Comparison of Biodiesel Production from High Free Fatty Acid, Crude Coconut Oil via Saponification followed by Transesterification or a Two-Stage Process

Surachai Jansri[1] and Gumpon Prateepchaikul[2]*

ABTRACT

Saponification followed by a transesterification process (SFT) or a two-stage process (TSP) were investigated for biodiesel production from high free fatty acid (FFA), crude coconut oil. In SFT, the effects of the concentration of NaOH solution on free fatty acid reduction were investigated. The oil from saponification after cleaning was used as a raw material to produce biodiesel. For TSP, the effects of methanol and H_2SO_4 on free fatty acid reduction were determined using various amounts of methanol catalyzed by H_2SO_4 and with different amounts of H_2SO_4 in methanol. Then, the de-acidified oil was used to produce biodiesel. All reactions were carried out at 60°C and monitored by titration and thin layer chromatography/flame ionization detection. The suitable conditions of SFT for obtaining 99% by weight methyl ester content were: 15 v% of water, 36 v% of methanol and 19.9 %wt/v of NaOH, yielding 45.6% in 26 h. Like methyl ester concentration, TSP could produce 86.6% yield of biodiesel under 5 v% of H_2SO_4, 37 v% of methanol and 2.5 %wt/v of NaOH in 14.25 h. Finally, the biodiesel cost was approximately 57.09 and 32.02 THB/L by SFT and TSP, respectively. Therefore, TSP was considered more suitable for producing biodiesel from high FFA crude coconut oil because it was quicker, cheaper and produced a higher yield.

Keywords: biodiesel, coconut oil, esterification, saponification, transesterification

INTRODUCTION

Energy is one of the important drivers of economic growth contributing to the development of Thailand. Fossil fuels produce the majority of Thailand's energy for motivating the industrial, agricultural and transportation sectors, which has resulted in a continuous increase in the import of fossil diesel fuel. In addition, the fossil diesel fuel causes significant pollution problems, such as increasing greenhouse gases and sulfur dioxide (Ma and Hanna, 1998; Gerpen *et al.*, 2004; Marchetti *et al.*, 2005). Therefore, alternative weal fuels are being investigated as a substitute for imported petroleum and to reduce pollution problems in Thailand. Moreover, alternative fuels can help balance growth on the demand side. Consequently, biodiesel, made from vegetable oils and animal fats, is one of the possible alternative fuels for diesel engines.

[1] The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok 10140, Thailand.

[2] Department of Mechanical Engineering, Faculty of Engineering, Prince of Songkla University, Songkhla 90112, Thailand.

* Corresponding author, e-mail: gumpon.p@psu.ac.th

Generally, transesterification is used to produce biodiesel from vegetable oil or animal fat that contain low free fatty acid (FFA) (Ma and Hanna, 1998). Crude coconut oil (CCO) (un-degummed and containing high FFA) is considered as a feed stock to produce biodiesel. It was found that in the production of biodiesel from CCO by transesterification, the high FFA in the CCO can react with the metallic alkoxide to produce soap (saponification) (Ma and Hanna, 1998; Brown *et al.*, 2003). This reaction causes lower yield and washing difficulties (Ma and Hanna, 1998; Tongurai *et al.*, 2001; Gerpen *et al.*, 2004; Marchetti *et al.*, 2005; Veljkovié *et al.*, 2006; Prateepchaikul *et al.*, 2007). At present, acid-catalyzed transesterification, enzyme-catalyzed transesterification, supercritical techniques and MeOH can be used to produce biodiesel from CCO having high FFA content (Ma and Hanna, 1998). However, MeOH was chosen for producing biodiesel from the CCO in this work because of the need for biodiesel generation at low temperature and low pressure.

The two-stage processes can be categorized into two types: 1) saponification followed by tranesterification (SFT) (Tongurai *et al.*, 2001) and 2) esterification followed by transesterification (TSP) (Veljkovié *et al.*, 2006; Prateepchaikul *et al.*, 2007). Both types aim to reduce the high FFA content to less than 1 wt% in the first step and additionally, to convert the first step product into an ester by alkali-catalyzed transesterification (Ma and Hanna, 1998; Tongurai *et al.*, 2001; Veljkovié *et al.*, 2006; Prateepchaikul *et al.*, 2007). Currently, although both types of the two-stage process are well known for biodiesel production from vegetable oils having high FFA content, no research has compared the advantages of the two. Therefore, the maximum benefit of each type of two-stage process was investigated.

