Transforming Rapeseed Oil into Fatty Acid Ethyl Ester (FAEE) via the Noncatalytic Transesterification Reaction

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A simple methodology for producing biodiesel is presented. The noncatalytic transesterification was carried out via the thermochemical process because the main driving force of biodiesel conversion was temperature rather than pressure. Noncatalytic transformation of rapeseed oil into fatty acid ethyl ester (FAEE) was performed in a continuous flow system under ambient pressure in the presence of activated alumina, charcoal, and carbon dioxide (CO_2). The biodiesel conversion methodology introduced in this work enables the esterification of fatty acids (FFAs), and transesterification of triglycerides to be combined into a single process and leads to a 97.5 (±0.5)% conversion efficiency of biodiesel within 1 min at 420–500°C. The new process has high potential to achieve a breakthrough in minimizing the cost of biodiesel production owing to its simplicity and technical advantages. © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 1468–1471, 2013
Keywords: biodiesel, fatty acid methyl ester (fame), fatty acid ethyl ester (FAEE), porous materials, carbon dioxide (CO_2)

Introduction

Approximately 85% of all petroleum-derived oil is used as fuel in the transportation sector.[1] This intensifies the importance and urgency of developing renewable energy alternatives to satisfy community needs, diversify energy sources, obtain a secure energy supply, and reduce environmental impacts.[1,2] Thus, among biofuels, biodiesel has been regarded as an attractive alternative, because it is relatively easy to adapt current engine technology and distribution networks to biodiesel.[3] Controversially, the high cost associated with lipid feedstocks for biodiesel has been considered a major impediment to the widespread use of biodiesel worldwide.[4,5] The same analogy has been put forward in regard to the bioethanol industry. Moreover, the ethical dilemma of using biodiesel feedstocks that compete with food resources has to be considered in a fully transparent manner when proposing this technology as an alternative energy source on a large scale.[6] These considerations have prompted the development of second- and third-generation biodiesels.[7–14]

In general, methanol (MeOH) has been commonly and commercially used to produce the biodiesel known as fatty acid methyl ester (FAME) via the transesterification process using homogeneous catalysts (i.e., KOH, NaOH, and H_2SO_4).[6,15–17] However, some recent studies have highlighted the use of ethanol (EtOH) instead of MeOH to transform various lipid feedstocks into biodiesel (i.e., fatty acid ethyl ester (FAEE)) because of the potential toxicity of MeOH and its typical production by the petroleum industry.[18–21] In contrast to MeOH, EtOH is a major renewable energy source, because bioethanol can be produced globally from starch- or sucrose-based feedstocks.[22] Thus, using EtOH would enhance the sustainability of biodiesel and minimize its environmental impact.[3,23,24] Furthermore, our promising and long-standing efforts to produce bioethanol from lignocellulosic biomass will likely achieve success in the near future, which would expedite the use of EtOH to produce biodiesel (i.e., FAEE). In addition, performing the transformation to biodiesel in the presence of conventional homogeneous catalysts is not desirable in terms of environmental impact, because of the sequence of transesterification and washing processes involved.[25–27] For example, the washing process leads not only to the generation of wastewater, but also to the inevitable loss of biodiesel.[3,28]

Thus, alternative methods of biodiesel production via transesterification with heterogeneous catalysts under subcritical conditions, and via noncatalytic synthesis under supercritical conditions, have been examined to resolve the problematic aspects of the conventional biodiesel conversion process.[29,30] Noncatalytic conversion under supercritical conditions is usually carried out at temperatures and pressures higher than 250°C and 100 bars, respectively.[29,31] Under these conditions, the reactions nearly reach completion; yet, despite these advantages, high-processing costs have been considered the main obstacle to use of this prospective technology. For this reason, economically viable biodiesel transformation technology must be developed and implemented. Thus, the main objective of this work is to describe the production of FAEE via the newly developed noncatalytic transesterification process under ambient pressure (i.e., 1 bar). In addition, this work aimed to clarify the optimal operational conditions such as temperature, pressure, and feeding rates of raw materials for noncatalytic FAEE conversion.

