289j Solid Acid Catalyzed Esterification of Free Fatty Acids in Oil Using Co_2 Enhanced Media

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The potential applications of alkyl esters include intermediates for value added products and a renewable, biodegradable, and nontoxic diesel fuel substitute, biodiesel[1-4]. The production of alkyl esters typically occurs via the transesterification of vegetable oils with alcohols using alkaline catalysts in a batch process. Large scale use of alkyl esters, and biodiesel, is currently prohibitively expensive due to costs associated with purifying the oil feedstock [1,5]. Cheaper feedstocks are available, but the high free fatty acid and water content lead to increased separation costs [6] and decreased catalyst efficiency [7].

This paper presents the results of exploiting dense CO_2-enahnced media to esterify the free fatty acids in waste oil. Recently, solid acid catalysts have been reported as environmentally beneficial alternatives to sulfuric acid for the esterification of palmitic acid in soybean oil using methanol [8]. However, acid sites accessibility can be an issue depending on the solid acid used. In addition, supercritical methanol has been used for the simultaneous methyl esterification of free fatty acids and transesterification of triglycerides [9]. However, the high temperatures and pressures required for supercritical methanol are cost prohibitive. The use of CO_2 to expand the reaction mixture can result in decreased mass transfer limitations at milder pressures and temperatures than supercritical methanol conditions. In addition to the phase behavior results presented, the effect of a) the CO_2-expanded media, b) the incorporation of co-solvents such as hexane, c) the feedstock composition, and d) the type of solid acid catalyst employed on the methyl ester yield is discussed.

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