MATERIALS AND METHODS

Materials

CCO (un-degummed and containing FFA around 20.38 wt %) from a local coconut oil mill in Had Yai, Songkhla, Thailand, was used as a raw material for biodiesel production. Sulfuric acid (H_2SO4), sodium hydroxide (NaOH) and methanol (CH_3OH, abbreviated to MeOH) of 98% purity commercial grade were purchased from a local chemical store in Had Yai, Songkhla, Thailand. Analytical grade sodium hydroxide pellets, sodium periodate, potassium hydrogen phathalate, ethanediol and bromothymol blue were purchased from Ajex Fine Chem., New Zealand. Sulfuric acid, diethyl ether, iso-propanol and hexane, also of analytical grade, were purchased from Lab Scan Analytical Science, Thailand. Analytical grade phenolphthalein and formic acid were purchased from Merck KGaA, Germany. Benzene, analytical grade, was purchased from Honeywell, Germany.

Public utility equipment

The consumption of electricity and water, used in each process, was measured with a kilowatt-hour meter (Wu Chi Electrical Co., Ltd.: model no. DD862) and a water meter (Nicety Water & Electricity Material Co., Ltd.: model no. LXSC-15E~50E), respectively. Both pieces of equipment were purchased from a local construction equipment store in Had Yai, Songkhla, Thailand.

Apparatus

Biodiesel production from high FFA content crude coconut oil by SFT and TSP was carried out in a 1000-ml beaker equipped with a magnetic bar and thermocouple. The solution was heated by a hotplate stirrer and the solution was stirred at a fixed stirring speed (300 rpm) at all times, except during saponification.

Saponification followed by transesterification in the batch process (Figure 1)

To commence *saponification* (*de-acidified process*), CCO was weighed and heated to 60°C. Then, the heated CCO was titrated to confirm the acid value (gram NaOH per litre CCO). The sodium hydroxide solution was prepared (consisting of NaOH, additional NaOH,
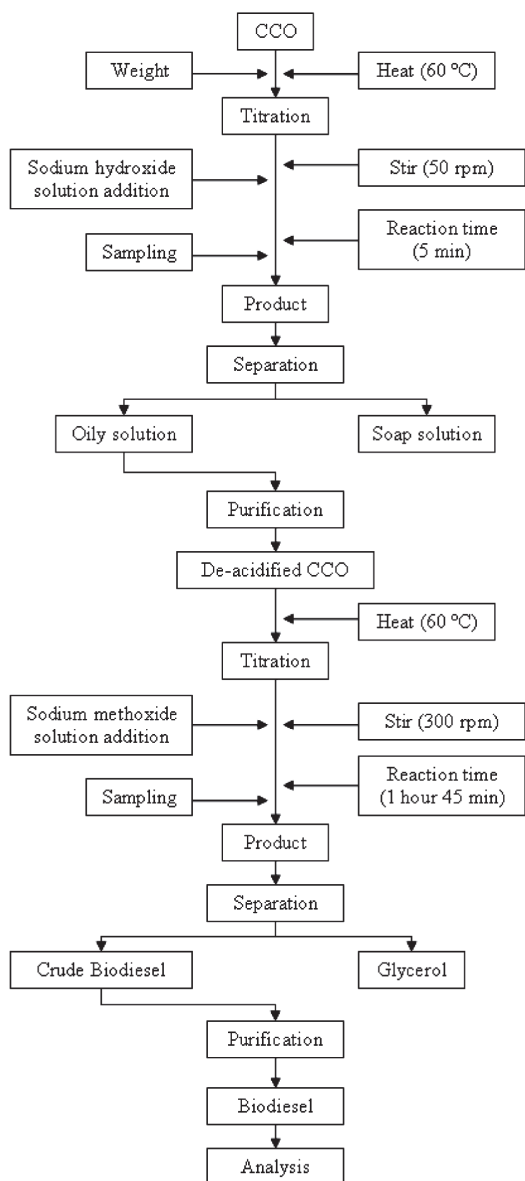

Figure 1 Schematic diagram of saponification followed by transesterification process.

and water). Next, the sodium hydroxide solution was slowly added to the heated oil, while the solution was stirred at 50 rpm for 5 min. Gravity was used to separate the soap solution (the bottom phase) from the oil for a period of 5 h. Afterward, the soap was drained out using a separating funnel. Subsequently, the oily solution (the top phase) was washed with water at ambient temperature. Finally, before producing biodiesel from the de-acidified CCO by transesterification, the cleaned oil was heated until the oil was clear. The effect of the amount of water was determined as 10, 12.5 and 15 v% based on the initial CCO catalyzed by sodium hydroxide using a titration method (non-additional). Amounts of 0, 0.5 and 0.75 %wt/v of additional sodium hydroxide in 10 v% of water based on the initial CCO were considered to determine the FFA conversion.