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Materials and Methods

Sample preparation

For the experiment, rapeseed oil was obtained from a local supermarket. Crude fatty acids (Daejung Chemical & Metals Co., Ltd., Incheon, Korea) contain various fatty acids, but the most abundant are in the $C_{16–18}$ range, such as hexadecanoic acid and oleic acid. Among them, oleic acid is dominant (~70%).

Lipids feedstocks of biodiesel were characterized in terms of acid value (AV). AV is expressed as the amount of KOH in mg necessary to titrate all of the FFAs contained in 1 g of oil. The AV is determined by the following equation: where V is the volume of KOH solution used to titrate the sample (mL), c is the concentration of the KOH solution (M), and m is the mass of the sample.

Activated alumina (Daejung Chemical & Metals Co., Ltd., Incheon, Korea) and charcoal were used for the experiment. The activated alumina and charcoal were characterized in terms of surface area and pore distribution using a BELSORP-mini II (BEL Japan Co., Ltd.). The surface area and pore distribution of activated alumina and charcoal were 297.350 and 0.2527 m^2 g^{-1}, and 5.4112 and 31.7249 nm, respectively.

Noncatalytic biodiesel conversion via the thermochemical process

A tubular reactor (TR) made of 1-inch outer diameter (OD) quartz tubing (Chemglass® CGQ-0800T-13), and a 1-inch Stainless Ultra-Torr® Vacuum Fitting (Swagelok SS-4-UT-6-400) was used. Charcoal or activated alumina was packed into the reactor with a volume of 120 mL. The required experimental temperature, which was in the range 250–500°C, was achieved using a split-hinged tubular-type furnace (AsOne®, Japan); the temperature was simultaneously monitored by an S-type thermocouple to ensure that the target temperature had been met. An insulation collar (high-temperature Duraboard insulation) at the end of the furnace was used to block heat transfer during operation and to protect the quartz tubing. Oil feedstock and primary alcohol (MeOH and/or EtOH) were continuously introduced into the tubular reactor using a gear pump (microannular gear pump MZR®-2905, Germany), and a high-performance liquid chromatography (HPLC) pump (Lab Alliance® PN#F40SFX01, USA).

All gases used in the experiments were of ultrahigh purity and obtained from Daesung Industrial Gases Co., Ltd. All gas flow rates were set using Brooks® mass flow controllers (Brooks SLA5800 Series). A computer-aided control system with LabVIEW® (National Instruments, USA) was employed.

After the reaction, the mixture was allowed to settle for 2 h before the glycerin layer and top layer, which included the biodiesel (FAME or FAEE) fraction, were separated, then removed into separate bottles, and weighed and analyzed via gas chromatography-mass spectrometry (GC/MS; HP-7890A/5975C MSD). The GC/MS and GC/flame ionization detector (FID) instruments were calibrated with the Supelco® FAME Mix (Lot # LB-80557). DB-WAX (J&W 127-7012) and HP-5MS (19091S-413E) GC columns were employed. The EN14103 method was used for the FAME and FAEE conversion.

Results and Discussion

We reported that the main driving force of noncatalytic biodiesel conversion in our previous work was not pressure, but temperature.[32,33] For example, noncatalytic transformation of the biodiesel lipid feedstocks into FAME was achieved in the presence of porous materials, in which case the transformation can be enhanced by the presence of carbon dioxide (CO_2).[32,33] Thus, the thermal energy enables the activation energy of the transesterification reaction to be reached without catalysts, which directly leads to the noncatalytic biodiesel conversion in the continuous flow system. In addition, CO_2 not only enhanced the bond dissociation in the alcoholysis reaction, but also blocked the reversible transesterification reaction.[32,33] Considering the average size of triglycerides (i.e., 2 nm), porous materials with numerous meso- and macropores were suitable for the noncatalytic conversion to biodiesel.[32,33] For example, by means of adsorption and/or absorption, numerous pores provide space for the reaction between the liquid phase of the biodiesel lipid feedstock (i.e., free fatty acids (FFAs) and triglycerides), and the gas phase of MeOH to occur.[32,33] Therefore, in order to investigate the noncatalytic conversion to FAEE on a fundamental level, the reactivities for conversion to FAME and FAEE were compared for various molar ratios of MeOH and EtOH (i.e., 0:1, 1:1, 1:2, and 1:3) at 380°C.

