

# Catalytic and Noncatalytic Esterification and Transesterification by Subcritical Methanol

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**Abstract**—The model reactions of benzoic acid (BA) esterification and ethyl benzoate (EB) transesterification by subcritical methanol were carried out for the first time at 220°C without catalysts in order to decrease the acid wastes from an industrially important reaction of the synthesis of biodiesel components. Methanol under these conditions is both a solvent and a catalyst. Benzoic acid is esterified in quantity even when the ratio of BA to methanol is 1 : 3. Benzoic acid transesterification occurs with 82% conversion and a BA-to-methanol ratio of 1 : 10. A process is proposed for biodiesel manufacturing from vegetable oil under the specified conditions and in the presence of a solid acid catalyst (sulfated  $\text{TiO}_2$ ,  $\text{SnO}_2$ , or  $\text{Al}_2\text{O}_3$ ). With the use of sulfated  $\text{TiO}_2$ , biodiesel fuel yields can reach 98% at 170°C. Our results can be used in the large-scale production of biodiesel fuel components because they show a way to seriously decrease costs for recycling acid emissions and the load on the environment.

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