For the *transesterification process*, de-acidified CCO was heated until the temperature reached 60°C. Then, the acid value of the heated CCO was checked to prepare the amount of sodium hydroxide required for neutralization. The sodium metoxide solution (consisting of MeOH and NaOH (neutralizing agent and catalyst)) was added slowly into the oil. The reaction was performed until the reaction time was reached. Next, agitation was stopped and the final solution was left for 1 h in a separating funnel to separate the glycerol (the bottom phase) from the crude biodiesel (the top phase). Variations in the amount of MeOH of 23 and 36 v% in 0.5 wt% sodium hydroxide based on the initial CCO as a catalyst were used to investigate the biodiesel production. Finally, the condition of the cleaned biodiesel was verified by quantitative and qualitative analysis.

Two-stage batch process. Before reducing the FFA content by *esterification* (the *first stage process*) (Figure 2), the FFA content of the CCO was analyzed. Next, it was weighed and heated to 60°C. Then, MeOH was added slowly into the beaker and mixed for 5 min. After that, H_2SO_4 (catalyzed in esterification) was added

slowly to the flask and mixing was performed until the reaction time was reached. Finally, the stirring was stopped and the final solution was poured into a separating funnel and left for 2 h to separate into two phases: a top phase (the oily phase, consisting of oil, methyl ester, un-reacted MeOH and some impurities) and a bottom phase (the waste phase or black phase, consisting of water, un-reacted MeOH and sulfuric acid). The top phase was kept to produce biodiesel by transesterification. The effect of the amount of MeOH at 15, 17, and 19 v% catalyzed by 5 v% of sulfuric acid based on initial CCO was determined. In addition, the effect of the amount of sulfuric acid at 4.5, 5 and 5.5 wt% using 15 v% MeOH based on initial CCO was determined. While the pre-treatment CCO was heated until the solution temperature reached 60° C in first step of *transesterification (the second stage process)*, the oil was titrated to verify the acid value to prepare the amount of NaOH for neutralization. As with the transesterification of SFT, the sodium methoxide solution was prepared and added slowly into the beaker.

All reactions were carried out at 60°C and the reactions were continued for the required time, when agitation was stopped and the final solution was poured into the separating funnel for 1 h to separate the glycerol from the crude biodiesel. An amount of 20 v% of MeOH and 0.5 %wt/v of sodium hydroxide based on initial CCO was used to investigate the methyl ester (ME) conversion. Finally, after cleaning the product, the quantity and quality of the biodiesel were verified.

Purification method of final biodiesel production

The final products of saponification and biodiesel production were cleaned by wet washing four times with water at ambient temperature. For the first two times, a 1:1 volume ratio of water to product was sprayed over the surface of solution. After 15 min, the waste water was drained from the bottom of the funnel. For the third cleaning, water with the same amount of product was also sprayed over the surface of solution and then air bubbles were introduced into the solution for 15 min. The solution was left for 15 min and waste water was drained. The fourth washing was similar to the third, except that the air bubbles were introduced throughout the night, for about 8 h. Finally, after draining the waste water, the cleaned solution was heated until it was clear.
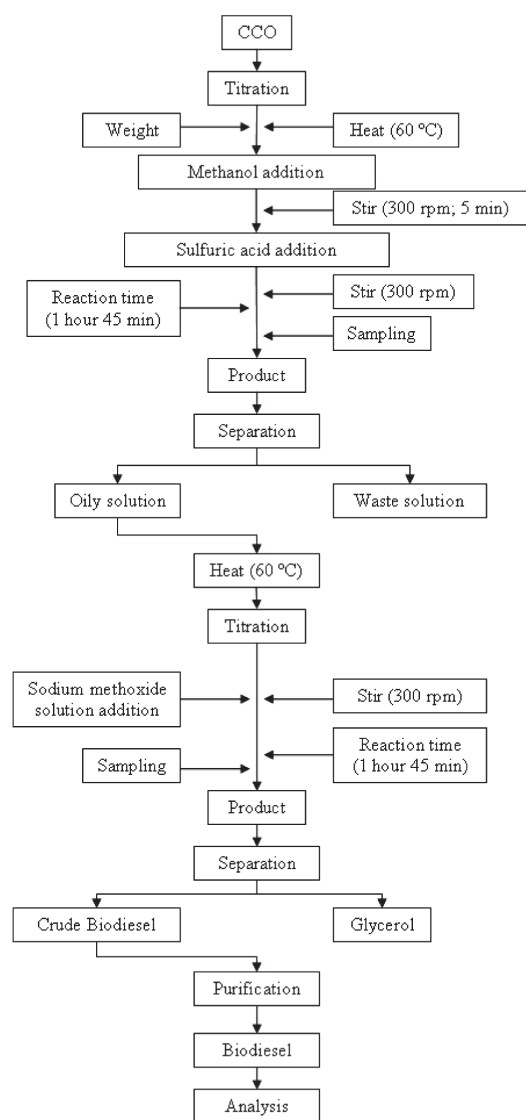

