

DEACIDIFICATION AND ESTERIFICATION OF WASTE COOKING OIL: COMPARISON OF THE COUPLED PROCESS WITH STAND-ALONE CATALYTIC ESTERIFICATION AND EXTRACTION PROCESSES

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The free fatty acids in waste oil with high acid value were removed and transformed into fatty acid methyl esters by the extraction-reaction coupled process. The de-acidification efficiency and esterification conversion in the extraction-reaction coupled process were studied and compared with those in the stand-alone extraction process and the esterification process, respectively. Compared with cross-current batch extraction, the de-acidification efficiency of the extraction-reaction coupled process was equivalent to that of seven equilibrium stages in the conditions of the oil/methanol mass ratio of 1:1 at 60 °C. Compared with the esterification process, the esterification conversion of the coupled process was 90.3%, which is much larger than 46% in the esterification process at the reaction time of 32 minutes. Based on these findings, it is suggested that the extraction-reaction coupled process is a very effective and promising method for biodiesel production from oils having high acid value.

Keywords: Biodiesel; Cation-exchange resins; High FFA oil; Extraction; Esterification

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INTRODUCTION

Biodiesel, which consists of fatty acid methyl ethers (FAMES) from vegetable oils and animal fats, is an alternative, non-toxic, biodegradable, and renewable liquid fuel (Shahid et al. 2008). There has been an increasing interest in biodiesel. However, biodiesel has currently not been widely produced in the world. The major bottleneck is the high cost of feedstock used for biodiesel production (Kulkarni et al. 2006). The raw feedstock costs constitute approximately 70 to 95% of the overall biodiesel production costs (Zhang et al. 2003). Many researchers have looked into the use of cheap low quality waste oils as raw feedstock for biodiesel production (Canakci et al. 2007; Watanabe et al. 2005; Zafiroopoulos et al. 2007). However, the process for biodiesel production with waste oil is very challenging due to the presence of considerable free fatty acids (FFAs) in the feedstock. Transesterification catalyzed alkali is the most common way to produce biodiesel because of rapid reaction rate and low level of corrosion toward the equipment. If this process is used to convert waste oil to biodiesel, FFAs in the waste oil will react with the alkaline catalysts to form a large amount of unwanted soap by-products, and the saponification also consumes alkaline catalysts, resulting in a lower transesterification rate, a lower yield of biodiesel, and a higher catalyst cost. The separation of the soap

formed also complicates the process and adds to the costs (Veljkovic et al. 2006).

The general methods to remove FFAs from oil are neutralization, steam distillation, extraction by alcohol, and esterification by acid-catalysis (Liu et al. 2002). Neutralization for deacidification has many limitations (Liu et al. 2001). Some of glyceride can be saponified by alkali, and the separation of glyceride from the formed soapstock is very difficult, which results in a large loss of glyceride. Steam distillation for deacidification requires a high temperature and consumes a large amount of energy consumption but with a low efficiency (Liu et al. 2001). Extraction by alcohol for deacidification needs a great amount of solvent and many extraction stages because of the limited solubility of FFAs in alcohol (Pina et al. 2000; Turkay et al. 1991). Esterification by acid-catalysis makes best use of FFAs in oil and transforms FFAs into FAMES by esterification. Both homogeneous acid catalysts and solid acid catalysts may be used. Homogeneous acid catalysts are difficult to recycle, need to operate at high temperatures, and give rise to serious environmental and corrosion problems (Loterio et al. 2005; Canakci et al. 2003). Solid acid catalysts offer significant advantages of eliminating separation, corrosion, toxicity, and environmental problems (Clark et al. 2002; Okuhara et al. 2002). However, the esterification between FFAs in oil and methanol catalyzed by solid acid catalysts is a liquid-liquid-solid heterogeneous reaction, and therefore is slow due to the dominating influence of the mass transfer resistance.

