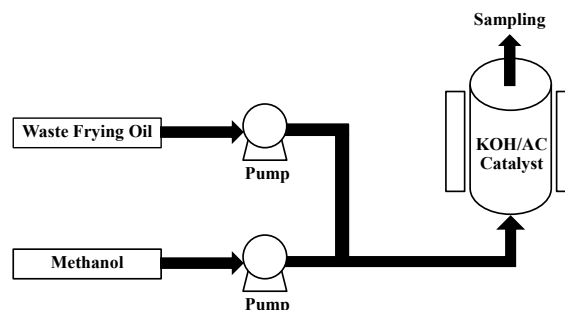
Fig. 1 Scheme of the packed bed reactor for the continuous transesterification.

dissolving KOH in distilled water. AC was divided in 50 g portions and placed in beakers. KOH solution (750 ml) with initial concentration of 0.40 g/ml was added. AC together with the KOH solution was then agitated at ambient temperature for 24 h. The amount of adsorbed KOH was measured by gravimetrical method [13].

Catalyst characterization

The morphology of AC and KOH/AC catalyst was conducted using a scanning electron microscope (SEM). The SEM images of the representative sample were obtained from a Camscan-MX 2000. Characterization by N_2 adsorption-desorption isotherms at 77 K were obtained using a Quantachrome instrument (Autosorb-1 Model No. ASIMP.VP4). The surface area was calculated using the Brunauer-Emmett-Teller (BET) equation and the mean pore diameter and pore volume was obtained by applying the Barret-Joyner-Halenda method on the desorption branch [20].

Instrumentation

The continuous transesterification was performed in a packed bed reactor. The scheme of the packed bed reactor is shown in Fig. 1. The reactor consists of a water-jacketed stainless steel column with an external diameter of 60 mm and a height of 345 mm. The column was packed with KOH/AC solid-base catalyst. WFO and methanol were fed into the system using two separate raw material pumps. The reaction temperature was controlled by a heater to keep constant temperature with an error of ± 1.0 °C. The temperature difference between the inlet and the outlet was below 1.0 °C during all the runs. Temperature and pressure of the system were monitored by temperature indicator and pressure gauges. The sample obtained was purified by reduced pressure distillation to remove excess methanol and water generated during reaction.

Continuous transesterification reaction

The synthesis of FAME from WFO and methanol was carried out in a packed bed reactor with flow rate of reactant 1 ml/min. The effects of reaction temperature (50–80 °C), methanol to oil molar ratio (10:1–30:1), catalyst bed height (100–300 mm), reaction time (1–3 h), and reusability of catalyst (1–4 times) on the conversion to methyl ester were studied. Composition of the methyl ester was analysed with a gas chromatograph equipped with a flame ionization detector and a capillary column 30 m × 0.32 mm × 0.25 μm (DB-WAX, Carbowax 20M).

RESULTS AND DISCUSSION

Characterization of catalyst

In general, the high porosity of AC provides a large surface area for attachment of alkoxides. The amount of adsorbed KOH was measured by gravimetrical method. The total loading content of the potassium salts was 30.1% by weight based on the weight of AC. Fig. 2 shows the SEM images of AC and KOH/AC which illustrate the porous nature of the materials. The figure shows that the metal loading affected the partial metal coverage on AC surface. When metal loading was increased, AC was covered with metal almost all the surface, increasing the active sites[14]. The photograph showed a good dispersion of KOH on the surface of AC. Based on these results, after loading of KOH, AC retained its structure that was important for catalysis and therefore the potassium species were found highly distributed upon the surface of the support[1].

The physical properties of AC and KOH/AC are summarized in Table 1. The AC had a large BET surface area (898.6 m^2/g) and pore volume (0.905 cm^3/g), and presented a uniform pore size. KOH/AC presented lower values for surface area (284.2 m^2/g) and pore volume (0.211 cm^3/g) relative to AC. The significant reduction in BET surface area from virgin AC to the KOH/AC catalyst with 30.1 wt% indicates filling of KOH molecules into the AC pores[13]. It can be seen that the catalyst resulted in a strong increase in the active sites. This assumption is supported by the SEM images of AC and KOH/AC.

