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Thesis Title:

**Transesterification using Ultrasonic Spray of Triolein Containing CaO into Methanol Vapor in a 3-Phase Reactor**

The objective of this research is to investigate the influence of heterogenous transesterification variables (feed flowrate, temperature, catalyst loading, an initial ratio of methanol to triolein as 6:1, initial volume of triolein and reactor's height) on the yield of methyl ester (biodiesel) of triolein with methanol by using CaO as catalyst. The reaction was carried in the experimental 3-phase reactor (triolein-MeOH-CaO), which the ultrasonic spray was used to generate many small liquid droplets. The reaction mechanism and kinetics parameters are investigated and determined, respectively.

**Chapter 1 Introduction** describes the background and explains the principles of biodiesel production. A review of suitable process for biodiesel production and the main factors affecting to FAME yield such as type of catalyst, catalyst loading and size, alcohol to oil ratio and reaction temperature and time is described in this section. A brief explanation of ultrasonic assisted transesterification is presented and the surface kinetic is described. The objective of this study is introduced as well as the structure of this thesis.

**Chapter 2 Experimental set up** introduces the chemicals used as raw materials and equipment for analyzing the composition of ester. Also, the experimental devices are presented. The catalyst preparation, experiment procedure and methyl ester analysis is described in detail.

**Chapter 3 Effects of variables on methyl ester yield** investigates the effect of key parameters such as flow rate of triolein, reaction temperature and CaO loading on the methyl ester yield. The efficiencies of 3-phase experimental reactor and 2-phase conventional reactor are compared. There is also the investigation of initial MeOH: Triolein ratio as 6:1 for the transesterification in 3-phase reactor to compare the methyl ester yield to none of methanol at the beginning of reaction. The effects of initial volume and spraying distance of triolein for 3-phase reactor on methyl ester yield is also observed. Finally, the methanol and methyl ester are determined during reaction. The parameter, time-totalized area, is also defined and it's strong correlation on methyl ester yield and the rate determining step of the transesterification is explain in this section. The results were summarized as follows:

It was discovered that the optimum triolein flow rate of 6 ml/min produced the highest yield of methyl ester due to the highest surface area of the triolein droplets being generated by ultrasonic spray. The higher temperature favored this endothermic reaction, although methanol solubility was decreased, and methyl ester yield receiving 23.8% at 100°C was observed. The methyl ester yield increased with additional CaO loading from 1 to 3 wt%. This trend changes when comparing 5wt% and 7 wt%. A 5 wt% CaO loading showed a higher yield of methyl ester than 7 wt% because content of CaO that exceeds a certain optimal level results in a higher bulk density, which generated droplets with larger sizes, resulting in less total surface area of the droplets. In addition, a higher content of CaO (7%wt) absorbed and traps more methyl ester in the CaO. The 3-phase system with an initial 6:1 methanol ratio showed higher of methyl ester yield than the experiment without the initial 6:1 methanol ratio when the experiment was continued until 120 min. The initial volume of triolein (80, 100, 200 ml) and spraying distance (10,20 cm) was not observed to have significant effect on the methyl ester yield. However, the small difference in yield of the initial volume of triolein came from the liquid circulating characteristic and catalyst mixing. The observed methyl ester in the circulation tube was about 3.4 wt% comparing the yield before entering the circulation tube as 19.44 wt% at 60 min of reaction time. It was confirmed that the reaction still occurs in the tube. The time-totalized surface area was the key factor affecting the methyl ester yield.

**Chapter 4 Reaction mechanism** estimates droplet residence time during falling in the 3-phase reactor, which was then used to calculate the actual mass of methanol in triolein mixture by gas absorption rate in spherical liquid droplet model. The kinetic model is based on adsorption isotherm, which was derived and proposed for 3 cases of reaction rate. The modeling of the transesterification in the 3-phase reactor was considered and proposed. The methanol balance in triolein mixture with reaction was used to simulate the actual mass of methanol remaining in the mixture after the reaction and methanol consumed rate equation, both of which are required to estimate methyl ester yield. The influence of time totalized surface area for the three flow rates of triolein (2.5, 6.0, and 9.0 ml/min) on the methyl ester mole was examined again. Regarding the effectiveness evaluation of the 3-phase reactor in comparing directly and conveniently with other research, the reaction rate of the transesterification was similarly evaluated by assuming that the overall reaction rate was obeyed as pseudo-first-order kinetics. Therefore, the rate of transesterification and kinetics parameters were determined and compared with other works. The results were summarized as follows:

The residence time of droplets in the reactor directly depends on the flow rates of triolein, which relates to the droplet diameter. The droplet's residence time of 2.5, 6.0, and 9.0 ml/min were estimated as 0.98, 0.98 and 0.32 s, respectively. The remaining methanol and methyl ester produced during transesterification was determined by doing the methanol balance around the methanol reaction inside the reactor. The methanol reaction rate constant was appropriately estimated as $4.95 \ x \ 10^{-3} \ min^{-1}$.
This methanol rate constant estimated was used to calculate the mole of methyl ester produced, which moderately agreed with the experiment results. Both methyl ester from the calculation and the experiment shows in good agreement and are strongly dependent on the time totalized droplets' surface area. It was found that rate constant, $k$ and activity energy, $E_a$ were 1.21 - 3.7x10$^{-2}$ min$^{-1}$ and 36.1 kJ mol$^{-1}$, respectively, which the higher $k$ and lower $E_a$ when compared other works supports the conclusion that our 3-phase setup enhanced the reaction.

**Chapter 5 Conclusions** summarizes the findings obtained from this study and provides recommendations for prospects. It was confirmed that 3-phase reactor enhances the transesterification especially during the beginning of the reaction in case of without methanol at the starting and the time-totalized surface area was the key factor affecting the methyl ester yield.