

Biodiesel Production from Palm Oil Using a Downflow Bubble Column Reactor

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Abstract: The objectives of this research were to develop a biodiesel production process from palm oil using a downflow bubble column reactor and study the effects of reaction temperature, methanol-to-oil molar ratio and catalyst (NaOH) concentration. The conversion of triglycerides to methyl esters was determined by nuclear magnetic resonance spectroscopy. The optimum condition for transesterification of palm oil and methanol catalyzed by NaOH was found to be: methanol-to-oil ratio of 6:1, NaOH concentration of 0.5 wt.% and reaction temperature of 50 °C. At the optimum condition, the conversion of 95.7% was achieved. A mathematical model was developed based on three-steps first-order kinetics with a mass transfer factor to describe the experimental results. It was found that the developed mathematical model well described the production of biodiesel using a downflow bubble column reactor.

Key words: Palm oil, transesterification, biodiesel, mathematical model, bubble column reactor

INTRODUCTION

World energy demand has climbed up steadily in the recent decades and fossil fuel is still the main source of energy for transportation. Prolonged political instability, particularly in major oil-producing countries, global warming and increasing environmental problems prompt many countries to rely less on the fossil fuel and more on renewable and environmental friendly types of energy. In Southeast Asian countries, biodiesel from palm oil constituent a significant portion of the substituted fuel (Mukherjee and Sovacool, 2014). Converting palm oil to biodiesel not only reduces the imported energy cost but also helps to stabilize the price of palm oil.

One challenge in producing biodiesel by transesterification of palm-oil with alcohol is to overcome the mass transfer step which is normally the slow and rate-limiting step (Aniya *et al.*, 2015). In practice, this is done by using powerful agitation in stirred tank reactors to create micro-mixing where the reaction can occur readily with minimum mass transfer resistance (Orgill *et al.*, 2013). In this research, we have explored the potential of a Downflow Bubble Column Reactor (DBCR) for producing biodiesel by transesterification of palm oil with methanol. DBCR was pioneered by as a type of gas-liquid contactors having no moving part and low energy consumption to give the same or even better level of mixing intensity than in stirred-tank reactors. Bubble

column reactors also provide more degree of freedom for process operation and control (Kantarci *et al.*, 2005). They have been used successfully in gas-liquid processes including biodiesel production process (Nabetani *et al.*, 2012; Wulandani *et al.*, 2015; McClure *et al.*, 2015). However, most of the applications of bubble column reactors to biodiesel production in literature require alcohol in the vapor state in order to form bubbles needed for efficient mixing. This consumes high energy. One promising application of bubble column reactors was the study by Alenezi *et al.* (2013) who produced biodiesel using 2.5 L downflow liquid contactor reactor. The conversion of 96.5% was obtained within 2.5 min at 40°C. The liquid alcohol was used to create sufficient mixing. However, the size of the reactor was very small. In this study therefore we investigated the transesterification of palm oil with methanol using a 14-L DBCR. The effects of methanol-to-oil molar ratio, reaction temperature and catalyst (NaOH) concentration were studied in order to find an optimally operational condition. A mathematical model was developed based on three-steps first-order kinetics with a mass transfer factor to describe the experimental results.

MATERIALS AND METHODS

Experimental: Food-grade refined palm oil (with a major fatty acid composition of palmitic 37%, oleic 46% and

