Rapid Synthesis of Biodiesel Fuels at Room Temperature in the Presence of Dimethyl Ether

Guoqing Guan, Katsuki Kusakabe,* Nozomi Sakurai, and Kimiko Moriyama
Department of Living Environmental Science, Fukuoka Women's University,
1-1-1 Kasumigaoka, Higashi-ku, Fukuoka 813-8529

(Received August 2, 2007; CL-070828; E-mail: kusakabe@fwu.ac.jp)

Vegetable oil such as corn, sunflower, rapeseed, soybean, and palm oil was completely transesterified into biodiesel fuel at short time because of high mass-transfer rate in the homogeneous solution formed by adding environmental-friendly solvent of dimethyl ether (DME).

Biodiesel fuel is considered to be a cleaner-burning diesel fuel made from natural, renewable sources such as vegetable oils or animal fats.[1–3] Various processes have been developed to produce biodiesel fuels.[4–11] Transesterification of vegetable oils and animal fats using methanol to produce biodiesel fuels is a two-phase reaction in which methanolysis occurs only in the methanol phase. However, oil has a limited solubility in methanol so that vigorous mechanically mixing and/or heating are necessary to improve the mass transfer between the two phase.[12,13] Boocock et al. first reported that the addition of tetrahydrofuran (THF) as a cosolvent into the methanol–oil system would form an oil-dominant one-phase system in which methanolysis rate rose dramatically.[14,15] THF can be flashed off with the excess methanol for reuse because of the similar boiling points of THF (67 °C) and methanol (65 °C). THF is a widely used solvent but it tends to form peroxide on storage. DME has little toxicological effect on health and the environment, and it exists as a gas in ambient conditions. It can be desolved in methanol as well as oils. Therefore, DME would serve as an environmentally friendly solvent for the homogenization of a methanol–oil system under slightly pressurized conditions and would separate easily after depressure. Both DME and methanol can be obtained from various resources such as natural gas, coal, and biomass. Therefore, it is possible to produce biodiesel fuels from biomass energy sources without using any fossil resources. For this study, the transesterification of vegetable oils such as corn, sunflower, rapeseed, soybean, and palm oil to biodiesel fuels was investigated in the presence of an alkaline catalyst dissolved in the homogeneous mixture of methanol, oil, and DME.

Corn, rapeseed, soybean, and palm oils of reagent grade were obtained from Wako, Japan. Sunflower oil for cooking use was purchased. The oils were not purified before use, and their chemical compositions are similar to those reported in the literature.[1] The reactor used was a pressure-proof glass cylinder (Volume = 10 mL, HPG-96-1, Taiatsu Techno®, Japan). Dehydrate methanol containing KOH and vegetable oil was put into the reactor. The molar ratio of methanol to oil was fixed at 6 and the weight concentration of KOH based on the oil was varied from 0.1–1 wt %. The DME cylinder was connected to the reactor, and DME was introduced into the reactor at approximately 500 kPa. The reactor was immersed in a constant temperature bath (25 °C) fitted with a shaker. The reaction was carried out at the shaking speed of 2.6 Hz. Prior to the reaction, the solubility tests were carried out by changing the composition of methanol, oil, and DME without a KOH catalyst. In several minutes, the reacted solution divided into an upper ester phase and a lower glycerol phase. After opening the reactor to release pressure, concentrated acetic acid was added to the reacted solution to terminate the reaction. The solution then was centrifugated at 6000 rpm for 20 min. The upper layer was rinsed several times with deionized water to remove the residual inorganic components. Concentrations of unreacted oils remaining in the synthesized biodiesel fuels were analyzed by a high-performance liquid chromatography (HPLC, TOSOH, Japan) equipped with a silica-gel column (Shimpack CLC-SIL, Shimadzu, Japan) and a refractive index detector using a mobile phase of *n*-hexane/2-propanol = 99.5/0.5 (v/v). Column temperature was kept at 40 °C. Concentrations of ester components in the biodiesel fuels were analyzed by a FID-GC (Shimadzu GC-8A, Japan) with a Silar 10C 10% Uniport HP glass column. Column temperature was kept at 190 °C and helium was used as the carrier gas.

Transesterification of various vegetable oils was performed when the molar ratio of methanol to oil was 6 at the KOH concentration of 1 wt % based on the oil. The sample was recovered after vigorous shaking for 20 s. No peak for the oils in the HPLC chromatogram was observed, suggesting that these types of vegetable oils had been completely transferred into biodiesel fuels. Table 1 indicates the compositions of the obtained biodiesel fuels. The biodiesel fuels obtained from corn, sunflower, rapeseed, and soybean oils was mainly composed of methyl oleate (C18:1) and methyl linolate (C18:2). The biodiesel fuels obtained from palm oil contained mainly methyl palmitate (C16) and methyl oleate (C18:1). These were approximately consistent with the composition of fatty oils in each.[1] Homogenization was accomplished by the DME/methanol molar ratios as shown in Table 1. When the DME/methanol molar ratio was decreased, the corn oil conversion was decreased because of the immiscibility of the oil and methanol (see ESI). Mean-