Effect of transesterification parameter

The effects of reaction temperature on the conversion of WFO to FAME was studied by varying the temperature from 50–80 °C, and keeping fixed 25:1 methanol to oil molar ratio, 250 mm catalyst bed height, and 1 ml/min flow rate of reactant with atmospheric pressure. Fig. 3 shows that an increase
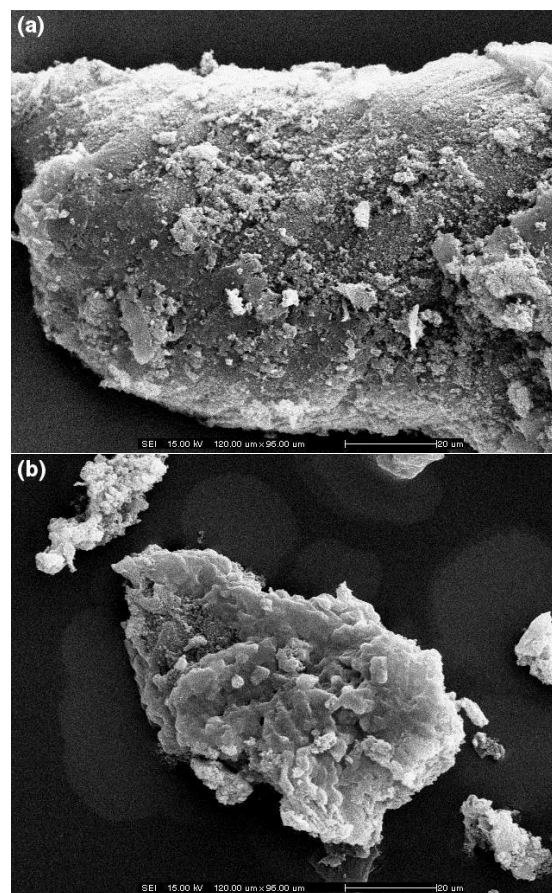

**Fig. 2** SEM micrograph of samples: (a) AC and (b) KOH/AC.

Table 1 Physical properties of AC and KOH/AC.

Physical property	Material	
	AC	KOH/AC
BET surface area (m^2/g)	898.6	284.2
Pore volume (m^3/g)	0.905	0.211
Mean pore diameter (Å)	45.22	92.43

in temperature led to higher reaction conversions. At the beginning of reaction, conversion increased because reactant contacted fresh catalyst. Then the conversions decreased due to slightly deactivated but stabilized catalyst, and the conversions reached steady state at all temperatures. At 50 °C, the least conversion (61.6%) was observed. At 60 °C, the reaction conversion was highest (86.3%). Increasing the temperature to 70 and 80 °C, a fluctuation was observed with lower conversion. The temperatures of 70 and 80 °C were higher than the boiling point of methanol (65 °C). Therefore the vapour-liquid phases of the reaction
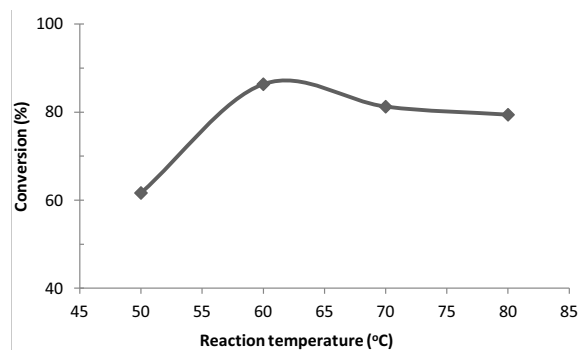
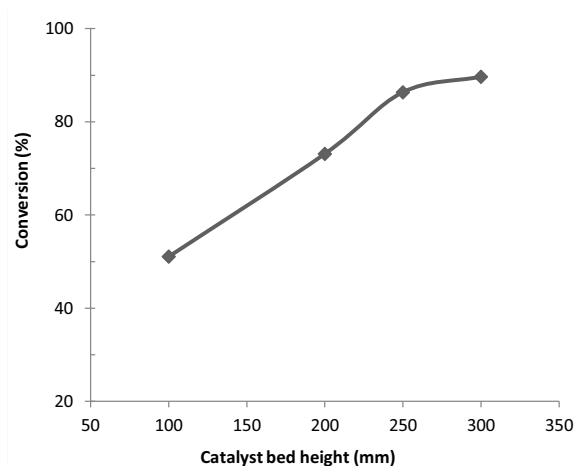**Fig. 3** Effect of reaction temperature on the conversion of transesterification in packed bed reactor.
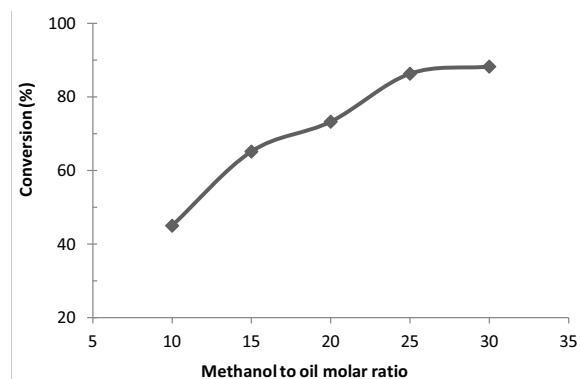
Fig. 4 Effect of methanol to oil molar ratio on the conversion of transesterification in packed bed reactor.