Figure 2 Schematic diagram of esterification, followed by transesterification.

Sampling and analysis

Samples during SFT and TSP were taken periodically and the composition of the solution monitored by thin layer chromatography/flame ionization detector (TLC/FID) and by a titration technique. After adding the catalyst in each step, a sample of 10 mL was withdrawn from a retention time of 0, 60, 75, 90, and 105 min (Prateepchaikul *et al.*, 2007) except in saponification, when the solution was sampled at 0, 1, 2, 3, 4 and 5 min during the retention time. Each sample was stopped immediately by freezing (May, 2004). Before analyzing the concentration of triglyceride (TG), diglyceride (DG), monoglyceride (MG), FFA and ME with TLC/FID, impurities in the samples were removed by washing three times with 250 mL hot water (80°C) (Jansri *et al.*, 2007). In addition, the FFA contents of the cleaned samples from saponification and esterification were analyzed by a titration technique.

Analytical methods

The acid value of the initial oil and the final product of SFT and of TSP were determined by the acid-base titration technique, except that a standard solution of sodium hydroxide was used instead of the standard solution of potassium hydroxide. A 4-mL sample was withdrawn by pipette and then the sample was diluted with 15 mL iso-propanol using 5% wt/v of phenolphthalein as an indicator. The solution was titrated with 0.1 mol/L sodium hydroxide solution until the solution reached the end point. The acid value of the sample ratio in gram of sodium hydroxide to litre of oil was determined. The compositions of the cleaned sample were analyzed by TLC/FID. Analysis was performed using an Itronscan MK6 with Chromarod type S-III quartz rod (Mitsubishi Kagaku Iatron Inc., Japan). The flame ionization detector used 160 mL/min of hydrogen flow rate and 2.0 L/min of air flow rate. The samples were diluted in hexane and then spotted on each rod, which was coated with an alumina/silica substance

(the stationary phase). The rods were developed in the first mobile phase (hexane/diethyl ether/formic acid in the volume ratio of 50:20:0.3 v/v/v) for 20 min. Before developing the rods in the second mobile phase (hexane/benzene in the volume ratio of 1:1 v/v) for 30 min, the rods were air-dried for 5 min. After that, the rods were oven-dried at 105°C and the composition of each sample was analyzed. The mass ratio of ME, TG, DG, MG and FFA was determined by scanning with 30 sec/rod of scan speed (Prateepchaikul *et al.*, 2007).

RESULTS AND DISCUSSION

Saponification followed by transesterification in the batch process

The effect of the amount of water on FFA reduction via SFT was investigated using the amounts of water of 10, 12.5, and 15 v% based on the initial CCO catalyzed using only NaOH in the titration technique. The saponification reaction was performed at 60°C. The results are shown in Figure 3 and indicate that 10, 12.5, and 15 v% of water based on the initial CCO could reduce the FFA content from 20.38 wt% to less than 4.73, 4.93 and 1.5 wt%, respectively.

