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## Supercritical carbon dioxide-mediated esterification in a microfluidic reactor

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### ABSTRACT

The immiscibility of vegetable oil and alcohol during the initial step in biodiesel synthesis has slowed down the process resulting to increase production costs. Thus, process intensification techniques that would enhance mixing or molecular interactions of the reactants, and enable short reaction time should be carried out in order to increase yield and minimize costs. We proposed coupling of two process intensification schemes in enhancing molecular interactions, *i.e.* the use of supercritical carbon dioxide as a solvent and microfluidic device, as applied to esterification of oleic acid (OA) with methanol (MeOH). We found this superior over the commonly applied microwave. Hence, we further explored the influences of reaction temperature, OA-to-MeOH molar ratio, residence time, water contents, pressure and catalyst addition on the oleic acid methyl ester (OAME) yield. Results showed that at temperature range of 60 to 120 °C and pressure of 10 MPa, the esterification reaction proceeds even without any catalyst in less than 1 min. Addition of relatively small amount of catalyst (0.1 wt% H<sub>2</sub>SO<sub>4</sub>) dramatically increased the yield 4-fold to 90%. Recirculation of the product even without a catalyst significantly increased yield. The experimental analysis confirms the applicability potential of the microfluidic reactor in the non-catalytic biodiesel synthesis.

### 1. Introduction

With the impending fossil fuel depletion, massive researches have focused in developing sustainable alternatives such as biodiesel (BDF) for internal combustion engines. BDF has attracted intense attention as it is a renewable, biodegradable and carbon neutral alternative for petroleum [1–3]. Recently, waste and non-edible oils were evaluated as suitable feedstock for BDF synthesis, which would enable BDF pricing market competitive [4–6]. Since waste oils contain significant amounts of free fatty acids, esterification process has been developed as another route for BDF synthesis. In this process, fatty acids react with alcohol to produce alkyl esters in the presence of acid catalyst. The fatty acids and alcohol are immiscible, hence there is a high mass transfer resistance (or low collision coefficient) between the two reacting molecules at the beginning of the esterification process. This is heightened as homogeneous acids, *i.e.* sulfuric acid, intended to catalyze the reaction preferentially co-locates in the alcohol phase [7,8]. As a result, the overall reaction rate is slowed down resulting to higher production costs [9]. With such a challenge, process technologies which are energy efficient, environment-friendly and with low residence time and higher

molecular collision should be carried out [10].

To address the immiscibility problems, we proposed the use of environmentally benign supercritical carbon dioxide (hereby abbreviated as SCCO<sub>2</sub>) as a solvent for reaction. Both reactants, methanol (hereby abbreviated as MeOH) and oleic acid (hereby abbreviated as OA), are known to be soluble in SCCO<sub>2</sub> even at low pressure conditions [11,12]. Besides, unlike the commonly used organic solvent such as hexane, separation of the products can be easily carried out by simple depressurization steps. For enhancement of reaction rates, two of the promising process intensification techniques related to improving molecular collision and interactions are microwave irradiation (MW) and the use of microfluidic device. MW has attracted interest in accelerating reactions since heating is produced within the system by the molecular motion of absorbing polar molecules. This is known as the reversed heating phenomena, which increases the chance for reacting molecules to collide and interact [13,14]. The collision of molecules are also thought to contribute to the reaction, and is considered as non-thermal effect of MW irradiation [15]. On the other hand, a microfluidic reactor has an internal diameter of a few millimeters and which allow for continuous-flow processes. Processing in microscale enhances heat and

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molecular collision due to short diffusion paths and large surface areas, thus, making it easy to operate and control even with sudden temperature changes [16]. With these characteristics, the use of a microfluidic reactors could bring about development of more energy efficient and cost-effective processes. For industrial applications, instead of scaling up, numbering up of microfluidic reactors to meet the required throughput can simplify the rigorous conventional process design methodology. These devices have been applied in the direct synthesis of hydrogen peroxide from hydrogen and oxygen [17]; lignin oxidation [18]; and in the direct conversion of syngas to dimethyl ether [19] at a safer, cleaner and more efficient way. Furthermore, coupling these devices with supercritical fluid (SCF) further intensifies the process since SCF can easily penetrate the sample matrix and induce miscibility [20]. Thus, performing supercritical fluid-based processes in a microfluidic device has a great potential for process intensification.

In this work, preliminary experiments were carried out to compare the application of two process intensification technologies, namely MW irradiation and microfluidic reactor for the synthesis of oleic acid methyl ester (OAME) from OA and MeOH. The microfluidic device was complemented with the use of environmentally benign SCCO<sub>2</sub> to further intensify the process. Due to the superiority of the latter approach, various process variables were investigated to increase the OAME yield.

## 2. Experimental methodology

### 2.1. Experimental set-up

Batch MW irradiation experiments for the synthesis of OAME were carried out using a  $\mu$ Reactor EX (Shikoku Instrumentation Co., Ltd.) equipped with a fiber optic thermometer for temperature measurement and a condenser for MeOH reflux were attached as shown in the schematic diagram (Fig. 1). It is capable of generating up to 1000 W of MW power.

