BIODIESEL PRODUCTION USING SUPERCRITICAL TERT-BUTYL METHYL ETHER (MTBE) AND ALCOHOLS

Nowadays, researches on biodiesel have attracted a tremendous attention as a consequence of the world facing the challenges due to depletion of fossil fuel reserves, global warming issues, and environmental pollution problems. Since biodiesel production increases rapidly in recent years, the overproduction of the main by-product glycerol, obtaining approximately 10% is unavoidable, leading to the significant decrease of price in the market. To circumvent this problem, biodiesel production without generating glycerol is needed. Thus, a new approach of biodiesel production using supercritical MTBE was proposed in this study. Experimental investigations were carried out in a temperature range of 200–500 °C under a pressure of 10 MPa and a fixed oil-to-MTBE molar ratio of 1:40 over 3–15 min. MTBE could react with triglyceride under supercritical conditions, generating fatty acid methyl ester (FAME) and glycerol tert-butyl ether (GTBE). No glycerol was observed under these reaction conditions. The FAME yield increased with temperature from 200 to 400 °C, but it decreased above 400 °C due to thermal decomposition.

Considering that supercritical conditions require elevated temperatures and high pressures, large amounts of heat must be added. To recover the heat efficiently, a novel spiral reactor was proposed in this study. Ethanol was firstly selected as a simple reactant. Experiments were performed at reaction temperatures of 270–400 °C, a fixed pressure of 20 MPa, oil-to-ethanol molar ratio of 1:40, and reaction times of 3–30 min. The results revealed that the spiral reactor employed in this study was not only as effective as conventional reactor in terms of transesterification reactor but also superior in terms of heat recovery. The quantitative analysis of the heat recovery efficiency was 85.5%. Thus, it was concluded that spiral reactor is a good candidate of reactor for biodiesel production under supercritical conditions.

Owing to the successful recovery of heat for biodiesel production using spiral reactor and considering the good merits of biodiesel production conducted under supercritical MTBE conditions, the study of effectiveness of spiral reactor for biodiesel production in supercritical MTBE is interesting. Using a fixed oil-to-MTBE molar ratio of 1:40 and a pressure of 10 MPa, experiments were performed at 250–400 °C and over 6–30 min. It was observed that the spiral reactor performed well for biodiesel production in supercritical MTBE, affording a higher FAME yield compared to the conventional flow reactor for the same residence time. In addition, the spiral reactor employed here was effective for biodiesel production using MTBE under supercritical conditions owing to the successful recovery of heat.

Since supercritical MTBE method was conducted at high pressure, the investigation of pressure effect on product composition as well as reaction kinetics is crucial. Transesterification reactions were carried out at various pressures (10–30 MPa), temperatures (300–400 °C), reaction time (3–30 min), and a fixed oil-to-MTBE molar ratio of 1:40. The effect of pressure on final product composition as well as reaction rate was negligible for the conditions employed here. This negligible effect could be attributed to the almost constant density of MTBE.

Finally, reaction behavior of biodiesel production under supercritical methanol, ethanol, and MTBE conditions was compared in this study. A series of experiments were carried out at reaction temperatures of 270–400 °C, reaction times of 3–30 min, a pressure of 20 MPa, and oil-to-reactant molar ratio of 1:40. The results showed that biodiesel yield increased with reaction time and temperature for all cases. Under the same reaction conditions, supercritical methanol method gave the highest yields of biodiesel. At 270 °C, biodiesel yield in supercritical MTBE was higher than that in supercritical ethanol owing to the solubility effect, whereas above 270 °C, biodiesel yield in supercritical ethanol was higher than that in supercritical MTBE due to the bulkier structure of MTBE.