In addition, the effect of the amount of NaOH on the reduction of the FFA content was
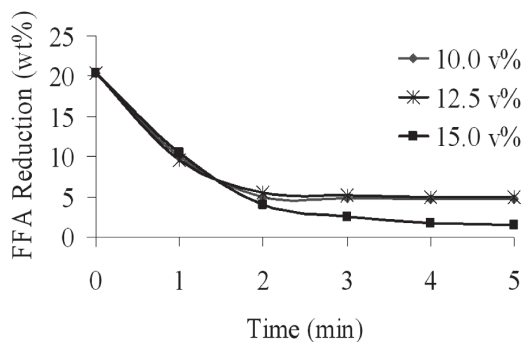

Figure 3 Effect of adding water on FFA reduction without addition of extra sodium hydroxide at 60°C.

investigated under conditions of 0, 0.5, and 0.75 % wt/v of additional NaOH in 10 v% of water, based on the initial CCO reacted at 60°C. The results are shown in Figure 4 and indicate that the high FFA content in the CCO could not be reduced to less than 4 wt% with any of the additional amounts of sodium hydroxide.

The investigations of both effects found that increasing the amount of water had a greater influence on the FFA reduction than did the additional amount of NaOH. Although the concentration of FFA in the CCO could not be reduced to less than the theoretical limit of 1 wt%, the lowest was selected to produce biodiesel. Therefore, the most suitable amount of water was 15 v% based on the initial CCO by non additional NaOH and was selected to treat the FFA contained in the CCO by the saponification process at 60°C.

The treated CCO was used as raw material for investigating the conversion of ME production under conditions of 23 and 36 v% of MEOH in 0.5 %wt/v of NaOH, based on de-acidified CCO at 60°C. When the reaction time was reached, the results (Figure 5) indicated that TG could be converted into ME at more than 75 and 99 wt% (TLC/FID) with amounts of MeOH 23 and 36 v%, respectively, based on the FFA reduction of the CCO. At lower concentrations of MeOH, there were difficulties in the reaction
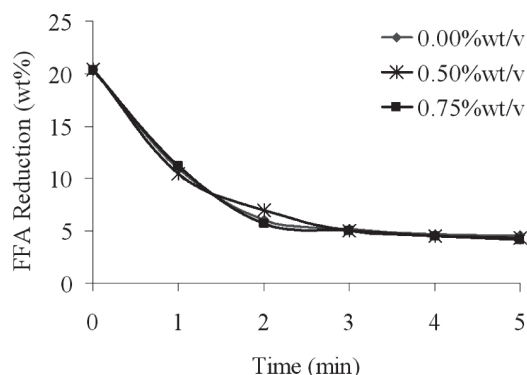
converting the TG in the de-acidified CCO into ME because the CCO had a greater content of high saturated fatty acids (90 wt%) than other oils (Wikipedia, 2009) and MeOH could evaporate during the reaction because of its lower vapor pressure (Department of Alberta Department of Chemical and Materials Engineering, 2009). Therefore, the higher ME conversion of 99 wt% was observed under the higher concentration of MeOH.

Two-stage biodiesel production batch process

The effect of the amount of sulfuric acid (catalyst) at 4.5, 5 and 5.5 v% based on initial CCO was investigated with regard to reducing the FFA content in MCPO by esterification using 15 v% MeOH, based on initial CCO at 60°C. The results (Figure 6) indicated that 4.5, 5.0 and 5.5 v% of sulfuric acid, based on the initial CCO could reduce the FFA content from 20.38 wt% to less than 3.40, 3.10 and 3.80 wt%, respectively. It was found that sulfuric acid had an influence on the FFA reduction, but that no amount of sulfuric acid based on initial CCO could reduce the FFA content to less than 1 wt%. However, some sulfuric acid was necessary to promote the reaction, so that amount of sulfuric acid that reduced the FFA the most, was selected. Consequently, 5 v% sulfuric
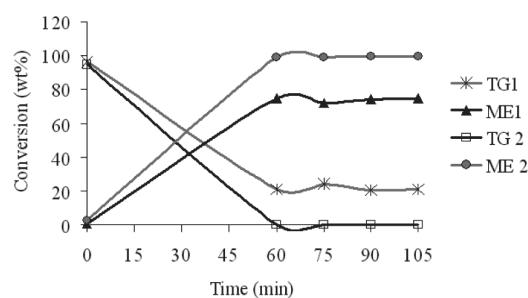
Figure 4 Effect of adding sodium hydroxide on FFA reduction using 10 v% water, based on initial CCO at 60°C.