Flow reactions were performed using the microfluidic device shown in Fig. 2. This apparatus consisted of a carbon dioxide (CO<sub>2</sub>) pump (Teledyne, ISCO, Japan), UFLC pump (LC-20AD, Shimadzu, Japan), micro device (SUS316L, Kobe Steel Co., Japan) and an oven. Fig. 3 shows the schematic diagram of the microfluidic reactor used in the experiments. The internal diameter of the microfluidic device is 0.9 mm while the length is 500 mm. The cross-section has a semi-circle shape. It is housed inside a stainless steel casing with dimensions of 200 × 100 mm, and can be operated at a maximum pressure of 20 MPa.

### 2.2. Experiments for non-catalytic biodiesel synthesis

For MW experiments, oleic acid (Wako, Osaka, Japan) and methanol (Wako, Osaka, Japan) at 1:4 ratio were placed in a 100-mL-three-necked flask. The flask was placed inside the cavity of the MW apparatus, attached to the fiber optic thermometer and condenser.

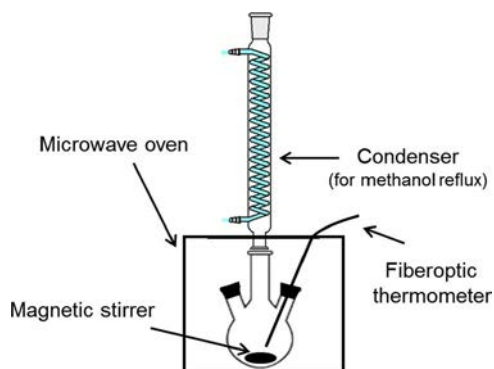


Fig. 1. Schematic diagram of microwave-experimental apparatus.

Stirring was provided using magnetic bar. After setting up the apparatus, the mixture was stirred for a few minutes, then MW was irradiated at 200 W for the specified duration. The reaction temperature was maintained between 60 and 70 °C. After each reaction, the mixture was cooled down to room temperature and collected for GC-FID analysis.

Similarly, a mixture of the OA and MeOH prepared at specified molar ratios were used for microfluidic reactions. The mixture was pumped into the reactor at a constant flowrate (0.02–0.1 mL/min) and with the same flowrate as CO<sub>2</sub>. Experiments on the synthesis of OAME was carried out at a pressure of 10 MPa and temperatures of 60 to 120 °C. Samples were immediately collected at the outlet and also subjected to GC-FID analysis.

### 2.3. GC-FID analysis of reaction products

Gas chromatographic method with flame ionization detection (GC-FID) was used to analyze the reaction products, especially for the presence of OAME. Components separation was carried out in a capillary column CP-SIL 8CB-MS (GL Sciences, Tokyo, Japan). Hexane (Wako, Osaka, Japan) was used as a solvent, and 2, 6-dimethylnaphthalene (Wako, Osaka, Japan) was used as an internal standard. Analysis was operated under programmed temperature conditions: 40 °C for 10 min, increased by 30 °C/min until 250 °C, maintained for 1 min then increased by 10 °C/min until 320 °C was reached then maintained at 10 min (detector and injector temperatures of 300 and 270 °C, respectively), injection volume of 0.2  $\mu$ L and helium as carrier gas (150 kPa). The yield was calculated following Eq. (1):

$$\text{Yield (\%)} = \frac{\text{OAME concentration } \left(\frac{\text{mol}}{\text{L}}\right) \times 100}{\text{OA feed concentration (mol/L)}} \quad (1)$$

## 3. Results and discussion

### 3.1. Preliminary studies on the non-catalytic biodiesel synthesis using MW and SCCO<sub>2</sub>-microfluidic reactor

We initially explored the intensification of non-catalytic biodiesel synthesis employing batch reaction through MW heating. We hypothesized that inherent internal and localized heating facilitate esterification reaction in a shorter reaction time. MeOH, being a polar solvent, acts as the microwave absorber system. First, a 5-min non-catalytic esterification reaction was performed, which resulted to a very poor yield of 0.62 wt% (Fig. 4–1). In order to improve the yield, we added a small amount of sulfuric acid (0.1 wt%). Yields were 22.1% at 60 °C and 30 s (Fig. 4–2) and 36% at 70 °C and 60 s (Fig. 4–3) at an OA-to-MeOH ratio of 1:4. Indeed, both the addition of the acid catalyst and the increase in temperature has increased the yield but still remains relatively low.

Due to the limitations in our reactor for high-temperature experiments, we benchmarked our results with that of Melo-Junior et al. [21]. They carried out the reactions at elevated temperatures since esterification is an endothermic process and increasing temperatures could drive the equilibrium towards product formation [22]. At 150 °C, their uncatalyzed yield amounted to about 3% (Fig. 4–4). Further increasing to 200 °C yielded 25% and 60% at reaction times of 5 and 30 min (Fig. 4–5 and 4–6), respectively. Because of the relatively low yield obtained using MW-assisted batch reaction and we cannot elevate reaction temperatures, we decided to explore the use of a microfluidic device which would enable us to carry out a continuous process at elevated temperatures.

Using an OA: MeOH ratio of 1:4 and 60 s at 120 °C, the yield already reached 19% (Fig. 4–7). As in the majority of researches which compared continuous-flow microfluidic device with batch processes, the continuous process outperforms the batch process under specified

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