Effect of nitrogen bubble for biodiesel production from used cooking oil

N Wiriya¹, R Kokoo², K Wichianwat¹, P Jiamrittiwong¹,³, T Srisurat¹∗

¹Faculty of Science, Energy and Environment, King Mongkut’s University of Technology North Bangkok, Rayong Campus, Nonglalok, Bankhai, Rayong 21120, Thailand
²Department of Chemical Engineering Faculty of Engineering, King Mongkut’s University of Technology North Bangkok, Bangkok 10800, Thailand
³Research and Development Center for Chemical Engineering Unit Operation and Catalyst Design (RCC), STRI Building, King Mongkut’s University of Technology North Bangkok, Bangkok 10800, Thailand

*thanarak.s@sciie.kmutnb.ac.th

Abstract Biodiesel is alternative energy produced using natural raw materials. The famous reaction used to produce biodiesel is transesterification. In the commercial scale, the mixing process is the crucial step for transesterification. Electric stirring motor used to mix raw materials in the conventional process consumes a lot of energy. This results in high production cost. In this research, bubbling technique was used to replace the electric stirring motor. Waste nitrogen gas obtained from the gas separation industry was fed to the bubble column filled with used sunflower oil and other reactants. Microbubbles of nitrogen gas were generated in the column. The results showed that the product yields obtained from the stirring technique is higher than the bubbling technique by 2.63% at the same operating time. In case of energy consumption, the bubbling technique can reduce electricity used by 50% compared with the stirring technique.

1. Introduction
Fossil fuel is mainly used as energy to push our society, economy and basic infrastructure [1]. Most fossil fuel used in transportation. There is a tendency for higher fuel consumption resulting in the shortage of fossil fuel in the next few decades [2]. Nowadays, there is widespread use of renewable energy i.e., solar cell, wind turbine and biodiesel which is produced from vegetable oils via transesterification process as shown in Figure 1. Biodiesel can be used as B100 and blends with petroleum diesel such as B5. However, the production cost of biodiesel is still high because of starting raw materials and operating cost [3].
Mixing agitation technology is often used in chemical industry to perform a variety of reactions including the mixing of solids, liquids, and gases. For biodiesel production, the main performance indicator of mixing process is mixing time, flow patterns, and energy consumption [4]. The production cost of biodiesel can be decreased by reducing the energy consumption of mixing process. Therefore, the new mixing technique using microbubbles was applied to replace the stirring technique. Microbubbles were generated using waste nitrogen gas in the bubble column filled with used sunflower oil and other raw reactants. The process of mixing occurs when microbubbles float up leading to the circulation flow pattern in the bubble column. In this research, biodiesel yields and energy consumption of stirring technique and bubbling technique were studied.

2. Materials and method

The reactant used in this study is the used cooking sunflower oil (UCSO) that was fried for 12 h. [5]. Methanol (99.5%) and NaOH (99.5%) were obtained from Sigma-Aldrich. NaOH was dissolved in methanol (1% by weight of oil) and then mixed with 300 ml of UCSO in the beaker. The UCSO to methanol ratio was set at 1:6. The reaction temperature and pressure were set at 60°C and atmospheric pressure, respectively [6]. The reaction time of both techniques were also set at 60 min.

For stirring technique as shown in figure 2, the magnetic stirrer was used for mixing the reactants and the rotational speed was set at 400 rpm. After 60 min of reaction, biodiesel and glycerol were separated, washed, and dried [7]. Samples were analyzed by the GC-MS (Gas Chromatography Model Agilent Technologies 7890A and Mass Spectrometer Model Agilent Technologies 5975C).

For bubbling technique, the same reactants with stirring technique were used. Operating conditions i.e., temperature, pressure, and reaction time were identical to the stirring technique. Nitrogen gas was fed to glass diffuser equipped at the bottom of the beaker to generate microbubbles. Volume metric
flow rate was set at 0.5 L/min. An overview of the process was shown in figure 3. Before analysed by the GC-MS, samples were separated, washed, and dried [7]. After analyzed by the GC-MS, the percentage yields were calculated using Eq.1

\[ \text{FAME Yield} (\%) = \frac{\text{Weight of FAME}}{\text{Weight of oil used}} \times 100 \]  

(1)

3. Results and discussion
After analysed by the GC-MS, biodiesel obtained from the stirring process has percentage yield of 79.87\%, while bubbling process has percentage yield of 77.24\% (no significant difference in the percentage yield might be assumed). Although the stirring process can produce higher percentage yield by 2.63\% at the same operating time, this process consumes more energy than that of bubbling process described in a later section. The color of biodiesel obtained from both processes was analyzed using the method of ASTM D1500. The color values of biodiesel produced from the stirring process and the bubbling process are 0.5 and 0.5, respectively (Refer figure 4).
Figure 5 shows the chromatogram of the differences between UCSO after 12 h of fried and origin sunflower oil (OSO). Slight difference was observed. This is because the OSO might be oxidized and the composition has been changed.