mixture may be responsible for this fluctuation[21]. Thus the highest reaction temperature was limited to 60 °C for the transesterification of WFO in packed bed reactor.

The excess of methanol is necessary because it can increase the rate of methanolysis. Normally, stoichiometric molar ratio of methanol to oil is near 6:1 when the homogeneous alkali-catalysed process is used. However, it increases to 20:1, even 50:1, in the heterogeneous alkali-catalysed process to ensure high conversion[22]. The conversion of WFO achieved 86.3% at 60 °C and 250 mm catalyst bed height when the ratio of methanol to oil was 25:1 (Fig. 4). The more excess of methanol was fed, the higher conversion of WFO to FAME was achieved in the same reaction time. However, when the ratio was over 25:1, the increment of conversion was small.

The catalyst bed height in the packed bed reactor is associated with the residence time during continuous transesterification. The WFO conversion increased rapidly from 51.1% to 89.7% with the increase of the catalyst bed height from 100 to 300 mm.

Fig. 5 Effect of catalyst bed height on the conversion of transesterification in packed bed reactor.
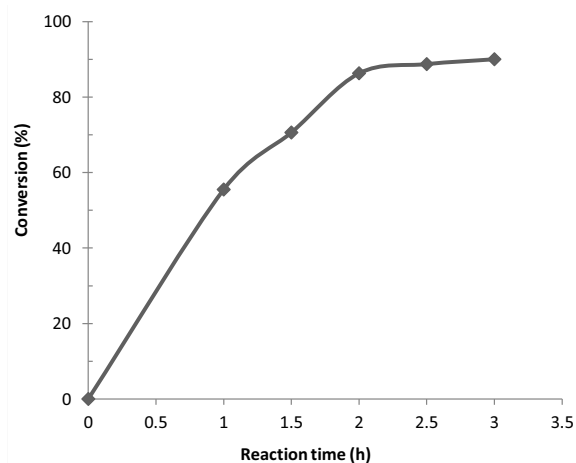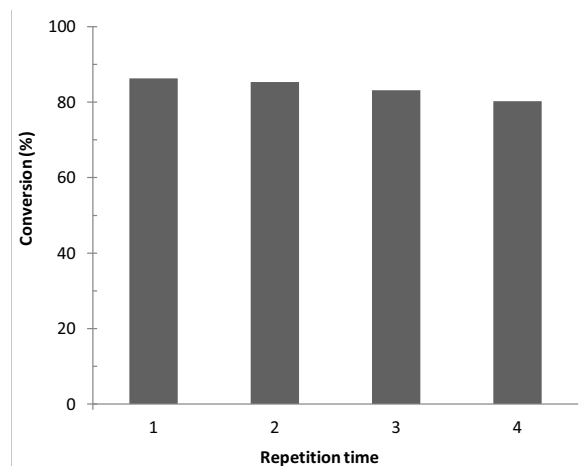

Fig. 6 Effect of reaction time on the conversion of transesterification in packed bed reactor.

In particular, WFO conversion was over 85% when catalyst bed height was over 250 mm (Fig. 5). It demonstrates that a high catalyst bed height provides a longer reaction time and more active sites to promote the reaction between WFO and methanol at a given flow rate[23].

The corresponding conversion of waste oil with the reaction time is shown in Fig. 6. The conversion of WFO increased from 55.5% to 86.3% with an increase of reaction time from 1 to 2 h. However, from reaction time 2–3 h, the conversion only increased a little. This can be explained by the fact that the transesterification reaction between WFO and methanol is reversible. When the reaction time is long enough, the hydrolysis reaction of FAME will start to generate more FFA

Fig. 7 Effect of repetition time on the conversion of transesterification in packed bed reactor.

Table 2 Reusability comparison between supported catalysts.

Catalyst	Repetition time	Conversion (%)	Reference
KOH/AC	4	80.3	This work
KOH/AC	3	89.3	Ref. 1
CaO/AC	4	70.1	Ref. 24
K$_2$CO$_3$/AC	3	97.4	Ref. 25

Table 3 The fuel properties of biodiesel.