In this study we investigated a combined process for deacidification of waste oil with high acid value, in which extraction of FFAs was coupled with esterification of FFAs. In this coupled process, the waste oil and methanol are pumped through a fixed-bed reactor containing solid acid catalyst. FFAs are extracted into the methanol phase from the oil phase, then react with methanol to form FAMES over the solid acid catalyst. The formation of FAMES would decrease the FFAs in the methanol, leading to an increased difference in FFA concentration between the oil phase and the methanol phase, and hence an increased mass transfer driving force favoring FFA extraction. The FAMES produced from the esterification of FFAs would move into the oil phase, which would decrease the FAMES in the methanol phase and thus favor the esterification reaction. In this way, the deacidification efficiency can be promoted in the coupled process.

In this work we study the coupled process of catalytic esterification and extraction of FFAs in waste oil. The deacidification efficiency in the coupled process was compared with that of the stand-alone extraction process, and the esterification conversion was compared with that of the stand-alone esterification process.

EXPERIMENTAL

Materials

The waste cooking oils (FFAs content: 27.4%, acid value: 55mgKOH/g oil, saponification value: 190mgKOH/g oil, water content: 0.75%) was purchased from a local company authorized to collect waste oils from local restaurants.

The catalyst used in the study is a strong acid cation exchange resin, named type 001×7. The resin was purchased from Hangzhou Huadong Pharmaceutical Co. Ltd. Its physical and chemical properties are listed in Table 1.

Table 1. Physical and Chemical Properties of Resin 001×7

Description	Strong acidic exchange resin, gel, sphere
Bead size (≥95.00%)	0.4-0.7 mm
Average pore diameter	/
Content of water	46-52%
Surface area	/
Porosity	0.37
Maximal cation-exchange capacity	4.5 mmol/g
Apparent density (wet)	0.77-0.87 g/ml
Real density (wet)	1.24-1.28 g/ml
Chemical stability	Insoluble in acidic, basic solution, and organic solvent
Thermal stability	Up to 120 °C
Corresponding Resins	Amberlite IR-120 , Dowex-50 , Lewatit-100

All other chemicals were obtained from local commercial sources and were analytically pure reagents.

Experimental Devices

Two devices were set up for this study. Device A (Fig. 1) was for stand-alone catalytic esterification, while Device B (Fig. 2) was for the coupled process.

Device A consisted of a glass column with a jacket, a pump, and a substrate tank. The inner diameter of the glass column was 2.7cm, and the length was 100cm. Five sample ports were installed on the side wall of the column, named as a, b, c, d, and e from the top down. The distances of the five sample ports to the top were 4.3cm, 24.3cm, 44.3cm, 64.3cm, and 84.3cm, respectively. The glass column was made into a fixed bed reactor when it was packed with the cation exchange resins, which were pretreated as described below. During reaction, the jacket was filled with running water at the reaction temperature, and the tank was filled with the mixture of methanol and FFAs. The mixture was pumped into the column from the top. The flow rate was controlled by a valve and measured with a flowmeter.

Device B is similar to Device A, except that the inner diameter of the glass column for Device B was 2.4cm, the length was 50cm, and the substrate mixture was pumped into the column from the bottom.

Pretreatment of Cation Exchange Resin

The first step was to remove impurities in the resins purchased. Fresh resins were soaked in distilled water for one or two days. After becoming fully expanded, the resins were packed into a glass column and washed with 2 mol/L HCl solution at 1 mL/cm²/min. The volume of the HCl solution used was 20 times of that of the resins. After the HCl washing, the resins were rinsed with distilled water until the pH of the eluate was 7.0. The resins were then washed with 1 mol/L NaOH solution at 1

mL/cm²/min. The volume of the NaOH solution used was 10 times of that of the resins. After the NaOH washing, the resins were rinsed with distilled water until Na⁺ in the eluate was no longer detectable. The procedure outlined above was repeated once.