Figure 5 Variation of FFA and ME during transesterification under conditions of 23 (TG 1 and ME 1) and 36 (TG 2 and ME 2) v% of MEOH in 0.5 %wt/v of NaOH, based on de-acidified CCO at 60°C.

acid based on the initial CCO was used as a catalyst for converting the FFA content into ME by esterification, because it could reduce the FFA content more than sulfuric acid levels of 4.5 and 5.5 v%. Then, the effect of the amount of MeOH on the conversion of FFA was investigated under conditions of 15, 17, and 19 v% in 5 v% of H_2SO_4 acid, based on the initial CCO at 60°C. The results (Figure 7) indicated that the FFA content could be reduced to less than 3.1, 1.7 and 2.0 wt% when the amount of MeOH was 15, 17, and 19 v%, respectively, based on the initial CCO used.

       As MeOH is known to evaporate at ambient temperature (Department of Alberta Department of Chemical and Materials Engineering, 2009), when the lower MeOH amount was used as a reagent, there was
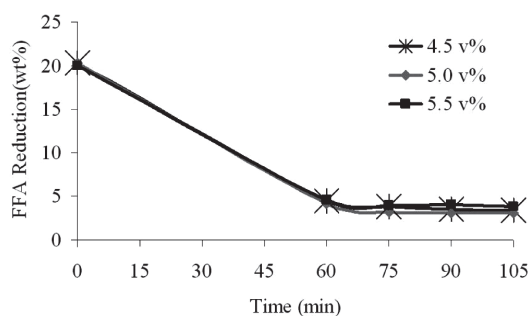

Figure 6 Effect of the amount of sulfuric acid on FFA reduction using 15 v% MeOH, based on initial CCO at 60°C.
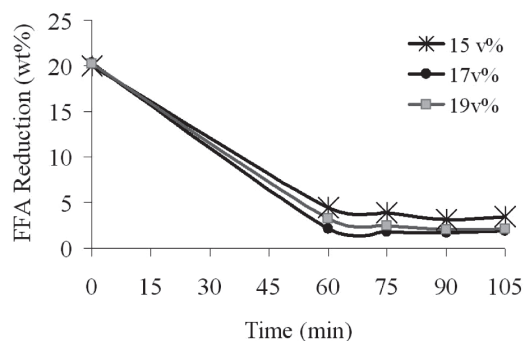

Figure 7 Effect of the amount of MeOH on FFA reduction using 5 v% sulfuric acid, based on initial CCO at 60°C.

insufficient MeOH to convert the FFA into ME. Therefore, the higher level of MeOH was considered preferable. On the other hand, when the higher amount of MeOH was used, the resultant FFA content in the CCO could not be reduced to less than 1 wt%. Therefore, 17 v% MeOH in 5 v% sulfuric acid, based on the initial CCO was considered suitable for converting FFA into ME by esterification (the first-stage process), even though the FFA content could not be reduced to less than 1 wt%.

       After separating the pre-treated CCO from the waste solution, the CCO was used to produce ME by transesterification under conditions of 20 v% MeOH and 0.5 %wt/v NaOH, based on the initial CCO at 60°C. The result indicated that CCO could be converted into ME to more than 99 wt%, as shown in Figure 8, although the conditions for transesterification in TSP used an amount of MeOH lower than that required for transesterification in SFT. This result was due to the MeOH in the transesterification of TSP being replaced by more un-reacted MeOH that remained from the pre-treatment of the CCO.

       Under suitable conditions, the reaction time was about 6 h for saponification followed by transesterification in the batch process, where saponification was used to convert the FFA contained in the CCO into soap. Then, the solution was washed by a spray and bubble technique until
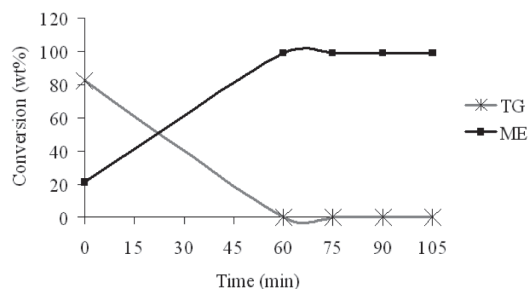

Figure 8 Variation of FFA and ME during transesterification under the condition of 20 v% in 0.5 %wt/v of NaOH, based on initial CCO at 60°C.