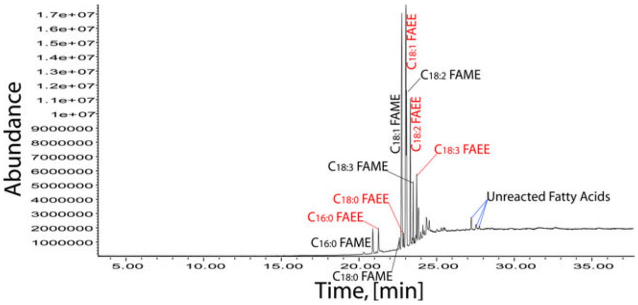

Figure 1. Representative chromatogram of biodiesel generated from rapeseed oil.

Experimental conditions: Temperature: 380°C. Molar ratio of MeOH to EtOH: 1:3. Volumetric feeding ratio of rapeseed oil to alcohol: 10:4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The volumetric flow rates of biodiesel feedstock (i.e., rapeseed oil) and primary alcohol (i.e., MeOH, EtOH, and mixture of MeOH and EtOH) were 10 mL min^{-1} and 4 mL min^{-1}, respectively. In addition, CO_2 was continuously fed into the TR at a flow rate of 100 mL min^{-1}. A representative chromatogram of the biodiesel derived from rapeseed oil is given in Figure 1.

The noncatalytic conversion of rapeseed oil to biodiesel was successfully carried out (i.e., ~98% of conversion efficiency), and representative major peaks, such as those of $C_{16–18}$-range FAME and FAEE, are labeled in Figure 1, which was well consistent with the literature review.[34] Other minor peaks identified as FAME and FAEE are left unlabeled for convenience, to make the chromatogram more visible.

One interesting observation is that the concentrations of FAMEs and FAEEs were similar for various molar ratios of MeOH to EtOH. Indeed, the area under the FAEE peaks had a marginal increase proportional to the molar ratio of MeOH and EtOH. However, as shown in Figure 1, no discernible increase of the FAEE peak area was observed even though the molar ratio of MeOH to EtOH was 1:3. This observation implies that MeOH has a relatively high reactivity in the noncatalytic transesterification reaction compared to EtOH in the noncatalytic transesterification reaction. Another interesting

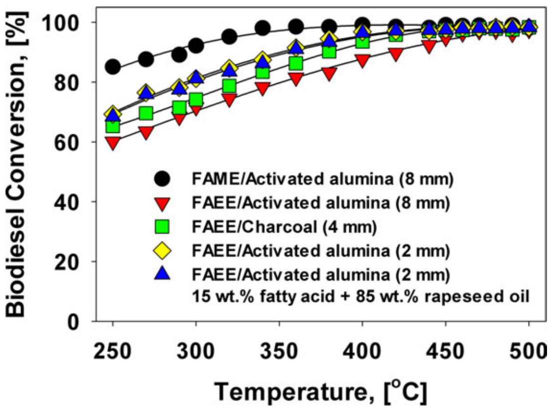

Figure 2. Biodiesel conversion of rapeseed oil at various temperatures, porous materials, and size of porous materials.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

observation is that the conversion efficiency of FAEE in the presence of pure EtOH decreased discernibly (i.e., ~83% conversion efficiency). This observation clarifies that the noncatalytic transformation of rapeseed oil into FAEE was enhanced by the simultaneous presence of both MeOH and EtOH. Thus, the reactivity for conversion to FAEE via the noncatalytic transesterification was relatively lower as compared to the case of FAME. Transforming rapeseed oil into FAEE would require more reaction time (i.e., retention time) in the TR. Thus, it is imperative to establish the optimal operation conditions such as the temperature and volumetric flow rate ratios of biodiesel lipid feedstock to EtOH.