Fuel properties	Biodiesel in this work	Thai standard	ASTM D6751-02
Kinematic viscosity at 40 °C (mm^2/s)	4.7	3.5–5.0	1.9–6.0
Density at 15 °C (kg/m^3)	891	860–900	870–900
Flash point (°C)	177	120	130
Cloud point (°C)	18	–	−3–12
Water content (wt%)	0.04	0.05 max	0.03 max

and alcohol. Thus from an economical point of view, it reveals that it is not necessary to spend a long time to increase the conversion of waste oil when the yield of FAME has been increased enough to avoid saponification and hydrolysis reaction in the transesterification reaction[24].

Reusability is one of the most important properties of a solid catalyst. In this experiment, the reactants and catalyst were introduced into the packed bed reactor for transesterification. KOH/AC catalyst was collected after the reaction and fresh reactants added without any treatment. WFO conversion, determined after each catalyst collection, was employed to evaluate the reusability. The operating conditions, i.e., a reaction temperature of 60 °C, methanol to oil molar ratio 25:1, and catalyst bed height 250 mm were determined by the operational parameters employed in the reactor. Under those conditions, a high WFO conversion was obtained (Fig. 7). WFO conversions exhibited no apparent decrease and surmounted 80% in every run for 4 times. As shown in Table 2, this value is within the range reported by other researchers[1, 25, 26]. This heterogeneous catalyst showed high stability and reusability for transesterification without loss of its catalytic activity during reaction. Small loss of the catalyst is an important factor for good catalyst reusability[27].

Characterization of biodiesel

The fuel properties of biodiesel obtained in this work are summarized in Table 3. It can be seen that most of its properties are in the range of fuel properties as described in the latest Thai and American standards for biodiesel[28–30].

CONCLUSIONS

This investigation showed that transesterification of WFO can be achieved by heterogeneous catalysis with KOH/AC. The optimum condition, which yielded a conversion of WFO of nearly 86%, was a reaction temperature of 60 °C, methanol/oil molar ratio 25:1, and reaction time 2 h with a catalyst bed height 250 mm in packed bed reactor. The experimental results show that KOH/AC had excellent activity and stability during transesterification. The catalyst was used for 4 times and no apparent activity loss was observed. The fuel properties of the biodiesel so obtained meet all biodiesel standards. As a solid catalyst, KOH/AC can decrease the cost of biodiesel and the steps of purification. It has potential for industrial application in the transesterification of WFO to FAME.

REFERENCES

1. Baroutian S, Aroua MK, Raman AAA, Sulaiman NMN (2011) A packed bed membrane reactor for production

of biodiesel using activated carbon supported catalyst. *Bioresour Tech* **102**, 1095–102.

2. Körbitz W (1999) Biodiesel production in Europe and North America, an encouraging prospect. *Renew Energ* **16**, 1078–83.

3. Agarwal AK, Das LM (2001) Biodiesel development and characterization for use as a fuel in compression ignition engines. *J Eng Gas Turb Power* **123**, 440–7.

4. Krawczyk T (1996) Biodiesel-alternative fuel makes inroads but hurdles remain. *Inform* **7**, 801–29.

5. Buasri A, Chaiyut N, Ketlekha P, Mongkolwatee W, Boonrawd S (2009) Biodiesel production from crude palm oil with a high content of free fatty acids and fuel properties. *CMU J Nat Sci* **8**, 115–24.

6. Simasatitkul L, Siricharnsakunchai P, Patcharavorachot Y, Assabumrungrat S, Arpornwichanop A (2011) Reactive distillation for biodiesel production from soybean oil. *Kor J Chem Eng* **28**, 649–55.

7. Du W, Xu Y, Liu D, Zhang J (2004) Comparativestudy on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors. *J Mol Catal B* **30**, 125–9.

8. Vicente G, Martínez M, Aracil J (2004) Integrated biodiesel production: a comparison of different homogeneous catalysts systems. *Bioresour Tech* **92**, 297–305.

9. Furuta S, Matsuhashi H, Arata K (2006) Biodiesel fuel production with solid amorphous-zirconia catalysis in fixed bed reactor. *Biomass Bioenerg* **30**, 870–3.

10. Shin J, Kim H, Hong SG, Kwon S, Na YE, Bae SH, Park WK, Kang KK (2012) Effects of ultrasonification and mechanical stirring methods for the production of biodiesel from rapeseed oil. *Kor J Chem Eng* **29**, 460–3.

