Alternative Route for Biodiesel Synthesis with Co-Production of Glycerol Carbonate

Zul Ilham1 and Shiro Saka2
1Biomass Energy Lab, Institute of Biological Sciences, Faculty of Science, Universiti Malaya 50603 Kuala Lumpur, Malaysia.
2Graduate School of Energy Science, Kyoto University 606-8501 Kyoto, Japan.

Email: ilham@um.edu.my

Abstract. As an alternative route from the conventional alkali-catalyzed biodiesel production, the supercritical dimethyl carbonate method had been proven to successfully produce biodiesel with the co-production of glycerol carbonate in a one-step and two-step non-catalytic methods. Biodiesel or fatty acid methyl esters (FAME) obtained were high in yield, comparable with supercritical methanol method and satisfy the international standards for use as biodiesel in engines. In this paper, key parameters for the processes such as reaction temperature, pressure, time, molar ratio of dimethyl carbonate to oil, the FAME yield, thermal decomposition, degree of denaturation, tocopherol content, oxidation stability and fuel properties were discussed. The optimized condition for supercritical dimethyl carbonate method is at 300°C/20MPa/20min/42:1 molar ratio of dimethyl carbonate to oil with a satisfactory yield of FAME at 97.4wt%. The extensive approach in this study is very important to complement mathematical model for optimization in the literatures, and to ensure that only high-quality biodiesel could be produced by supercritical dimethyl carbonate method under an optimized condition.

1. Introduction
The search for renewable energy from sustainable biomass resources is an ongoing process in order to offer alternative energy to the world. Among biomass-derived biofuels, biodiesel, chemically known as fatty acid methyl esters (FAME) possesses good properties that make it suitable for use as a direct substitute for petroleum diesel fuel. However, current commercial process requires the transesterification of oils with short-chained alcohols in the presence of alkaline catalyst, which overproduced crude glycerol as a by-product [1].

As biodiesel production is projected to increase in years to come, the by-product crude glycerol could be overproduced and potentially be a new type of waste, if new utilizations are not to be discovered. Apart from creating novel applications of glycerol or converting it into other valuable and useful derivatives [2,3], new production method of biodiesel without the production of glycerol is, therefore, worth to be explored. Previously, our laboratory developed an alternative new process for biodiesel production without producing glycerol by utilizing methyl acetate of carboxylate esters followed by conversion of the obtained fatty acids to FAME and triacetin was demonstrated for use as biodiesel [4]. Subcritical acetic acid treatment to convert oils and fats to fatty acids and triacetin followed by conversion of the obtained fatty acids to FAME in supercritical methanol has also been studied [5].
On this line of study, dimethyl carbonate was selected as a reactant for non-catalytic supercritical treatment and investigated for its potential for biodiesel production [6]. In addition, additional milder process was also studied by incorporating the supercritical dimethyl carbonate into a two-step method [7]. Without producing glycerol, both methods yielded high quality FAME and value-added by-product such as glycerol carbonate [8-10]. This paper presents the key parameters such as reaction temperature, pressure, time, molar ratio of dimethyl carbonate to oil, the FAME yield, thermal decomposition, degree of denaturation, tocopherol content, oxidation stability and fuel properties which are important to complement mathematical model of an optimization study in biodiesel synthesis.

2. Materials and Methods

2.1 Materials
Feedstock being used in this study was rapeseed oil as triglycerides. Free fatty acid content of the feedstock was less than 2wt%. Dimethyl carbonate (Tc=275°C, Pc=4.63MPa) was used as the solvent and glycerol carbonate, various authentic compounds of oleins, methyl esters and fatty acids such as palmitic, stearic, oleic, linoleic and linolenic acids were all obtained from Nacalai Tesque Inc. and Wako Pure Chemical Industries Ltd., Japan, all of which are of the highest purity available.