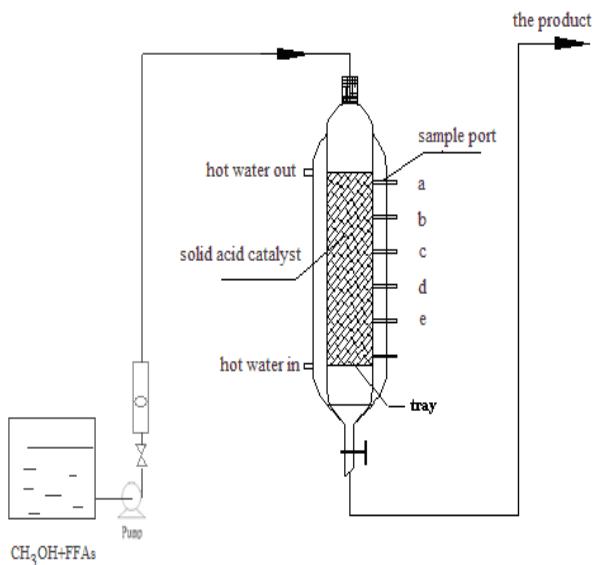


Fig. 1. The fixed-bed reactor

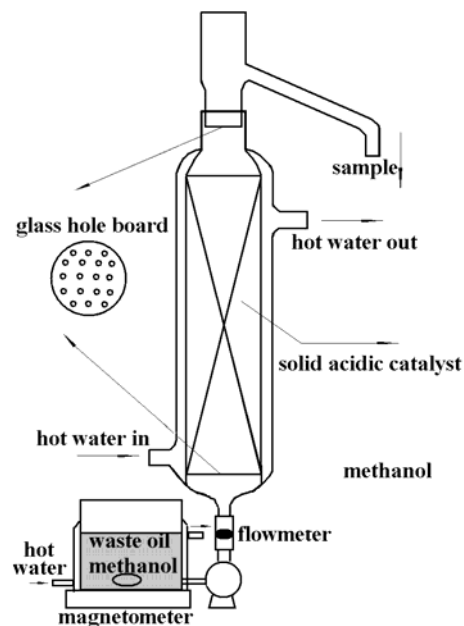


Fig. 2. The extraction-reaction column

Next, to activate catalyst groups, the resins were washed with 1mol/L HCl solution at 1 mL/cm²/min. The volume of the HCl solution used was 20 times of that of the resins. The resins were then washed with distilled water to remove excess HCl until the pH of the eluate was 7.0.

Finally, the treated resins were dried in a vacuum oven at 75°C overnight, and then immersed in methanol for later use.

Stand-alone Extraction and Esterification Process

Extraction of FFAs

The extraction of FFAs from the waste oil was carried out using a multistage cross-current batch process with methanol as the solvent. Waste oil was mixed with methanol in the mass ratio of 1:1, and the mixture was stirred vigorously in a sealed container for 1 hour at 60 °C. Then, the mixture was allowed to separate into two layers at 60 °C overnight. The acid values of the two layers were measured. Methanol in both phases was removed through evaporation at 60°C and 50 KPa. The acid value of the remaining oil was measured. The treated oil layer was mixed with fresh methanol in the mass ratio of 1:1, and the above process was repeated until the acid value of the oil layer was below 3 mgKOH/g oil. FFAs were obtained by evaporating methanol of the methanol phase, and the product was used in the esterification process. The treated oil phase was used to produce biodiesel by transesterification.

Esterification

The pretreated cationic exchange resins were packed into the glass column of Device A, as shown in Fig. 1, and rinsed with methanol. The column was heated and maintained at 60 °C by circulating the thermostated water through the jacket of the fixed bed reactor.

One part of FFAs extracted from the waste oil was mixed with 3 parts of fresh methanol, and the mixture was heated and kept at 60 °C in the substrate tank. To start the esterification reaction, the mixture was pumped through the fixed bed reactor at 3.3ml/min. FFAs reacted with methanol to form FAMES over the activated cation exchange resins. After the system reached steady state, the samples were withdrawn from the sample ports, and the contents of FFAs in the samples were determined by titration with KOH aqueous solution.

The Coupled Process

The pretreated cationic exchange resins were packed into the glass column of Device B shown in Fig. 2, and rinsed with methanol. The column was heated, and the temperature was maintained at 60 °C by circulating thermostated water through the jacket of the column.

