Supercritical Fluid Transesterification for the Catalyst-Free Production of Biodiesel

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Non-catalytic supercritical transesterification provides a new way of producing biodiesel fuel from bio-based oils (triglycerides). When the supercritical fluid (SCF) is used as a reaction medium, a small change in the pressure near the critical point of the fluid causes a significant change in density-dependent properties such as the solubility parameter, mass transfer, viscosity, and dielectric constant. Some unique advantages for conducting chemical reactions in SCF are: (1) reaction rates, yields, and selectivity can be adjusted by varying pressure and temperature; (2) environmentally-benign SCF such as supercritical CO₂, H₂O, and alcohol can be used instead of undesirable solvents; (3) mass transfer is improved for heterogeneous reactions; and (4) simultaneous separation and reaction may be accomplished for some reactions. Compared to conventional transesterification processes catalyzed by alkali or acid catalyst, the non-catalytic SCF method does not require the post-refining process for the removal of the catalyst. To find the supercritical reaction conditions that are best suited for the economical biodiesel production, experiments were conducted first with soybean oil. The soybean oil was treated with a supercritical methanol above the critical temperature and pressure at 239 °C and 8.1 MPa, respectively. The reaction parameters investigated were the reaction time and temperature at a constant pressure and a molar ratio (alcohol to triglycerides), and their effect on the biodiesel formation. Addition of a co-solvent, supercritical CO₂ (critical point at 31 °C and 7.3 MPa), increased the rate of the supercritical methanol transesterification reaction, making it possible to obtain high biodiesel yields at less harsh temperature conditions.