The following experimental work was carried out to investigate the effect of the temperature on the conversion of rapeseed oil to biodiesel, as depicted in Figure 2. The other experimental conditions, including the volumetric flow rates of biodiesel lipid feedstock, primary alcohols, and CO_2, were the same as those given in Figure 1. As can be seen in Figure 2, the conversion efficiency of FAME was noticeably higher than that of FAEE at the lower temperature regime. For example, the conversion efficiencies of FAME and FAEE derived from rapeseed oil at 250°C were ~83% and ~60%, respectively. However, the conversion efficiencies of FAME and FAEE were approximately similar in the high-temperature regime, above 420°C.

The observed conversion efficiency of FAEE in the presence of charcoal is interesting. For example, in previous work done by the authors reported that the conversion efficiency of FAME was nearly the same whether activated alumina or charcoal was used. However, as shown in Figure 2, the conversion efficiency of FAEE was discernibly higher when charcoal was used instead of activated alumina. This observation was consistent with the discussion in Figure 1. For example, transforming rapeseed oil into FAEE required a relatively longer retention time as compared to the case of FAME due to the low reactivity identified in Figure 1. Thus, the authors postulated that the pellet size of the porous materials affects the conversion efficiency of biodiesel. Thus, the following experimental work was carried out with crushed activated alumina in which the average pellet size was significantly reduced (i.e., 2 mm). The conversion efficiency of FAEE was significantly enhanced, as shown in Figure 2, which validates the authors' hypothesis. For example, the conversion efficiency of FAEE was enhanced approximately 18% when we employed 2 mm size of activated alumina. This enhancement was clearly shown in Figure 2. This observation validates that transforming rapeseed oil into FAEE need more retention time, as compare to the case of FAME. Thus, the average pore size and pellet size of the porous material could be crucial factors in the conversion to FAEE.

However, the conversion efficiency was changed as a function of pallet size, suggesting there are transport limitations, typically for a catalytic reaction. In order to get more detailed information, the same experimental work was carried out in the presence of the crushed cordierite honeycomb ceramic for catalyst support. The conversion efficiency of FAEE was less than 5%, which is consistent with the previous work. In addition, the experimental result with the sintered activated alumina (i.e., 1,500°C for 5 h) was similar to the case of cordierite. This observation suggests that pore size and retention time to activate the noncatalytic transesterification reaction is the crucial factor, which can be an evidence of noncatalytic transesterification reaction.

The effect of the presence of FFAs on the conversion efficiency of FAEE was also considered. As an example, 15 wt % of crude fatty acid was intentionally added to the biodiesel lipid feedstock (i.e., rapeseed oil), which is equivalent to an acid value of 30. As illustrated in Figure 2, the noncatalytic conversion to FAEE seemed to have a high tolerance to FFAs in the biodiesel lipid feedstock, which is consistent with the authors' previous work. For example, transforming rapeseed oil having 15 wt % of crude fatty acid into FAEE under the presence of 2 mm pellet size of activated alumina showed the similar conversion efficiency.

Finally, the optimal volumetric flow rate ratio of biodiesel lipid feedstock to EtOH was investigated, as shown in Figure 3. In this experiment, the transformation of biodiesel lipid feedstock into FAEE was carried out at 420°C under the various volumetric flow rate ratios of rapeseed oil to EtOH. As shown in Figure 3, a relatively high ratio of primary alcohol (i.e., EtOH) was necessary to reach the maximum achievable conversion to FAEE, as compared to that necessary for FAME. For example, the optimal volumetric flow rate ratios of biodiesel lipid feedstock to primary alcohol for conversion to FAME and FAEE were 0.2 and 0.3, respectively. This would imply that the conversion to FAEE is more difficult than that to FAME, which is consistent with the previous results shown in Figures 1 and 2.

