



Process Engineering Implications of Response Surface Analysis of Microwave-Induced Process Intensification of Coconut Oil Transesterification

J. R. Conejos-Edeza, S. A. Roces, F. T. Bacani and R. R. Tan*

Chemical Engineering Department, De La Salle University, 2401 Taft Avenue, Manila, Philippines

**Corresponding Author: email raymond.tan@dlsu.edu.ph*

Abstract: Biodiesel from vegetable oils is regarded as an important biofuel which is already produced commercially in many countries. The key step in the production of biodiesel is the transesterification of oil into methyl esters, a reaction which is both reversible and multi-phase. Hence, there are inherent difficulties which may be addressed through process intensification techniques such as microwave irradiation. This work discusses the process engineering implications of the results of 1st-order response surface methodology (RSM) optimization of microwave-based process intensification of the transesterification of coconut oil. Six experimental factors (catalyst dosage, methanol-to-oil ratio, reaction temperature, reaction time, alkali catalyst type and the presence of agitation) are considered. Although only catalyst dosage and the presence of agitation are found to have statistically significant effects on reactor performance, the negative results are nevertheless useful for process engineering decisions with respect to scale-up.

Key Words: microwave-based process intensification; transesterification; coconut biodiesel; response surface methodology; design of experiments

1. INTRODUCTION

Biodiesel is considered as a commercially significant biofuel as a partial substitute for diesel fuel. It is produced via the transesterification of vegetable and animal oils with light alcohols such as methanol or ethanol, yielding methyl and ethyl esters, respectively, which are light enough to be used in unmodified diesel engines without causing operational issues. In addition, biodiesel can potentially be produced from a broad range of raw materials depending on local availability (Demirbas, 2009). An extensive review of various commercial and “exotic” feedstocks for biodiesel production has

recently been reported (Razon, 2009). Global production of biodiesel was at about 15 billion L/y toward the end of the last decade, with the major feedstocks being palm, soybean and rapeseed oil (Sorda et al., 2010). In the Philippines, in particular, current legislation (i.e., the Biofuels Act of 2006) mandates blending of 2% biodiesel in the approximately 6 billion L/y of diesel sold (DOE, 2012), and the preferred feedstock is coconut oil, which is a major agricultural crop in the country.

The transesterification reaction presents significant difficulties in process engineering because it is both reversible and multi-phase. In practice, excess methanol is used to shift the reaction

equilibrium forward; however, the disadvantage of this approach is that it necessitates downstream recovery of the excess methanol and also complicates purification of the methyl ester phase. Also, the presence of multiple phases brings about significant mass transfer effects. One strategy for improving the performance of transesterification reactors is process intensification, which is defined as “*the strategy of reducing the size of chemical plant needed to achieve a given production objective*” (Cross and Ramshaw, 1986). For example, there has been increased interest in the use of microwave irradiation for process intensification in general (Leonelli and Mason, 2010) and biodiesel production in particular (Motasemi and Ani, 2012). This approach has been shown to be effective for transesterification of various feedstocks such as coconut oil (Nascimento et al., 2009), karanja oil (Kamath et al., 2011), kenaf seed oil (Rathana et al., 2009), Pongamia pinnata seed oil (Kumar et al., 2011), rapeseed oil (Hernando et al., 2007), soybean oil (Hernando et al. 2007), tallow (Liu et al., 2011) and waste cooking oil (Lertsathapornsuk et al., 2008; Chen et al., 2012). These studies all report drastic reductions in reaction times by one or two orders of magnitude, from about 1 – 2 hours in conventional systems down to several minutes with microwave irradiation. This reduction suggests the possibility of reducing reactor size by the same factor. The proposed mechanism is that, under microwave irradiation, molecular energy levels at interfacial boundaries are much higher than suggested by bulk temperatures (Leonelli and Mason, 2010); thus, the dramatic improvement in apparent reaction rates reported in the literature may be attributed to this peculiar feature of microwave heating, which is particularly favorable to multi-phase reactions such as transesterification.