it was clean, which took about 9 h. This was followed by the de-acidification of the oily solution to use as feedstock for producing biodiesel, which in turn took 1.25 h. The solution was left for 0.75 h to separate into biodiesel and glycerol. After separation, the final solution of crude biodiesel was washed (taking about 9 h). In total, the reaction time for producing biodiesel from high FFA content crude coconut oil by SFT was about 26 h. The alternative method for producing biodiesel from CCO having high FFA content was the two-stage biodiesel production batch process. In the first-stage process, 1.25 h of reaction time was required to convert the FFA in the CCO into ME, after which the solution was left for 2 h to separate the pre-treatment CCO out of the wasted solution. Then, the pre-treated oil was used to produce biodiesel by transesterification in the second-stage process, which required 1.25 h as shown in Figure 6. Subsequently, the solution was left for 0.75 h for separation into biodiesel and glycerol. This was followed by a wet washing technique at ambient temperature that took 9 h to clean the crude biodiesel. The total reaction time to produce biodiesel using this process was about 14.25 h.

Yield of biodiesel

The yield of biodiesel from each process was investigated under the suitable conditions. With the conversion of ME to more than 99 wt%, it was found that the yield of biodiesel using the SFT and TSP process was 45.6 and 86.6 v%, respectively, based on the initial CCO. The SFT process required less ME than TSP because the FFA and some TG, DG and MG in the CCO were converted into soap (waste) by the saponification reaction, which reduced the amount of the initial CCO available for the production of biodiesel via transesterification. For esterification, the result indicated that the amount of the pre-treatment CCO was nearly the same as the initial amount of CCO because FFA was generated into ME (product) by esterification. In addition, during

treatment of the FFA, some TG, DG and MG in the CCO were converted into ME by acid catalyzed transesterification. Moreover, excess MeOH was used in the first process. Therefore, after separating the waste solution out of the oily phase, ME and some un-reacted MeOH remained in the final solution of the esterification process. Consequently, the TSP process had the higher yield of the two processes.

Estimation the biodiesel production cost

The cost of raw materials, chemical reagents and public utilities, except for the fabrication and labor costs were used to estimate the cost of biodiesel produced in the study. Table 1 shows the variable costs from the study and show that although both processes were similar in the biodiesel cost per batch, they had different biodiesel costs in terms of yield. The cost of biodiesel per yield of TSP (32.02 THB) was cheaper than for SFT (57.09) by about 44% because of the higher yield of final product obtained. However, although the biodiesel production of TSP was the cheaper, it was still higher than the fossil diesel fuel price. Therefore, some costs, such as the amount of MeOH and H_2SO_4 should be reduced by recovering these from the un-purified final product.

CONCLUSION

Using the SFT process, the suitable conditions for producing 45.6% yield of biodiesel with 99 wt% ME content, based on the initial oil content were: 420 v% water including the purification process, 36 v% MeOH and 19.9 %wt/v NaOH, based on de-acidified CCO at 60°C and the total processing time was 26 h. Using the TSP process, the suitable conditions for producing 86.6% yield of biodiesel having 99 wt% ME content, based on the initial CCO were: 5 v% H_2SO_4, 37 v% MeOH, 2.5 %wt/v NaOH and 200 v% cleaning water, based on initial CCO at 60°C

Table 1 Unit variation cost and estimated cost of biodiesel production from high free fatty acid CCO.

Variable cost	Unit cost (THB)	Amount		Cost/batch (THB)		Cost/yield (THB/L)	
		A	B	A	B	A	B
Raw material*							
- CCO (L)	20	1	1	10.00	10.00	21.92	11.55
Chemical reagents*							
- MeOH (L)	18.75	0.36	0.37	6.75	6.94	14.80	8.01
- H2SO4 (L)	19.00	0.00	0.37	0.00	7.03	0.00	8.12
- Sodium hydroxide (kg)	25.68	0.20	0.05	5.14	1.28	11.27	1.48
Public utility**							
- Electricity (kwh)	2.50	0.40	0.39	1.00	0.98	2.19	1.13
- Water (L)	0.00775	4.20	2.00	3.15	1.50	6.91	1.73
Total (THB)				26.04	27.73	57.09	32.02

A = SFT;   B = TSP;   * = Price including 7% VAT and transportation cost;   ** = Household rates used in Thailand.

with a total operating time of 14.25 h. In addition, the biodiesel costs per yield from the SFT and TSP processes were 57.09 and 32.02 THB/L, respectively. The results indicated that TSP was suitable as a biodiesel production process using CCO having high FFA content, because this process was quicker, cheaper and produced a higher yield of biodiesel than SFT.

ACKNOWLEDGEMENT

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