Waste oil (named as “the feedstock”) was mixed with methanol at a mass ratio of 1:1, and the mixture was heated up and kept at a temperature of 60°C during the experiment. Then, the mixture was pumped into the fixed bed reactor at 2.61ml/min. After the system reached steady state, the sample was collected from the outlet of the extraction-reaction column. The collected sample was allowed to stand for 30 minutes and separate into two layers (The methanol layer was named as “the extract phase”, and the oil layer was named as “the raffinate phase”). Methanol in each of the two layers was removed by evaporation. The content of FFAs in each of the two treated layers was determined through titration. The contents of FAMES in the two treated layers were determined using gas chromatographic analysis.

Analytical Methods

Reaction time

In the fixed bed reactor, reaction time or residence time is the contact time between the fluid and resins. Plug flow of the fluid through the bed at a constant flowrate Q (ml /min) is assumed. The reaction time, t , was calculated by equation (1),

$$t = \frac{V_o}{Q} = \frac{\varepsilon V}{Q} = \frac{\varepsilon \frac{\pi}{4} d^2 h}{Q} \quad (\text{min}) \quad (1)$$

where V_o is the void volume of the bed (ml), V is the volume of the bed (ml), h is the height of the resin layer in the column (cm), d is the internal diameter of the column (cm), ε is the void fraction (having a value of 0.37 for the used resin), and Q is the flowrate (ml/min).

FFA concentration

The concentration of FFAs is indicated by the acid value, which is equal to the amount (mg) of KOH required to neutralize the FFAs in 1g of oil.

The acid value was determined according to GB/T5530-85 published by Standardization Administration of the People's Republic of China,

$$AV = \frac{V \times c \times 56.1}{m} \quad (2)$$

where AV is the acid value (mg KOH/g oil), V is the dissipative volume of KOH solution (ml), c is the concentration of KOH solution (mol/L), 56.1 is the molecular weight of KOH (g/mol), and m is the weight of the sample (g)

FAME concentration

The content of FAMES was determined according to Europe Biodiesel Standard EN14103 (Determination of ester and linolenic acid methyl ester contents).

A gas chromatograph (7890A, from Agilent Technologies Co., Ltd) and DB-Wax column (30 m×0.32 mm×0.50 μm) were used.

Analytical Conditions: Injector temperature: 250°C. Oven temperature: 200 °C, hold 8min; 10 °C /min to 230 °C, hold 10min. FID detector temperature: 300 °C. Carrier gas: nitrogen, flowrate 3ml/min. Methyl heptadecanoate (over 98% purity, chromatographic grade) used as internal standard for GC analysis of FAMES was purchased from Sigma Ltd. (USA).

Esterification yield

The coupled process. The purpose of the coupled process is to reduce FFAs in the oil feedstock through extracting and converting FFAs into FAME.

The content of FFAs in the oil was indicated by the acid value of the oil. The esterification rate of FFAs was calculated with equation 3,

$$\eta = \frac{m_F AV_F - (m_E AV_E + m_R AV_R)}{m_F AV_F} \quad (3)$$

where η is the esterification rate of FFAs in the coupled process (%). m_F , m_E , and m_R were the mass of the feedstock, the extraction phase, and the raffinate phase, respectively (g). AV_F , AV_E , and AV_R were the acid value of the feedstock, the extraction phase, and the raffinate phase, respectively (mg KOH/g oil).

Stand-alone esterification process. The stand-alone esterification rate was calculated using equation 4,

$$\eta = \frac{AV_0 - AV_i}{AV_0} \quad (4)$$

where η is the esterification rate of FFAs in the stand-alone esterification process (%), AV_0 is the acid value of the mixture into the fixed-bed reactor (mg KOH/g), and AV_i is the acid value of the samples drawn from the sample port (mg KOH/g).

RESULTS AND DISCUSSION

Deacidification of Waste Cooking Oil: Comparison of the Coupled Process with Stand-Alone Extraction Processes

The results from the extraction process and the coupled process are compared in Fig. 3. The acid value of raw waste oil is indicated by the blue histogram bar (first bar), the acid value of the waste oil treated by the coupled process is indicated by the yellow (right-most) bar, the acid value of the waste oil treated by the extraction process is indicated by the red columns, and the extraction stages are indicated by the numbers from 1st to 9th listed on the horizontal axis.