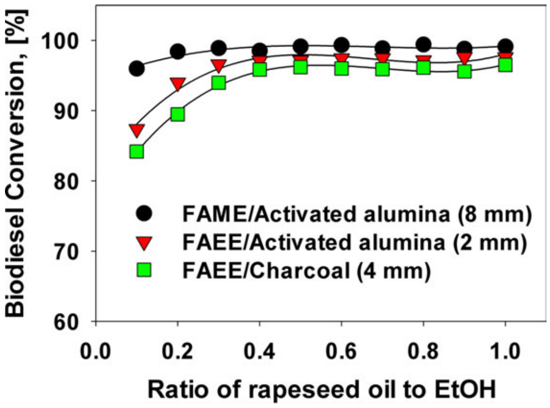

Figure 3. Biodiesel conversion of rapeseed oil at 420°C under various ratios of rapeseed oil to EtOH.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The novelty of our work is that transforming rapeseed oil into biodiesel was done under atmospheric condition and at a relatively high-temperature regime. For example, compared to the conventional and commercialized process (i.e., homogeneous catalyst, such as KOH and H_2SO_4), the conversion cost of biodiesel can be saved nearly 70% when we employ the heat exchanger. Noncatalytic conversion under supercritical conditions is usually carried out at temperatures and pressures higher than 250–350°C and 10–45 MPa, respectively, and a MeOH or EtOH-to-oil molar ratio of 42:1 compared to the stoichiometric ratio of 3:1. Thus, the production of biodiesel using porous materials and CO_2 presented here would be an alternative to the supercritical biodiesel conversion.

Conclusions

In this work, the conversion of FAEE was mechanistically validated under various experimental conditions, including various temperatures, volumetric flow rates of biodiesel feedstock, and porous materials. The effects of temperature and the pellet size of the porous material on the conversion of rapeseed oil to FAEE were crucial. Compared to the conversion to FAME, the noncatalytic conversion to FAEE needs more rigorous experimental and/or operational control.