2.2 Experimental Methods
Results presented in this study were obtained by utilizing the flow-type supercritical biomass conversion system developed previously in our laboratory [11-14]. In the flow-type reaction system as depicted in figure 1, where temperature and pressure could be constantly controlled, tubular reaction vessel made of Hastelloy C-276 was used and the flow capacity of this system was up to 600mL/h. Reaction time was calculated by dividing the volume of the flow-type reaction vessel tube by the volumetric flow-rate at the given conditions (equation 1). The working temperature and pressure employed in this study ranged in 270-400°C and 10-40MPa, respectively, all of which were monitored and controlled by thermocouple and pressure gauge. Details have been described in previous works [11-14].

\[
t = \frac{V}{(Fs (\rho s) + Fo (\rho o))}
\]

\(t\): Reaction time (sec)
\(V\): Tube volume (mL)
\(Fs\): Flow-rate of solvent (mL/sec)
\(Fo\): Flow-rate of oil (mL/sec)
\(\rho s\): Specific density of solvent at reaction condition over initial (g/mL)
\(\rho o\): Specific density of oil at reaction condition over initial (g/mL)

Figure 1. Flow-type supercritical biomass conversion system.
2.3 Fuel Properties Analysis
FAME being produced were also subjected to various tests for fuel properties to comply with international standards [15-17], all of which, were made according to the European Standard Methods [17]. In addition to those, isomerization of FAME and tocopherol content were analyzed by fourier transform infrared spectrometry (Shimadzu, FT-IR 8300) and Standard Methods for the Analysis of Fats, Oils and Related Materials 2.4.10 and 2.5.2 [15], respectively.

3. Results and Discussion

3.1 Effect of temperature and pressure
Temperature and pressure are crucial parameters in supercritical dimethyl carbonate because they allow the solvent properties of dimethyl carbonate to be adjusted. Table 1 shows the effect of temperature variation when reaction pressure is maintained at 20MPa in supercritical dimethyl carbonate. Increase in temperature was seen to accelerate the reaction, especially at conditions beyond the critical point of dimethyl carbonate (Tc=275ºC, Pc=4.63MPa). However, this is changed if the treatment time was prolonged to be 60min due to the thermal decomposition. Previous findings also supported this alleged statement [18].

The influence of reaction pressure on supercritical dimethyl carbonate is also very important as dimethyl carbonate could decompose to carbon dioxide and methanol under low reaction pressure high temperature [19]. The decomposition which happened at low reaction pressure could be observed when dimethyl carbonate was subjected to various temperatures and pressures under supercritical condition, and the mechanism is presented in figure 2. It could be seen that dimethyl carbonate tends to decompose at lower reaction pressures (5MPa and 10MPa), while being stable at higher pressures (20MPa and 40MPa), when treated for 30min. This phenomenon might be related to the cage effect of the solvent, explaining the enhancement of solvent reaction rate at high temperature and high pressure. This phenomenon is especially unique to dimethyl carbonate due to its thermodynamic properties. If high pressure is maintained, dimethyl carbonate could be stable up to 390 ºC [20]. These results presented beforehand showed the importance to describe temperature and pressure together in a specific reaction time for supercritical process optimization [21].

| Reaction Condition and Time (min) | FAME (wt%) | Yield (wt%) |
|----------------------------------|------------|-------------|
|                                  | Palmitate  | Stearate    | Oleate | Linoleate | Linolenate |
| 270ºC/20MPa                      |            |             |        |           |            |
| 15                               | 0.2        | 0.4         | 5.4    | 2.1       | 0.8        | 8.9        |
| 30                               | 3.2        | 1.2         | 34.2   | 4.5       | 5.2        | 48.3       |
| 60                               | 5.8        | 1.3         | 49.6   | 21.6      | 10.4       | 88.7       |
| 300ºC/20MPa                      |            |             |        |           |            |
| 15                               | 4.5        | 1.1         | 54.8   | 19.9      | 9.8        | 90.1       |
| 30                               | 5.6        | 1.3         | 56.9   | 23.6      | 10.2       | 97.6       |
| 60                               | 4.5        | 1.3         | 55.6   | 19.8      | 9.2        | 90.4       |
| 350ºC/20MPa                      |            |             |        |           |            |
| 15                               | 5.2        | 1.2         | 57.4   | 22.8      | 10.3       | 96.9       |
| 30                               | 5.1        | 1.4         | 56.8   | 21.1      | 10.0       | 94.4       |
| 60                               | 5.1        | 1.4         | 54.1   | 18.7      | 7.3        | 86.6       |
| 380ºC/20MPa                      |            |             |        |           |            |
| 15                               | 5.9        | 1.4         | 57.3   | 21.6      | 10.9       | 97.1       |
| 30                               | 6.0        | 1.4         | 57.5   | 21.5      | 10.8       | 93.2       |
| 60                               | 5.8        | 1.2         | 54.7   | 9.7       | 7.2        | 78.6       |
3.2 Effect of solvent to oil molar ratio and reaction time