Table 1. Compositions of the biodiesel fuels prepared from different vegetable oils[a]

Vegetable oil	DME/MeOH molar ratio	Ester compositions in the biodiesel fuels/wt %				
		Methyl palmitate (C16)	Methyl oleate (C 18:1)	Methyl linoleate (C18:2)	Methyl linolenate (C18:3)	Methyl arachidate (C20)
Com	1.12	9.2	32.8	54.2	3.3	0.50
Sunflower	0.98	6.2	41.6	51.5	0.25	0.45
Rapeseed	1.23	4.3	57.2	22.9	13.2	2.4
Soybean	1.31	9.3	26.7	54.1	8.5	1.4
Palm	1.27	42.4	45.1	11.6	0.32	0.58

[a] Methanol/oil = 6:1 on a molar basis; KOH concentration is 1 wt % based on the oil weight; vigorous shaking for 20 s.

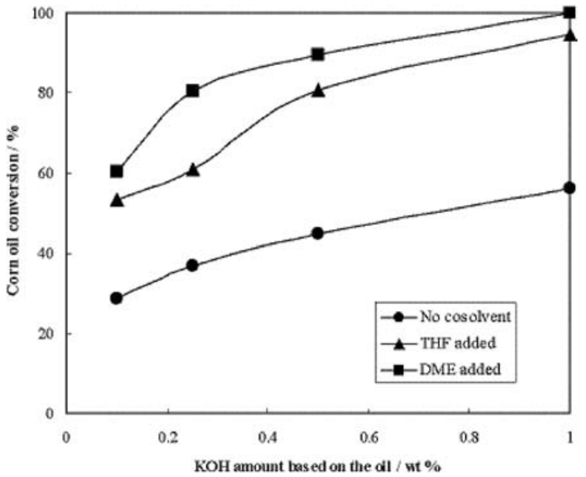

Figure 1. Corn oil conversion as a function of KOH concentration based on the weight of oil at 25 °C. MeOH/oil = 6:1 on a molar ratio, shaking frequency = 2.6 Hz, reaction time = 10 min.

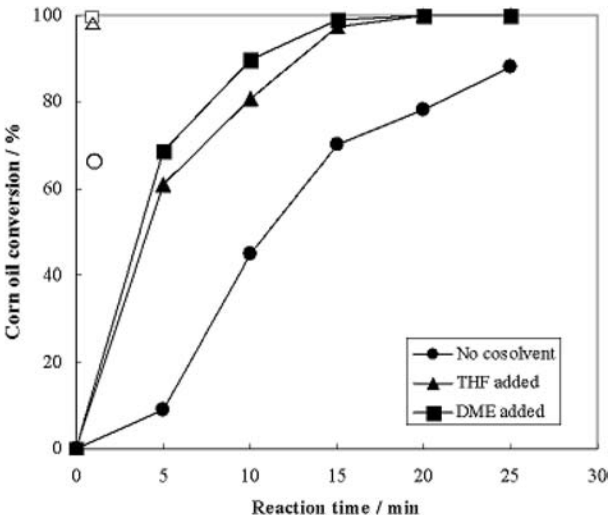

Figure 2. Corn oil conversion as a function of reaction time with a shaking frequency of 2.6 Hz at 25 °C. MeOH/oil = 6:1 on a molar ratio, KOH concentration = 0.5 wt %. □△○: 20 s vigorous shaking in the case of DME (□), THF (△) addition, and no cosolvent (○).

while, loss of DME was not observed during the reaction because it was not involved in the reaction at room temperature.

The effect of KOH concentration on the biodiesel fuel formation from corn oil was investigated. For comparison, transesterification of corn oil with THF (THF/methanol = 0.45 on a molar basis) and without any solvent was performed under the same experimental conditions. A slow shaking frequency of 2.6 Hz was chosen for a period of 10 min due to the high reaction rate in the homogeneous state. Figure 1 shows that the conversion of corn oil increased with increasing KOH concentration. When DME was used as a cosolvent, the highest conversion was obtained and reached 100% at KOH concentration of 1 wt %. When no solvent was added in the reaction system, the conversion became very low compared to a one-phase system. This means the mass transfer between two phases is the rate-determining step. A decrease in the usage of KOH due to the addition of DME is effective in reducing the use of water during separation in the biodiesel fuel production.

Figure 2 shows the conversion of corn oil as a function of reaction time with a shaking frequency of 2.6 Hz at a KOH concentration of 0.5 wt %. When either DME or THF was used, corn oil was completely converted to biodiesel fuel after 20 min of shaking. When vigorous hand shaking was continued for 1 min instead of slow shaking (2.6 Hz), 100 and 97% conversion was reached at a KOH concentration of 0.5 wt % for DME and THF additions, respectively. Also, 100% conversion was reached during a period of less than 20 s at a KOH concentration of 1 wt % for the DME addition as indicated in Table 1.

In conclusion, DME can be considered as an effective cosolvent in the biodiesel fuel production process. Rapid synthesis of biodiesel fuels was achieved in a one-phase reaction system containing DME. DME can be easily recovered from the obtained biodiesel fuel through a depressure procedure.

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