Figure 5. Comparison biodiesel between used sunflower oil and origin sunflower oil.

Figure 6 shows the chromatogram of the comparison of biodiesel obtained from both processes. There is no difference between these techniques noticed. This can be confirmed by the values listed in table 1, which represents the composition of methyl esters found in the samples. The compositions of methyl esters gained from both techniques are slightly different. This means that the stirring technique might be replaced by the bubbling technique.

Figure 6. Comparison of FAME via Stirrer and Nitrogen mixing process.
Table 1. Composition of fatty acid methyl esters obtained from stirring and bubbling mixing.

| Peak No. | Name                                                                 | Formula       | Stirrer mixing | Nitrogen mixing |
|---------|----------------------------------------------------------------------|---------------|----------------|-----------------|
| 1       | Methylene Chloride                                                   | CH₂Cl₂        | 1.81 %         | 1.57 %          |
| 2       | Cyclohexane, 1,3-dimethyl-, cis-                                     | C₈H₁₆         | 0.62 %         | 0.69 %          |
| 3       | Cyclopentane, 1-ethyl-2-methyl-, cis-                                | C₆H₁₄         | 0.55 %         | 0.71 %          |
| 4       | Cyclohexane, 1,2-dimethyl-, trans-                                   | C₆H₁₄         | 0.54 %         | 0.63 %          |
| 5       | Cyclohexane, 1,4-dimethyl-, trans-                                   | C₆H₁₄         | 0.72 %         | 0.71 %          |
| 6       | 2-Pentanol,1-(2methylene cyclopropyl)-4 methyl-                       | C₈H₁₆         | 0.44 %         | 0.74 %          |
| 7       | 3-Octyne                                                            | C₈H₁₆         | 1.61 %         | 1.32 %          |
| 8       | Cyclohexane, ethyl-                                                 | C₅H₁₀O        | 2.79 %         | 3.00 %          |
| 9       | Ethylbenzene                                                        | C₅H₁₀         | 0.85 %         | 0.81 %          |
| 10      | 9-Hexadecenoic acid, methyl ester, (Z)-                             | C₁₇H₃₂O₂      | 0.59 %         | 0.45 %          |
| 11      | Hexadecanoic acid, methyl ester                                      | C₁₇H₃₂O₂      | 9.95 %         | 9.37 %          |
| 12      | 9,12-Octadecadienoic acid (Z,Z)-, methyl ester                      | C₁₉H₃₄O₂      | 35.79 %        | 35.05 %         |
| 13      | 11-Octadecenoic acid, methyl ester, (Z)-                            | C₁₉H₃₄O₂      | 38.81 %        | 40.08 %         |
| 14      | 10-Octadecenoic acid, methyl ester                                  | C₁₉H₃₄O₂      | 1.56 %         | 1.51 %          |
| 15      | Octadecanoic acid, methyl ester                                      | C₁₉H₃₄O₂      | 3.31 %         | 3.28 %          |

The results listed in table 2 and table 3 show that bubbling technique used less energy than stirring technique by 50%. Although the same hot plate stirrer was used, the bubbling technique was used only heating mode resulting less energy consumption. However, the energy of feed nitrogen is not considered. This is because nitrogen can be supplied from the gas separation processes.

Table 2. Energy used in the Stirrer Mixing process.

| Stirrer Mixing Process | Electric power (Unit) |
|-----------------------|-----------------------|
| Stirring and heating  | 0.5                   |
| Hotplate Stirrer (Wash water) | 0.1 |
| Total Energy consumption | 0.6                  |

Table 3. Energy used in the Nitrogen Mixing process.

| Nitrogen Mixing Process | Electric power (Unit) |
|------------------------|-----------------------|
| Nitrogen gas (Waste 0.5 L/min) | -                    |
| Hotplate Stirrer (Transesterification, Heat) | 0.2 |
| Hotplate Stirrer (Wash water) | 0.1 |
| Total Energy consumption | 0.3                  |

4. Conclusion
Two techniques i.e., stirring and bubbling of mixing process for biodiesel production were studied. The percentage yield obtained from both techniques were slightly difference, while the energy consumption of bubbling technique was less than that of stirring technique by 50%. Therefore, bubbling technique might be used to replace the stirring technique.

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