To our knowledge, the only previously published investigation of microwave-intensified transesterification of coconut oil was the work of Nascimento et al. (2009). Our work investigates additional factors such as reaction temperature, choice of catalyst (NaOH and KOH) and the presence or absence of mixing. The rest of this paper is

organized as follows. The next section describes the overall experimental methodology. Systematic investigation is accomplished using design of experiments (DOE), and in particular, response surface methodology (RSM), which allows for rapid and efficient optimization of operating conditions through a sequence of phased experiments (Montgomery, 2005). Results of the two phases of experimentation are then reported, outlining the identification of statistically significant experimental factors and their subsequent optimization. Process engineering implications of the experimental results are also discussed. Finally, conclusions and prospects for future work are given at the end of the paper.

2. METHODOLOGY

The experimental set-up was adopted from the work of Rathana et.al., (2010) and is shown in Figure 1. It consists of a glass reactor vessel equipped with an inlet port for the reactants and another vertical port for the impeller shaft and a type K thermocouple. The latter is connected to a thermal control unit which ensures that the temperature within the reactor is maintained at the desired level. A refluxing condenser is used to retain volatile vapors in the reactor without undue pressure build-up. The entire assembly is then placed inside a modified 0.85 kW, 2.45 GHz household microwave oven (Whirlpool AVM585). Throughout this work, the reactor operates in batch mode, with each batch comprised of 100 g of coconut oil.

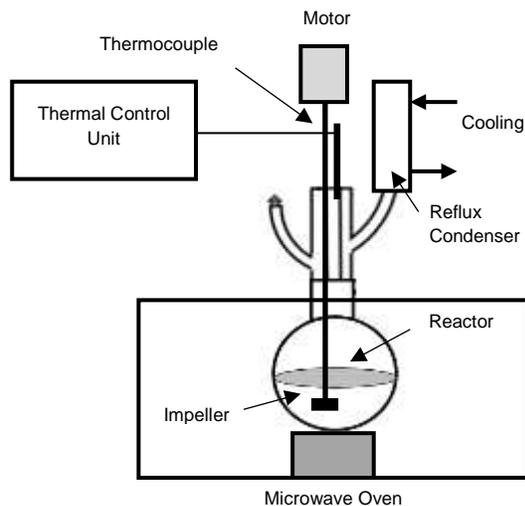




Fig. 1. Schematic Diagram of Microwave-Intensified Reactor

Commercially available refined, bleached, and deodorized (RBD) coconut oil was used as the feedstock in the work. The process utilized sodium hydroxide (NaOH) pellets and potassium hydroxide (KOH) pellets for the alkali-catalyzed transesterification process. The alcohol used is an analytical reagent grade methanol (MeOH). All these chemicals were sourced out from commercial suppliers. Analysis of the coconut methyl ester samples produced in this work was outsourced to an external analytical laboratory specializing in biodiesel samples. The determination of the total glycerol (TG) content was of particular interest for the RSM-based optimization of reaction conditions to achieve the best conversion levels. The presence of TG indicates the presence of both traces of free glycerol as well as bound glycerol in the form of mono-, di- and tri-glycerides (Monterio et al., 2008). Note that the presence of the latter species results from incomplete conversion of the vegetable oil into methyl ester; hence, after washing to remove free glycerol (thus leaving behind only bound glycerol).

A typical two-phase DOE approach was used to optimize conversion in the microwave-intensified transesterification. Phase I dealt with the determination of the statistically significant factors. Six initial factors were studied, namely, catalyst dosage (as OH⁻) per unit oil (x_1), methanol-to-oil mole ratio (x_2), presence of agitation (x_3), reaction temperature (x_4), reaction time (x_5), and type of catalyst (x_6). A $2^{(6-2)}$ fractional factorial experimental design with 16 runs was used in order to determine the statistically significant factors using percentage conversion as the response. The experimental factor levels are shown in Table 1; these values were determined based on literature and on preliminary tests.

DOE philosophy emphasizes phased experimentation, wherein results of each phase are used to plan subsequent experiments. Thus, in this work, the experimental design for Phase II is contingent on the results of Phase I, and thus will only be discussed in detail in a later section of this paper. Essentially, the statistically significant factors identified in Phase I of the study were investigated further to generate a second-order (i.e., linear-quadratic) polynomial regression model, which was then analyzed to determine the optimum reaction conditions to achieve maximum conversion. All statistical analysis results reported here were done using Microsoft Excel.