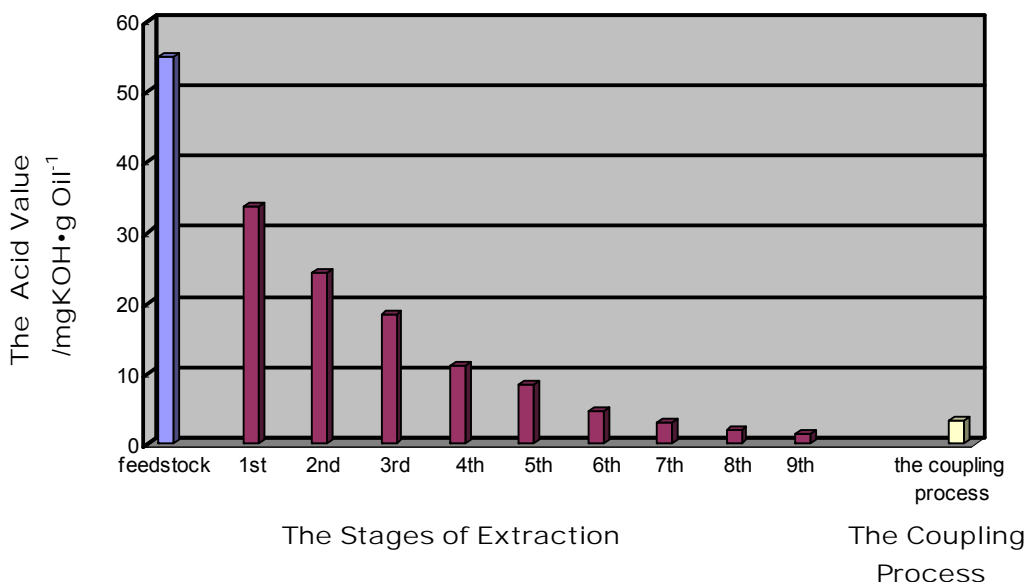


Fig. 3. Removal of FFAs from the waste oil as a function of number of extraction (the mass ratio of oil phase to methanol phase = 1:1, extraction temperature = 60 °C)

It is shown in Fig. 3 that seven equilibrium stages were necessary for the cross-current batch extraction process to decrease the acid value of the waste oil to 3.2mgKOH/g oil from 55mgKOH/g oil, and the usage of methanol was seven times the mass of the waste oil. This result may be attributed to the fact that FFAs in the waste oil were mainly long chain palmitic and oleic acids having low solubility in the methanol (Heryanto et al. 2007; Calvo et al. 2009). Table 2 showed the distribution of FFAs between the methanol phase and the oil phase at 1:1 methanol/oil mass ratio and 60°C. At equilibrium, the ratio of FFAs in the methanol phase to those in the oil phase (partition coefficient of FFAs) was relatively low. The partition coefficient was less than 1 when the acid value of the oil phase was less than 30 mgKOH/g oil. A low partition coefficient is an indication of a low de-acidification efficiency and the need for larger volume of

solvent, a longer extraction column, or more extraction stage numbers to remove FFAs from the raw oil using methanol.

Table 2. Extraction Equilibrium Data of FFAs between Methanol and Waste Oil

FFAs content in the methanol phase mgKOH/g	FFAs content in the oil phase mgKOH/g	partition coefficient of FFAs *
39.04	33.66	1.16
21.23	24.43	0.87
14.71	18.44	0.80
10.00	11.12	0.90
6.14	8.53	0.72
3.72	4.61	0.81
2.31	3.15	0.73
1.49	2.01	0.74
0.95	1.51	0.63

*the ratio of FFAs in the methanol phase to FFAs in the oil phase at extraction equilibrium

Compared with the cross-current batch extraction, the acid value of waste oil dropped easily to 3.2mgKOH/g oil from 55.0mgKOH/g oil in the coupled process, and only 30 minutes and methanol in the mass of waste oil were needed to complete the operation. The usage of methanol in the coupled process was reduced by a factor of 7, but the de-acidification efficiency was equivalent to the de-acidification efficiency of seven equilibrium stages in the cross-current batch extraction.