11. Samart C, Sreetongkittikul P, Sookman C (2009) Heterogeneous catalysis of transesterification of soybean oil using KI/mesoporous silica. *Fuel Process Tech* **90**, 922–5.

12. Hameed BH, Goh CS, Chin LH (2009) Process optimization for methyl ester production from waste cooking oil using activated carbon supported potassium fluoride. *Fuel Process Tech* **90**, 1532–7.

13. Baroutian S, Aroua MK, Raman AAA, Sulaiman NMN (2010) Potassium hydroxide catalyst supported on palm shell activated carbon for transesterification of palm oil. *Fuel Process Tech* **91**, 1378–85.

14. Buasri A, Chaiyut N, Nakweang C (2011) Preparing activated carbon from palm shell for biodiesel fuel production. *Chiang Mai J Sci* **38**, 572–8.

15. Ribeiro AM, Loureiro JM (2002) Simulation of toxic gases and vapours removal by activated carbon filters. *Chem Eng Sci* **57**, 1621–6.

16. Costa Neto PR, Rossi LFS, Zagonel GF, Ramos LP (2000) Produção de biodiesel alternativo ao óleo diesel através da transesterificação de óleo de soja usado em frituras. *Quim Nova* **23**, 531–7.

17. Zaher F (2003) Utilization of used frying oil as diesel engine fuel. *Energ Sourc* **25**, 819–26.

18. Gratuito MKB, Panyathanmaporn T, Chumnanklang RA, Sirinuntawittaya N, Dutta A (2008) Production of activated carbon from coconut shell: Optimization using response surface methodology. *Bioresour Tech* **99**, 4887–95.

19. Tongpoothorn W, Sriuttha M, Homchan P, Chanthai S, Ruangviriyachai C (2011) Preparation of activated carbon derived from *Jatropha curcas* fruit shell by simple thermo-chemical activation and characterization of their physico-chemical properties. *Chem Eng Res Des* **89**, 335–40.

20. Alba-Rubio AC, Vila F, Martín-Alonso DM, Ojeda M, Mariscal R, López-Granados ML (2010) Deactivation of organosulfonic acid functionalized silica catalysts during biodiesel synthesis. *Appl Catal B Environ* **95**, 279–87.

21. Hsieh LS, Kumar U, Wu JCS (2010) Continuous production of biodiesel in a packed-bed reactor using shell-core structural $Ca(C_3H_7O_3)_2/CaCO_3$ catalyst. *Chem Eng J* **158**, 250–6.

22. Zhang Y, Dubé MA, McLean DD, Kates M (2003) Biodiesel production from waste cooking oil: 1. Process design and technological assessment. *Bioresour Tech* **89**, 1–16.

23. Feng Y, Zhang A, Li J, He B (2011) A continuous process for biodiesel production in a fixed bed reactor packed with cation-exchange resin as heterogeneous catalyst. *Bioresour Tech* **102**, 3607–9.

24. Lu P, Yuan Z, Li L, Wang Z, Luo W (2010) Biodiesel from different oil using fixed-bed and plug-flow reactors. *Renew Energ* **35**, 283–7.

25. Buasri A, Ksapabutr B, Panapoy M, Chaiyut N (2012) Biodiesel production from waste cooking palm oil using calcium oxide supported on activated carbon as catalyst in a fixed bed reactor. *Korean J Chem Eng* (in press).

26. Fan M, Zhang P (2007) Activated carbon supported K_2CO_3 catalysts for transesterification of dimethyl carbonate with propyl alcohol. *Energ Fuel* **21**, 633–5.

27. Jiang ST, Zhang FJ, Pan LJ (2010) Sodium phosphate as a solid catalyst for biodiesel preparation. *Braz J Chem Eng* **27**, 137–44.

28. Chongkhong S, Tongurai C, Chetpattananondh P, Bunyakan C (2007) Biodiesel production by esterification of palm fatty acid distillate. *Biomass Bioenerg* **31**, 563–8.

29. Buasri A, Chaiyut N, Loryuenyong V, Pin-Ngern K, Tonprasert N, Dangnuan S (2012) Production of fatty acid methyl ester by esterification of waste frying oil with methanol using acidified silica as heterogeneous. *J Biobased Mater Bio* (in press).

30. Buasri A, Ksapabutr B, Panapoy M, Chaiyut N (2012) Synthesis of biofuel from palm stearin using an activated carbon supported catalyst in packed column reactor. *Adv Sci Lett* (in press).