Catalytic Effect of Metal Reactor in Transesterification of Vegetable Oil

Sir:

A paper on the noncatalytic transesterification of soybean oil appeared recently (1). The authors apparently considered that a reactive metal surface catalyzed the transesterification reaction, presumably from the observation that the reaction rates of mixtures containing metal shavings were increased compared with those in the absence of fine-mesh metal. Furthermore, the authors compared their results with ours (3).

In our papers (2,3), we reported a novel method for biodiesel production by a catalyst-free supercritical methanol treatment. In addition to the reaction temperature, we found that the molar ratio of methanol to vegetable oil and the reaction pressure are important reaction parameters in the noncatalytic transesterification. As discussed in detail in the paper (3), an increase of the molar ratio from 3.5 to 42 could increase methyl ester formation from 43 to 90% with 2 min of treatment at 350°C, whereas at a molar ratio of 6, the same treatment produced only about 60% methyl esters. The increase in yield with increasing methanol is a direct result of a second-order rate constant expression. On the other hand, the authors compared our results, which were carried out at a molar ratio of 42, with theirs at a molar ratio of 6 in methanol. The effect of the molar ratio on the yield of methyl esters at 230°C is demonstrated in Figure 1. Our results at a molar ratio of 6 (in methanol) were about two times higher than that reported by the authors (1). The difference may result from the catalytic effect of the metal reactor, as observed by the authors.

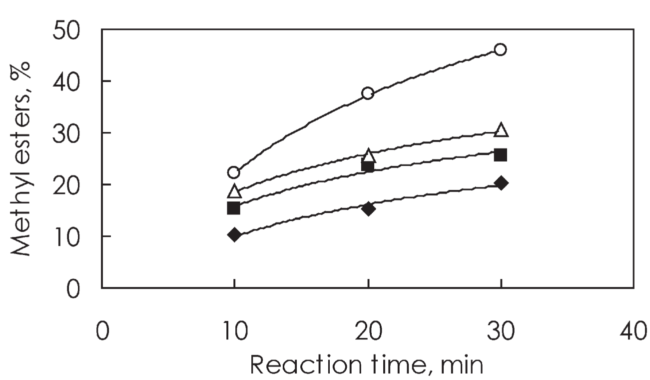

FIG. 1. Effect of molar ratio of methanol to rapeseed oil on the production of methyl esters in supercritical methanol at 230°C. (○) 42:1; (△) 12:1; (■) 6:1; (◆) 3:1.

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Besides molar ratio, the reaction pressure is also an important parameter (4). Our results showed that the reaction rate is linear with reaction pressure. Figure 2 presents the effect of pressure on the yield of methyl esters for rapeseed oil treated with supercritical methanol at 230°C. As one can see, the higher the reaction pressure, the better the conversion. No transesterification reaction occurred at atmospheric pressure. Furthermore, at 10 MPa, which is slightly above the critical pressure, methyl ester formation was highest. At still higher pressure, the conversion was almost constant, indicating that the reaction pressures were high enough to perform transesterifications. Pressure increases the solubility of methanol in oil. From this evidence, therefore, reaction pressure is one of the important variables for reaction rate enhancement.

Results obtained from treatment at lower and higher surface-to-volume ratios of the reactor confirmed that TAG conversions to methyl esters were similar, which implied that the reaction proceeded at the same reaction rate. As a consequence, regardless of the high pressure and high temperature treatment, our method could be available for scaling-up of the reactor. Scanning electron microscopy coupled with energy-dispersive X-ray analysis was carried out to identify the possible presence of trace metals from the reaction vessel in the reaction mixture. No nickel, chromium, or molybdenum was detected; only a trace amount of iron was observed, which was probably from the reaction vessel packing. This result indicated that the reaction vessel was not corroded. Therefore, even though it may be true that the metal reactor catalyzes the reaction as reported by Dasari *et al.* (1), the combined effect

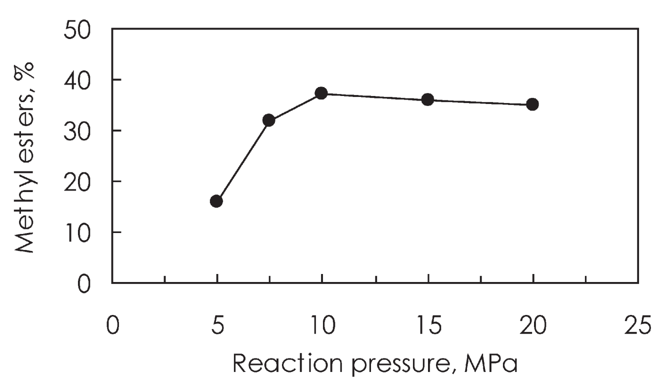

FIG. 2. Effect of reaction pressure in transesterification by supercritical methanol treatment for 20 min at 230°C at a molar ratio of 42:1 (methanol/rapeseed oil).

of a higher molar ratio and pressure is proven to yield important effects in enhancing the reaction rate of transesterification in a catalyst-free supercritical methanol treatment.

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