Stoichiometrically, 3 moles of dimethyl carbonate are required to react with 1 mole of triglycerides. In practice, however, excess amount of dimethyl carbonate is needed to drive the reaction in favor of the product in producing higher yield of FAME. In supercritical dimethyl carbonate, as more dimethyl carbonate is used, higher FAME yield can be obtained, but eventually, a plateau point is reached where more dimethyl carbonate does not help to increase the reaction rate. The point for esterification was found at the molar ratio of 14 (figure 3), while for transesterification, the optimum molar ratio was 42 (figure 4). This result is in good agreement with previous findings which showed similar trend with supercritical methanol [7,11-14]. This suggested that high molar ratio of dimethyl carbonate to oil helps facilitate the flow-type supercritical dimethyl carbonate processes for high yield of FAME. Supercritical dimethyl carbonate is best to be operated at high temperature and high pressure with high molar ratio of dimethyl carbonate to reach the optimum yield in a short reaction time. The ideal range of reaction time for supercritical dimethyl carbonate is determined to be less than 30min in order to prevent potential thermal deterioration of the FAME.

Figure 2. Mechanism of by-products formation at high- and low-pressure condition.

Figure 3. Effect of molar ratio on FAME yield from esterification of supercritical dimethyl carbonate at 300°C/20MPa/20min.
3.3 Potential isomerization of FAME
As shown earlier, prolonged reaction time over 60min at high temperature and pressure, i.e. 350°C/20MPa could have resulted in lower yield due to thermal decomposition. This is mostly due to the decomposition of poly-unsaturated fatty acids (methyl linoleate and methyl linolenate), which are more vulnerable to thermal decomposition than the mono-unsaturated fatty acid (methyl oleate) and saturated ones (methyl palmitate and methyl stearate) [21].

In addition, the isomerization of unsaturated FAME from *cis*-type double bonds to *trans*-type is always possible at this high temperature reaction, contributing to negative effect on cold flow properties of biodiesel, since *trans*-isomer generally has higher melting point than *cis*-isomer. Similar findings have been described in supercritical methanol method [18].

However, at the condition of 300°C/20MPa and preferably lower temperature under similar pressure, all FAME including the poly-unsaturated FAME were found to be stable as exposed to supercritical dimethyl carbonate [21].

3.4 Tocopherol content in preventing oxidation
The tocopherols (α-tocopherol, β-tocopherol and γ-tocopherol), which are natural antioxidants in oils, are also not stable at condition higher in temperature than 300°C at 20MPa. While tocopherols remained almost unchanged at milder temperatures, it decreased drastically at severe temperatures, therefore, deteriorating the oxidation stability of biodiesel (figure 5). These facts have to be observed by all researchers utilizing supercritical technology to ensure that the biodiesel being produced is high in quality and in compliance with the international standards. The optimization should not only focus on the process but also consider on the quality of the biodiesel.

**Figure. 4.** Effect of molar ratio on FAME yield from transesterification of supercritical dimethyl carbonate at 300°C/20MPa/20min.
3.5 Fuel properties of biodiesel from non-catalytic supercritical dimethyl carbonate

In the supercritical process, it should also be noted that the FAME could be reduced in quality, especially if a reaction takes place at a very severe temperature under low reaction pressure, i.e., 380°C/5MPa. Problems in quality could be resulted from the physical and chemical properties of FAME themselves as the major components of biodiesel, as well as minor fuel constituents arising due to poor transesterification condition. This emphasizes the necessity to evaluate the biodiesel properties according to the international standards and to define a supercritical condition by stating both temperature and pressure of the reaction.