The reason that the coupled process has higher de-acidification efficiency is that esterification has active effects on extraction. In the coupled process, the cation exchange resin (Resin 001×7) was used as not only packing for extraction but also as a catalyst for esterification. The resin can be wetted preferentially by methanol, compared to oil, because of a quantity of sulfonic groups on the surface of the resin, so the methanol phase was used as the continuous phase and the resin was immersed in the methanol phase, but the oil phase flowed through the extraction-reaction column in the form of drops. FFAs in the oil phase were first extracted into the methanol phase, then reacted with methanol into FAMES catalyzed by cation exchange resin. Esterification of FFAs resulted in the decrease of the content of FFAs in the methanol phase and the increase of the concentration difference of FFAs between the oil phase and the methanol phase. The increased driving force for mass transfer helped to improve the extraction efficiency and the de-acidification efficiency.

Another factor influencing the deacidification efficiency was the cation exchange resin used as the packing. The packing also improved mass transfer by breaking up large drops to increase interfacial area and promoted mixing in drops by distorting the shapes of the droplets.

Esterification of Waste Cooking Oil: Comparison of the Coupled Process with Stand-Alone Catalytic Esterification Processes

The reaction kinetics of FFAs in the stand-alone esterification process are shown in Fig. 4. It is shown that the esterification rate of FFAs increased, then decreased with increasing the usage of methanol. The esterification rate reached a peak at the

methanol/FFAs mass ratio of 3. Additionally, the esterification rate of FFAs increased with increasing residence time with maximum below 70% at 60min. The low yield was probably due to the accumulation of reaction products (FAME and water) in the reaction system, as the reaction is reversible. Removing water and/or FAMES during the reaction should help improve the esterification rate.

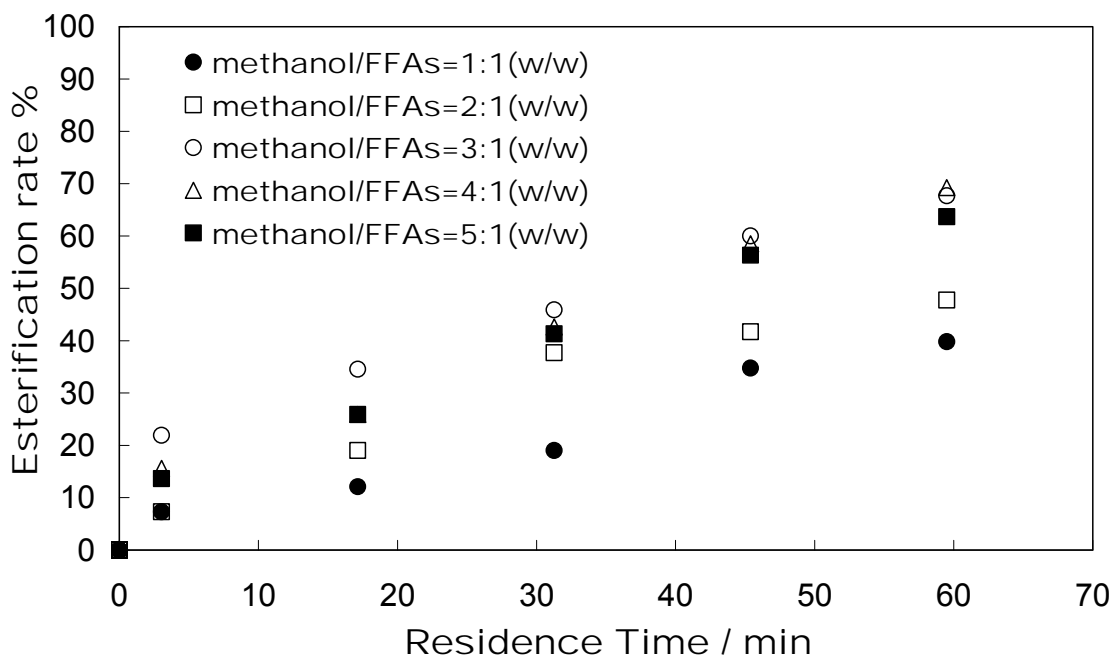


Fig. 4. Esterification of extracted FFAs as a function of residence time at different mass ratio of methanol/FFAs (reaction temperature = 60°C, and apparent velocity = 0.58cm/min)

Table 3 compares the coupled process with the stand-alone esterification process. It is shown that the esterification rate of FFAs in the coupled process was much larger than that in the stand-alone esterification process. The esterification rate of FFAs in the coupled process was 90.7%, but only 46% in the esterification process at the residence time of 32 minutes.