Literature Cited

1. Biermann U, Bornscheuer U, Meier MAR, Metzger JO, Schäfer HJ. Oils and fats as renewable raw materials in chemistry. *Angew Chem Int Ed*. 2011;50(17):3854–3871.
2. Huber GW, Cortright RD, Dumesic JA. Renewable alkanes by aqueous-phase reforming of biomass-derived oxygenates. *Angew Chem Int Ed*. 2004;43(12):1549–1551.
3. Lardon L, Helias A, Sialve B, Steyer J-P, Bernard O. Life-cycle assessment of biodiesel production from microalgae. *Environ Sci Technol*. 2009;43(17):6475–6481.
4. Bender M. Economic feasibility review for community-scale farmer cooperatives for biodiesel. *Bioresour Technol*. 1999;70(1):81–87.
5. Wassell Jr CS, Dittmer TP. Are subsidies for biodiesel economically efficient? *Energy Policy*. 2006;34(18):3993–4001.
6. Yusuf NNAN, Kamarudin SK, Yaakub Z. Overview on the current trends in biodiesel production. *Energy Convers Manage*. 2011;52(7): 2741–2751.
7. De Paola MG, Ricca E, Calabr V, Curcio S, Iorio G. Factor analysis of transesterification reaction of waste oil for biodiesel production. *Bioresour Technol*. 2009;100(21):5126–5131.
8. Netto CGCM, Andrade LH, Toma HE. Enantioselective transesterification catalysis by Candida antarctica lipase immobilized on superparamagnetic nanoparticles. *Tetrahedron Asymmetry*. 2009;20(19): 2299–2304.
9. Lin L, Ying D, Chaitep S, Vittayapadung S. Biodiesel production from crude rice bran oil and properties as fuel. *Appl Energy*. 2009;86(5):681–688.
10. Meng X, Yang J, Xu X, Zhang L, Nie Q, Xian M. Biodiesel production from oleaginous microorganisms. *Renewable Energy*. 2009;34(1):1–5.
11. Converti A, Casazza AA, Ortiz EY, Perego P, Del Borghi M. Effect of temperature and nitrogen concentration on the growth and lipid content of Nannochloropsis oculata and Chlorella vulgaris for biodiesel production. *Chem Eng Process*. 2009;48(6):1146–1151.
12. Umdu ES, Tuncer M, Seker E. Transesterification of Nannochloropsis oculata microalga's lipid to biodiesel on Al2O3 supported CaO and MgO catalysts. *Bioresour Technol*. 2009;100(11):2828–2831.
13. Khan SA, Rashmi, Hussain MZ, Prasad S, Banerjee UC. Prospects of biodiesel production from microalgae in India. *Renewable Sustainable Energy Rev*. 2009;13(9):2361–2372.
14. Um B-H, Kim Y-S. Review: A chance for Korea to advance algal-biodiesel technology. *J Ind Eng Chem*. 2009;15(1):1–7.
15. Lin L, Cunshan Z, Vittayapadung S, Xiangqian S, Mingdong D. Opportunities and challenges for biodiesel fuel. *Appl Energy*. 2011;88(4):1020–1031.
16. Samios D, Pedrotti F, Nicolau A, Reiznautt QB, Martini DD, Dalcin FM. A transesterification double step process – TDSP for biodiesel preparation from fatty acids triglycerides. *Fuel Process Technol*. 2009;90(4):599–605.
17. Zhang J, Jiang L. Acid-catalyzed esterification of Zanthoxylum bungeanum seed oil with high free fatty acids for biodiesel production. *Bioresour Technol*. 2008;99(18):8995–8998.
18. Li Y, Zhang X-d, Sun L. Fatty acid methyl esters from soapstocks with potential use as biodiesel. *Energy Conversion Manage*. 2010;51(11):2307–2311.
19. Allen CAW, Watts KC, Ackman RG, Pegg MJ. Predicting the viscosity of biodiesel fuels from their fatty acid ester composition. *Fuel*. 1999;78(11):1319–1326.
20. Moser BR. Preparation of fatty acid methyl esters from hazelnut, high-oleic peanut and walnut oils and evaluation as biodiesel. *Fuel*. 2012;92(1):231–238.
21. Knothe G, Cermak SC, Evangelista RL. Methyl esters from vegetable oils with hydroxy fatty acids: Comparison of lesquerella and castor methyl esters. *Fuel*. 2012;96(0):535–540.
22. Powell EE, Hill GA. Economic assessment of an integrated bioethanol-biodiesel-microbial fuel cell facility utilizing yeast and photosynthetic algae. *Chem Eng Res Des*. 2009;87(9):1340–1348.
23. Kiwjaroun C, Tubtimdee C, Piumsomboon P. LCA studies comparing biodiesel synthesized by conventional and supercritical methanol methods. *J Clean Product*. 2009;17(2):143–153.
24. Yee KF, Tan KT, Abdullah AZ, Lee KT. Life cycle assessment of palm biodiesel: Revealing facts and benefits for sustainability. *Appl Energy*. 2009;86(Supplement 1):S189–S196.
25. Yusuf C. Biodiesel from microalgae. *Biotechnol Adv*. 2007;25(3): 294–306.
26. Yusuf C. Biodiesel from microalgae beats bioethanol. *Trends Biotechnol*. 2008;26(3):126–131.
27. Singh M, Singh S, Singh RS, Chisti Y, Banerjee UC. Corrigendum to "Transesterification of primary and secondary alcohols using Pseudomonas aeruginosa lipase" Bioresource Technology 99 (2008) 2116–2120. *Bioresour Technol*. 2009;100(5):1884–1884.
28. Vicente G, Mart?ez M, Aracil J. Optimisation of integrated biodiesel production. Part II: A study of the material balance. *Bioresour Technol*. 2007;98(9):1754–1761.
29. Saka S, Isayama Y. A new process for catalyst-free production of biodiesel using supercritical methyl acetate. *Fuel*. 2009;88(7): 1307–1313.
30. Helwani Z, Othman MR, Aziz N, Kim J, Fernando WJN. Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review. *Appl Catal A*. 2009;363(1–2):1–10.
31. Isayama Y, Saka S. Biodiesel production by supercritical process with crude bio-methanol prepared by wood gasification. *Bioresour Technol*. 2008;99(11):4775–4779.
32. Kwon EE, Seo J, Yi H. Transforming animal fats into biodiesel using charcoal and CO2. *Green Chem*. 2012;14(6):1799–1804.
33. Kwon EE, Yi H, Park J, Seo J. Non-catalytic heterogeneous biodiesel production via a continuous flow system. *Bioresour Technol*. 2012;114(0):370–374.
34. Rashid U, Anwar F. Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil. *Fuel*. 2008;87(3): 265–273.

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