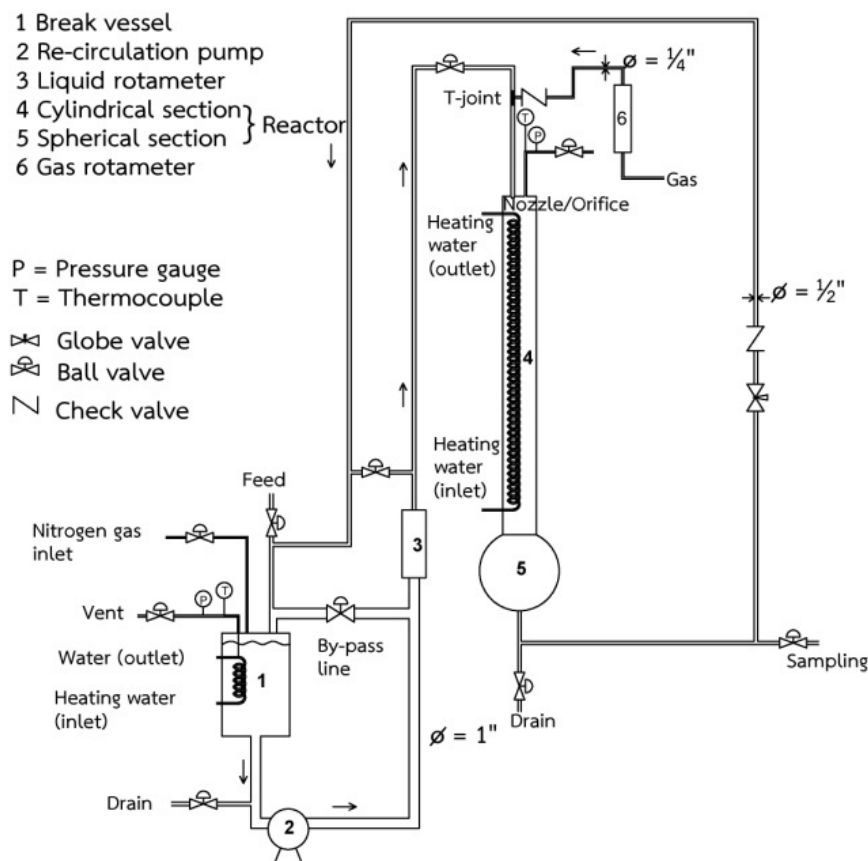


Fig. 1: Schematic diagram of 14-L DBCR

linoleic 11% acids) was purchased from Morakot Industries Co., Ltd (Thailand). Methanol (99.9%) and NaOH (>99%) were used. Chloroform-d (99.8%) was purchased from Merck for Mukherjee and Sovacool (2014) H NMR analysis.

The schematic diagram of DBCR is shown in Fig. 1. The break vessel and reactor column (1 m height) were made of quartz. The column consisted of 2 main parts: cylindrical and spherical sections connected by flanges and o-ring gaskets. The inside and outside diameters of the cylindrical column were 50 and 80 mm, respectively. Heating/cooling water was supplied to the outside layer of the column in order to control the reaction temperature. A spherical section had a volume of 5 L and diameter of 106 mm. This section was made to reduce velocity of liquid in the column. A 7-L break vessel was designed and used to prepare reagents (oil and NaOH/methanol solution) before entering into the column. Heating water was supplied to the break vessel in a similar way to the reactor column. Other parts including valves and pipes were made of stainless steel. In the upper part of the column and break vessel, 1/2 inch pipes were installed for

inlet liquid, 1/4 inch pipes for vent line (vent out the air during start-up). They were also equipped with pressure gauges and thermocouples. A centrifugal pump was used to circulate the liquid from break vessel through the reactor column on a continuous recycle loop at the flow rate of 0.08 m³/h.

The experiments started by filling palm oil into the break vessel and heating the oil to required reaction temperatures. The heated oil was then fed into the column. Next, NaOH/methanol solution was added to the break vessel. The reaction time started when the column was fully filled with the mixture of NaOH/methanol and oil solution. Small liquid bubbles were created throughout the cylindrical section of the reactor column to facilitate mass transfer across oil and methanol phases. The experimental range in this study included the reaction temperature (40-50°C), methanol-to-oil molar ratio (3:1-8:1) and the NaOH concentration (0-1 wt.% of oil).

Analysis of methyl esters: Samples were taken from the sampling point at the bottom of the reactor column. The conversion of triglycerides to methyl esters was

determined using proton nuclear magnetic resonance (¹H NMR) spectroscopy (Bruker 300 MHz) with chloroform-d as a solvent. The calculation was based on Eq. 1 (Silva *et al.*, 2015):

$$\%C_{ME} = 100X \left(\frac{2I_{CH3}}{3I_{CH2}} \right) \quad (1)$$

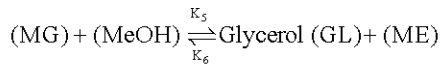
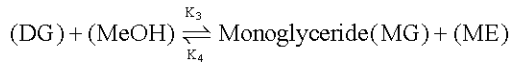
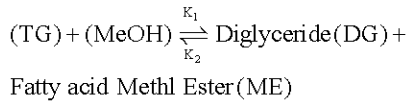
Where:

$\%C_{ME}$ = Percentage of conversion to methyl esters

I_{CH3} = Integral of the signal at chemical shift of 3.66 ppm representing the CH₃ of the methoxy group in methyl esters

I_{CH2} = Integral of the signal at 2.27 ppm representing the CH₂ of the ester

Kinetic modeling: It is widely accepted that transesterification of Triglycerides (TG) and methanol (MeOH) obeys the following reaction steps:



Some researchers have developed slightly different versions of kinetic model for transesterification of triglycerides with alcohol. However the most widely used model in describing the reaction is that by Yusuff *et al.* (2014) and it was modified to take into account the non-ideal mixing (thus significant mass transfer resistance) by Promraksa as follows:

$$\frac{dC_{TG}}{dt} = -k_1' C_{TG} C_{MeOH} + k_2 C_{DG} C_{ME} \quad (2)$$

$$\frac{dC_{DG}}{dt} = k_1' C_{TG} C_{MeOH} - k_2 C_{DG} C_{ME} - k_3 C_{DG} C_{MeOH} + k_4 C_{MG} C_{ME} \quad (3)$$

$$\frac{dC_{MG}}{dt} = k_3 C_{DG} C_{MeOH} - k_4 C_{MG} C_{ME} - k_5 C_{MG} C_{MeOH} + k_6 C_{GL} C_{ME} \quad (4)$$

$$\frac{dC_{GL}}{dt} = k_5 C_{MG} C_{MeOH} - k_6 C_{GL} C_{ME} \quad (5)$$

$$\frac{dC_{ME}}{dt} = k_1' C_{TG} C_{MeOH} - k_2 C_{DG} C_{ME} + k_3 C_{DG} C_{MeOH} - k_4 C_{MG} C_{ME} + k_5 C_{MG} C_{MeOH} - k_6 C_{GL} C_{ME} \quad (6)$$

$$\frac{dC_{MeOH}}{dt} = -k_1' C_{TG} C_{MeOH} + k_2 C_{DG} C_{ME} - k_3 C_{DG} C_{MeOH} + k_4 C_{MG} C_{ME} - k_5 C_{MG} C_{MeOH} + k_6 C_{GL} C_{ME} \quad (7)$$

C_{TG} , C_{DG} , C_{MG} , C_{ME} , C_{MeOH} , C_{GL} are the concentrations of triglycerides, diglycerides, monoglycerides, fatty acid methyl esters, methanol and glycerol, respectively. k_1 - k_6 are pseudo-first order rate constants according to the reaction steps shown above. α is mass transfer factor which approaches 1 when mass transfer is sufficiently high and mass transfer resistance is negligible. In practice this model needs further simplification in order to be more tractable because there are still too many parameters (6 rate constants and one mass transfer factor) to be estimated simultaneously. Since in three reaction steps, the same type of reaction occurs in series until three fatty acids in triglyceride are completely converted to three molecules of fatty acid methyl esters and they are catalyzed by the same concentration of NaOH simultaneously. Hence, it is reasonable to assume that the ratio of rate constant (β) k_2/k_1 , k_4/k_3 and k_6/k_5 are approximately of the same order of magnitude. With this assumption we then needed only to estimate k_1 , k_3 , k_5 , α and β . Therefore, we obtained the following simplified equations from Eq. 2-7:

$$\frac{dC_{TG}}{dt} = -k_1' (C_{TG} C_{MeOH} - \beta C_{DG} C_{ME}) \quad (8)$$

$$\frac{dC_{DG}}{dt} = -\frac{dC_{TG}}{dt} - k_3 (C_{DG} C_{MeOH} - \beta C_{MG} C_{ME}) \quad (9)$$

$$\frac{dC_{MG}}{dt} = k_3 (C_{DG} C_{MeOH} - \beta C_{MG} C_{ME}) - \frac{dC_{GL}}{dt} \quad (10)$$

$$\frac{dC_{GL}}{dt} = k_5 (C_{MG} C_{MeOH} - \beta C_{GL} C_{ME}) \quad (11)$$

$$\frac{dC_{ME}}{dt} = -\frac{dC_{TG}}{dt} + k_3 (C_{DG} C_{MeOH} - \frac{C_{MG} C_{ME}}{\beta}) + k_5 (C_{MG} C_{MeOH} - \frac{C_{GL} C_{ME}}{\beta}) \quad (12)$$

$$\frac{dC_{MeOH}}{dt} = \frac{dC_{TG}}{dt} - k_3 (C_{DG} C_{MeOH} - \frac{C_{MG} C_{ME}}{\beta}) - k_5 (C_{MG} C_{MeOH} - \frac{C_{GL} C_{ME}}{\beta}) \quad (13)$$