Basically the differences between the two processes are largely due to the differences in reaction equilibrium between the two processes. In the stand-alone esterification process, the reaction products (FAME and water) can accumulate in the reaction system, which can block the esterification. However, in the coupled process, FAMES generated from the esterification could be extracted back into the oil phase, which can be expected to decrease the concentration of FAMES in the methanol phase, accelerate the esterification of FFAs in the methanol phase, and promote the esterification conversion.

Mass Balance of the Coupled Process

A mass balance of the coupled process was carried out, and the material flow in the coupled process is shown in Table 4.

Table 3. Comparison of the Esterification Process and the Coupled Process

	Esterification process	Coupled process
Feedstock	FFAs extracted from waste oil	waste oil having FFAs (55mgKOH/g oil, 0.274g FFAs/g oil)
Usage of methanol	methanol/FFAs=3:1(w/w)	methanol/waste oil= 1:1(w/w) methanol/FFAs in waste oil=3.65:1 (w/w)
Temperature	60°C	60°C
Flow speed	flowrate:3.3ml/min apparent velocity :0.58cm/min	flowrate:2.61ml/min apparent velocity : 0.58cm/min
Reaction time	32min	32.2min
Esterification rate	46%	90.7%

Table 4. Material Flow in the Coupled Process

	Flow in		Flow out			
	oil	methanol	the oil phase		the methanol phase	
			Before evaporation	After evaporation	Before evaporation	After evaporation
Mass (g)	96.8	96.8	86.5	12.7	106.2	84.8
AV (mgKOH/g)	55.0	/	1.74	11.87	3.22	4.03
FAMEs (%)	/	/	9.35	63.76	16.07	20.21
Reduction of FFAs			0.08628 mol	24.16 g		
Production of FAMEs (theory)			0.08628 mol	25.88 g		
Production of FAMEs (experiment)			0.08398 mol	25.19 g		
Relative error			2.6% (mol)	2.6% (wt)		

It was shown that the amount of FAMEs calculated from the reduction of FFAs using the esterification equation approximated the amount of FAMEs obtained in the experiment. The relative difference was 2.6%. The difference may be attributed to experimental error or to the methanolysis of triglyceride with strong acidic ion-exchange resin. Garcia et al. (2008) and Kulkarni et al. (2006) studied the production of biodiesel using a solid acidic catalyst. They thought that acidic catalyst can catalyze both esterification of FFAs and transesterification of oil. Garcia et al. found that the methanolysis conversion of soybean oil could reach 98.6% at 120°C, 1hr, and 5wt% sulfated zirconia catalyst (Garcia et al. 2008). Furuta et al. obtained over 95% conversion of soybean oil at 250°C using titanium- and aluminum-doped zirconias (Furuta et al. 2006). In the coupled process, the effect of catalysis of the strong acidic ion-exchange resin on the transesterification of triglyceride has not been studied. But the data in Table 4 shows that the methanolysis conversion of triglyceride with Resin 001×7 was low. This may be due to the mild reaction conditions (60°C).

CONCLUSIONS

The extraction-esterification coupled process is a promising method for biodiesel production from low quality waste cooking oil. The coupled process has high de-acidification and esterification efficiency due to the reciprocal effect between esterification and extraction. The de-acidification efficiency of the coupled process was equivalent to that of seven equilibrium stages. The esterification extent of the coupled process was over 90% under mild reaction conditions. In addition, the coupled process can offer significant advantages of eliminating separation, corrosion, toxicity, and environmental problems. The coupled process is worth studying further. Many factors, such as the catalyst, the oil/methanol mass ratio, the reaction temperature, the apparent velocity, and the residence time, can affect the coupled process. Further studies of the coupled process are necessary.

