CHAPTER I

INTRODUCTION

1.1. Background

The demand for biodiesel, the fatty acid-alcohol esters derived from, typically, triglyceride in vegetable or animal oils/fats and methanol or ethanol, as an alternative and potentially sustainably renewable fuel for diesel engines, is increasing steadily due to economic and environmental issues. These include increases in the crude oil price, as well as the dwindling but limited supplies of the non-renewable conventional diesel. Before the 1990s, the relatively high price of biodiesel that was mainly produced from virgin or refined vegetable oils, was the most serious obstacle to its development and its use could not economically compete against conventional diesel [1]. However, due to the relatively high price of conventional diesel at present, biodiesel produced from both refined and used vegetable or animal oils/fats became competitive [2]. On the other hand, the global warming issue makes biodiesel attractive as it has a closed carbon cycle and can effectively reduce the CO_2 emission burden from transportation and industry. For instance, biodiesel decreases the net CO_2 emission by 78% compared with conventional [3, 4]. Furthermore, biodiesel emits a lower level of CO, SO_x and unburned hydrocarbons after combustion than that from conventional diesel [5]. Finally, biodiesel has the potential to be a sustainable renewable resource. Therefore, research on biodiesel production technologies has received continuous attention globally.

Conventional biodiesel production process using either strong acidic or basic catalyst is performed at 30 - 60 °C and atmospheric pressure. This process has some disadvantages such as; long reaction time (over 30 min), wastewater treatment needed, soap and low quality crude glycerol by-products, and some non-recoverable chemicals needed [6]. The novel biodiesel production in supercritical methanol has advantages such as short reaction time (lower than 30 min) and less wastewater produced. Moreover, the supercritical methanol process does not require any additional chemicals, and the by-product is high purity glycerol. The more detailed advantages of the biodiesel production in supercritical methanol were discovered recently. For example, it was found that free fatty acids, that posed some problems in conventional method, did not affect the supercritical methanol process. Also, the supercritical methanol is easier to improve than conventional process because the overall configuration is not complex [6, 7].

The improvement of biodiesel production in supercritical methanol has been reported continuously. Firstly, the use of carbon dioxide and propane was introduced by Chinese researchers in order to reduce temperature, pressure and methanol to vegetable oil molar ratio at the optimal condition [8]. Secondly, the continuous production of biodiesel via transesterification in supercritical methanol in a lab-scale reactor was successfully attempted in Thailand [9], Japan [10] and China [11]. Thirdly, many useful data were reported, such as an axial dispersion number in tubular reactor for biodiesel production in supercritical methanol [12], heat recovery process for biodiesel production in supercritical methanol [13], and vapor-liquid phase equilibria of the major components such as vegetable oil, methyl esters and glycerol with supercritical methanol [14-19]. The details of reports are summarized in the literature review section.

Data from lab-scale reactor successfully attempted in our laboratory were used for constructing a scale-up reactor. As we tested the reactor, it was found that the high viscosity of vegetable oil posed a problem on the pumping system. This problem was solved by an addition of some co-solvents such as THF and hexane [20]. However, the methyl ester content in biodiesel obtained from this scale-up reactor was lower than that from the lab-scale reactor.

1.2. Objectives

1.2.1. To investigate effects of co-solvents on methyl ester content in biodiesel produced from transesterification of vegetable oil in supercritical methanol.

1.2.2. To develop residence time estimation method for continuous production of biodiesel in supercritical methanol by the Equation of state.

1.2.3. To develop a biodiesel process using supercritical alcohol that produces biodiesel that conforms to the standard biodiesel specification of Thailand at approximately 10 liters per day.

1.3. Scope of dissertation

1.3.1. Effect of co-solvents (THF and hexane) employed to reduce viscosity is investigated in 250-mL and 5.5-mL batch reactors by 2^k factorial design.

1.3.2. Residence time estimation procedure based on the inconstant fluid properties is developed.

1.3.3. Additional effects such as interference of co-solvents, thermal degradation of unsaturated fatty acids, contaminants in crude vegetable oil, pressure, delayed quenching time and development of compressibility of mixture on ME content are studied and used to improve the biodiesel production with supercritical alcohol process.