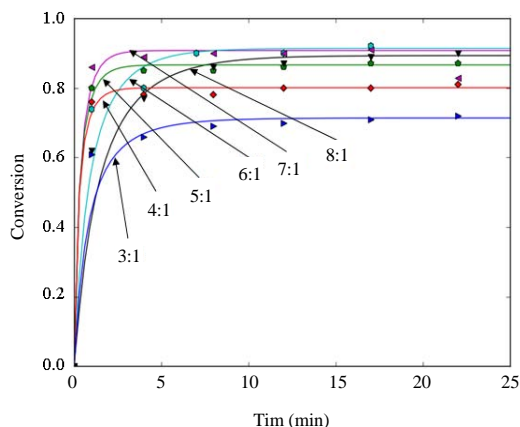


Fig. 2: The predicted and experimental conversions at various methanol-to-oil ratio at 40°C, NaOH 0.5 wt. %

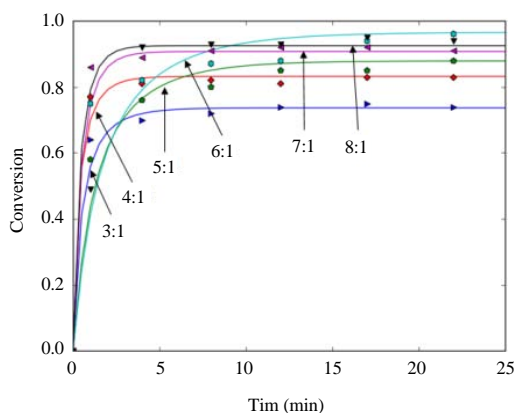


Fig. 3: The predicted and experimental conversions at various methanol-to-oil ratio at 50°C, NaOH 0.5 wt. %

This system of ordinary differential equations with the corresponding initial conditions was solved numerically using scipy module and a python program. It was then used to fit the experimental results and estimate the model parameters. We defined and fixed k_3 and k_5 where their values were taken from Giulio Santori *et al.* (2012) who reported that the values of k_3 and k_5 (alcohol-to-oil molar ratio 6:1, reaction temperature 55°C) of 11 and 0.3 l/mol min, respectively.

RESULTS AND DISCUSSION

Effect of methanol-to-oil molar ratio: The stoichiometry of the transesterification reaction requires alcohol-to-oil molar ratio of 3:1 to complete the reaction. However, most researchers found that more alcohol was required to drive

the reaction toward ester products (Keera *et al.*, 2011). In this research, methanol-to-oil molar ratio was varied from 3:1-8:1 and the effect of this variable on conversion is shown in Table 1. The parameters (k'_1 , β) and simulated conversions were reported and compared with the conversions obtained from the experiments. The values of simulated conversions were found to be closed to the experimental conversions, suggesting that the developed model can fit very well to experimental data in this study. Figure 2 and 3 show the effect of methanol-to-oil molar ratio on conversions at 40 and 50°C, respectively. We found that at 40°C, the equilibrium conversion increased significantly with methanol-to-oil molar ratio from 3:1-5:1 and was slightly different when the ratio was further increased to 8:1. Similarly, at 50°C the equilibrium conversion increased with methanol-to-oil molar ratio from 3:1-6:1 and reduced with the ratio of 7:1-8:1. This is due to the excess amount of methanol which increases the solubility between glycerol and ester phases. When more glycerol remains in the ester phase, it drives the equilibrium backward (Talebian *et al.*, 2013; Farooq *et al.*, 2015; Choedkiatsakul *et al.*, 2014). As a result, the equilibrium conversion decreases. The maximum conversion (95.7%) was obtained at the methanol-to-oil ratio of 6:1 at 50°C. At 40°C, the highest conversion was 91.7% at the ratio of 6:1. As can be seen from these values, the advantage of using DBCR for biodiesel production is that it requires small molar ratio of methanol-to-oil (6:1). Previous researchers have reported larger molar ratio of methanol-to-oil for optimum production of biodiesel, i.e., 9:1 with 0.75 wt% NaOH at 55°C (Sinha *et al.*, 2008), 10.44:1 with 1.22 wt% KOH at 66.8°C (Verma and Sharma, 2016) and 11.06:1 with 1.43 wt.% at 56.6°C (Dwivedi and Sharma, 2015).

When comparing the conversions at 40°C with those at 50°C, increasing the reaction temperature did not give different conversions significantly. Most conversions were >90% under optimum conditions. Therefore, biodiesel production can be carried out with DBCR at low temperature (e.g., 40°C). This could save energy and it is an advantage of DBCR.

Effect of NaOH concentration: Table 2 shows the parameters (k'_1 , β) and simulated conversions in comparison with the conversions obtained from the experiment. The values of simulated conversions were found to be closed to the experimental conversions suggesting that the developed model can fit very well to the production of biodiesel with DBCR.