In addition, it is crucial to monitor the temperature and pressure due to the marked effect of supercritical condition on the stability of dimethyl carbonate itself. If dimethyl carbonate subjected to high temperature and high pressure below or beyond the real optimum supercritical condition, dimethyl carbonate could decompose to reduce the yield of both FAME and value-added by-products. Therefore, current trend in many recent publications by describing an optimization study based on only minimum sets of experiments and a response surface methodology analysis without acknowledging the whole key parameters by experimental works could not really represent a real optimized condition. To ensure that the FAME produced in supercritical dimethyl carbonate are satisfactory as biodiesel, its fuel properties were also studied. The results were compared with Japanese, EU and US standards. Overall, the FAME from this two-step method satisfied all requirements for international biodiesel standards except for the specification stated for oxidation stability [21]. As mentioned earlier, oxidation stability is an important parameter to prevent deterioration and could be improved with addition of antioxidant or by utilizing oils with lower levels of unsaturated fatty acids.

4. Concluding Remarks

Based on the data presented, this study stressed the importance to address all key parameters such as reaction temperature, pressure, time, molar ratio of dimethyl carbonate to oil, the FAME yield, degree of denaturation, thermal decomposition and oxidation stability towards real optimization of supercritical dimethyl carbonate for the production of a high-quality biodiesel. The optimum condition for supercritical dimethyl carbonate is preferably in a controlled condition below 300°C and at high pressure more than 20MPa, reaction time less than 30min to achieve a high yield of FAME at 97.4wt%. Conclusively, an experimental process optimization is very important to compliment optimized mathematical model in order to produce high quality biodiesel with maximum yield which is suitable for use in diesel engines.
References

[1] Crocker M (Ed.) 2011 *Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals* (Royal Society of Chemistry, London)

[2] Silva GPD, Mack M and Contiero J 2009 *Biotechnol. Adv.* 27 p 30-39

[3] Saka S, Goembira F and Ilham Z 2011 *Bioresour. Technol.* 102 p 3989

[4] Saka S and Isayama Y 2009 *Fuel* 88 p 1307-1313

[5] Saka S, Isayama Y, Ilham Z and Xin J 2010 *Fuel* 89 p 1442-1446

[6] Ilham Z and Saka S 2009 *Bioresour. Technol.* 100 p 1793-1796

[7] Ilham Z and Saka S 2010 *Bioresour. Technol.* 101 p 2735-2740

[8] Ilham Z and Saka S 2011 *Lipid Technol.* 23 p 10-13

[9] Yao T (Ed.), *Zero Carbon Energy Kyoto 2010* (Springer, Berlin, 2010)

[10] Yao T (Ed.), *Zero Carbon Energy Kyoto 2011* (Springer, Tokyo, 2012)

[11] Saka S 1999 *Jasco Report* 3 Saka S 1999 *Jasco Report* 3 p 28-31

[12] Saka S and Kusdiana D 2001 *Fuel* 80 p 693-698

[13] Kusdiana D and Saka S 2001 *J. Chem. Eng. Japan* 34 p 383-387

[14] Kusdiana D and Saka S 2004 *Appl. Biochem. Biotech.* 115 p 793-801

[15] JOCS, Japan Oil Chemists’ Society Standard Methods for Fats and Oils (JOCS, Tokyo, 1996)

[16] ASTM, American Society for Testing and Materials Standard Test Methods (AOCS, Pennsylvania, 2007)

[17] CEN, European Committee for Standardization Standard Test Methods (CEN, France, 2003)

[18] Ilham Z and Saka S 2016 *SpringerPlus* 5 p 1-6

[19] Ilham Z and Mansor MRA 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* 877 p 012029

[20] Ilham Z, Hakimi MI, Mansor MRA and Goembira F 2019 *IOP Conf. Ser.: Earth Environ. Sci.* 361 p 012022

[21] Ilham Z and Saka S 2012 *Fuel* 97 p 670-677

Acknowledgements

The principal idea for this work was pioneered by Emeritus Professor Shiro Saka and was supported by JICA Project for AUN/SEED-Net Short Term Research Program in Japan and Universiti Malaya (IF015-2020), of which, the authors highly acknowledged.