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REFERENCES CITED

- Calvo, B., Collado, I., and Cepeda, E. A. (2009). "Solubilities of Palmitic Acid in Pure Solvents and Its Mixtures," *J. Chem. Eng. Data* 54, 64–68
- Canakci, M., and Van Gerpen, J. (2003). "A pilot plant to produce biodiesel from high free fatty acid feedstocks," *Transactions of the ASAE* 46, 945-954.
- Canakci, M. (2007). "The potential of restaurant waste lipids as biodiesel feedstocks," *Bioresource Technology* 98, 183-190.
- Clark, J. H. (2002). "Solid acids for green chemistry," *Accounts of Chemical Research* 35, 791-797.
- Furutaa, S., Matsuhashi, H., and Arata K. (2006). "Biodiesel fuel production with solid amorphous-zirconia catalysis in fixed bed reactor," *Biomass and Bioenergy* 30, 870-873.

- Garcia, C. M., Teixeira, S., Marciniuk, L. L., and Schuchardt, U. (2008). "Transesterification of soybean oil catalyzed by sulfated zirconia," *Bioresource Technology* 99, 6608-6613.
- Shahid, E. M., and Jamal, Y. (2008). "A review of biodiesel as vehicular fuel," *Renewable and Sustainable Energy Reviews* 9, 2484-2494.
- Heryanto, R., Hasan, M., Abdullaha, E. C., and Kumoro, A. C. (2007). "Solubility of Stearic Acid in Various Organic Solvents and Its Prediction using Non-ideal Solution Models," *ScienceAsia* 33, 469-472
- Kulkarni, M. G., and Dalai, A. K. (2006). "Waste cooking oil-an economical source for biodiesel: A review," *Industrial and Engineering Chemistry Research* 45, 2901-2913.
- Kulkarni, M. G., Gopinath, R., Meher L. C., and Dalai, A. K. (2006). "Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification," *Green Chemistry* 8, 1056-1062.
- Liu, X., Kan, J. Q., and Chen, Z. D. (2002). "Discuss on technology of removing FFA from vegetable oil with high acid value," *China Oils and Fats* 3, 24-26.
- Liu, D. C., and Su, W. Y. (2001). *Edible Vegetable Oil and Vegetable Protein*, Chemical Industry Press, Beijing.
- Lotero, E., Liu, Y., Lopez, D. E., Suwannakarn, K., Bruce, D. A., and Goodwin, J. G. (2005). "Synthesis of biodiesel via acid catalysis," *Industrial & Engineering Chemistry Research* 44, 5353-5363.
- Okuhara, T. (2002). "Water tolerant solid catalysts," *Chemical Reviews* 102(10), 3641-3665.
- Pina, C. G., and Mejrelles, A. J. A. (2000). "Deacidification of corm oil by solvent extraction in a perforated rotating disc column," *Journal of the American Oil Chemists' Society* 77, 553-559.
- Turkay, S., and Civelekoglu, H. (1991). "Deacidification of sulfur olive oil: Single-stage liquid-liquid extraction of miscella with ethyl alcohol," *Journal of the American Oil Chemists' Society* 68, 83-86.
- Veljkovic, V. B., Lakicevic, S. H., Stamenkovic, O. S., Todorovic, Z. B., and Lazic, M. L. (2006). "Biodiesel production from tobacco (*Nicotiana tabacum* L.) seed oil with a high content of free fatty acids," *Fuel* 85, 2671-2675.
- Watanabe, Y., Pinsirodom, P., Nagao, T., Kobayashi, T., Nishida, Y., Takagi, Y., and Shimada Y. (2005). "Production of FAME from acid oil model using immobilized *Candida Antarctica* lipase," *Journal of the American Oil Chemists Society* 82, 825-831.
- Zafiroopoulos, N. A., Ngo, H. L., Foglia, T. A., Samulski, E. T., and Lin W. B. (2007). "Catalytic synthesis of biodiesel from high free fatty acid-containing feedstocks," *Chemical Communications* 3670-3672.
- Zhang, Y., Dubé, M. A., and Mclean, D. D. (2003). "Biodiesel production from waste cooking oil: Economic assessment and sensitivity analysis," *Bioresource Technology* 90, 229-240.

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