Figure 4 and 5 show the effect of NaOH concentration (0-1.0 wt.%) on conversions at 40°C and 50°C, respectively. As expected, very small amount of biodiesel was produced with 0% NaOH. Incomplete transesterification was observed with NaOH concentrations of 0.1 and 0.3 wt.%. When NaOH

Table 1: Parameters of the kinetic model and comparison in conversions of different methanol-to-oil molar ratio at 40 and 50°C, NaOH 0.5 wt.%

MeOH:Oil	$k_1' = k_1\alpha$	β	Simulated conversion (%)	Experimental conversion (%)
At 40°C				
3:1	1.5	0.23	71	71.9
4:1	4.0	0.28	80	81.3
5:1	3.0	0.28	87	87.3
6:1	0.9	0.25	91	91.7
7:1	2.0	0.35	90	90.9
8:1	0.4	0.50	89	89.7
At 50°C				
3:1	2.5	0.19	73	74.3
4:1	3.0	0.22	83	83.3
5:1	0.7	0.25	87	87.7
6:1	0.5	0.10	96	95.7
7:1	1.5	0.35	91	91.3
8:1	1.5	0.35	93	94.3

Table 2: Parameters of the kinetic model and the comparison in conversions of different NaOH concentrations at 40 and 50°C

NaOH (wt.%)	$k_1' = k_1\alpha$	β	Simulated conversion (%)	Experimental conversion (%)
At 40°C, MeOH:Oil = 5:1				
0	0.02	380.00	4.0	4.0
0.1	0.10	3.50	42.0	42.1
0.3	0.80	0.55	77.0	77.2
0.5	2.00	0.28	87.0	87.3
0.7	1.00	0.20	90.0	90.5
1	0.80	0.08	96.0	96.2
At 50°C, MeOH:Oil = 6:1				
0	0.05	300.000	4.5	4.8
0.1	0.07	2.500	54.0	53.8
0.3	0.50	0.550	83.0	82.6
0.5	0.50	0.125	94.0	95.7
0.7	1.50	0.160	95.0	94.8
1	5.00	0.120	97.0	96.2

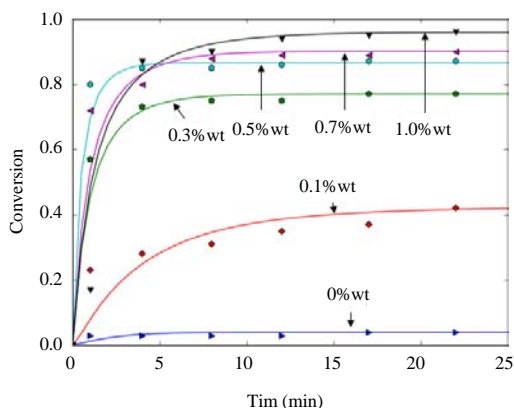


Fig. 4: The predicted and experimental conversions at various NaOH concentrations at 40°C and methanol-to-oil ratio of 5:1

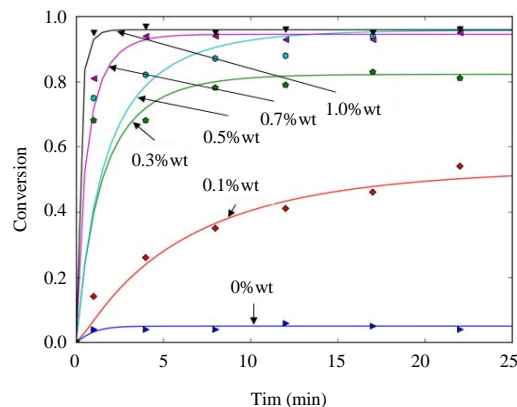


Fig. 5: The predicted and experimental conversions at various NaOH concentrations at 50°C and methanol-to-oil ratio of 6:1

concentration was increased from 0.1-0.3 wt.%, the conversions considerably increased. However, after 0.5 wt.%, conversion increased slightly. The NaOH concentration of 1 wt.% was found to have detrimental effect on quality of biodiesel. No clear separation between ester and glycerol-rich layers was observed during settling process. Moreover, more soap was found in the process of washing biodiesel with warm water. This is due

to that excess amount of alkali catalyst promotes more saponification (Keera *et al.*, 2011; Choedkiatsakul *et al.*, 2014; Dharma *et al.*, 2016; Chuah *et al.*, 2015).

CONCLUSION

The Downflow Bubble Column Reactor (DBCR) is a promising reactor that can be used to produce biodiesel

successfully without any stirrer. The DBCR required low methanol-to-oil molar ratio (e.g., 6:1) and low reaction temperature (e.g., 40°C) in order to provide conversion satisfactorily.

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