Table 1. Levels of Factors for the Fractional Factorial Design

Factors	Symbol	Coded Levels	
		-1	+1
Catalyst dosage (m_{OH}/m_{oil})	x_1	0.002	0.004
Methanol-oil mole ratio	x_2	6:1	9:1
Agitation (RPM)	x_3	0	120
Temperature (°C)	x_4	50	60
Reaction time (min)	x_5	5	9
Catalyst type	x_6	KOH	NaOH

3. RESULTS AND DISCUSSION

Conversion levels from Phase I range from 83.79 – 93.33% under the various conditions tested; the purpose of this experimental phase is to determine if the observed variations can be attributed to changes in the experimental factors. The screening of factors was done via analysis of variance (ANOVA) at a level of significance of 0.05. The P-values were used to check the statistical significance of each factor, as shown in Table 2. Note that the P-value is defined as the probability that an apparent effect arises purely by chance; thus, a low P-value for any factor implies that it is likely to have a real (i.e., statistically significant) effect on the response (Montgomery, 2005). In this case, a P-value ≤ 0.05 indicates that the observed effect of a



particular experimental factor on conversion is statistically significant.

Table 2. Statistical Significance of Factors from Phase I

Factors	Effect	P-value
Catalyst dosage (m_{OH}/m_{oil})	+	0.034
Methanol-oil mole ratio	+	0.079
Agitation (RPM)	+	0.023
Temperature ($^{\circ}C$)	+	0.959
Reaction time (min)	+	0.441
Catalyst type	-	0.063

It can be seen that only catalyst dosage (x_1) and agitation (x_3), with P-values of 0.034 and 0.023, respectively, have statistically significant positive effects on conversion levels. In other words, the results indicate that increasing catalyst dosage and using agitation can be expected to increase conversion. The latter clearly results from the increase in interfacial surface area, resulting in more intimate contact between the reacting phases. This preliminary result is then used as a basis for planning Phase II, as described in the next section. On the other hand, all other factors are found not to have any statistically significant effect on conversion for the range of values tested (as shown in Table 1). This in itself is an interesting result which has useful process engineering implications, which are as follows:

- As methanol-to-oil ratio (x_2) is found to have no statistically significant effect on conversion when varied from 6:1 to 9:1. Thus, from a process engineering perspective, a ratio of 6:1 (corresponding to 100% excess methanol) is preferable, as it reduces problems associated with downstream separation and recovery of the excess methanol in both ester and glycerol phases. This is an interesting result since, in the case of conventional transesterification, use of excess methanol is a strategy often used to improve

conversion levels, at the expense of complicating downstream processing.

- Temperature (x_4) is also found to have no statistically significant effect on conversion when varied from $50^{\circ}C$ to $60^{\circ}C$; thus, lower operating temperature is preferable as it will reduce the energy intensity of the process.
- Reaction time (x_5) does not have a statistically significant effect on conversion between the values of 5 to 9 minutes. This result implies that the reaction rapidly approaches equilibrium in 5 minutes or less. Thus, from a process engineering standpoint, shorter reaction times are preferred as these imply that smaller, less expensive reactors can be used for any given throughput.
- Choice of catalyst (x_6) has no statistically significant effect on conversion, thus indicating that KOH and NaOH are equally effective as catalyst.

In Phase I, it was found that catalyst dosage (x_1) and agitation (x_3) have statistically significant effects on conversion levels. Additional experiments were then done in Phase II to investigate the effects in more detail. As the other three quantitative experimental factors (methanol-oil ratio, temperature and reaction time) from Phase I were found to be statistically insignificant, these were set to the lower values of the ranges given in Table 1; KOH was also selected as the catalyst in all of the tests. Also, because mixing was already found to have a statistically significant positive effect on conversion, all additional experimental tests were performed with agitation. Note that catalyst dosage (x_1) was at the intermediate value for five replicate runs (i.e., the coded factor level of 0 corresponds to an actual value of 0.003) which also allows an assessment of the repeatability of the results. For these five replicates, the observed conversion was $87.23 \pm 4.29\%$. In addition, one run each was performed at extreme values of x_1 (coded values of -1.4 and $+1.4$, corresponding to real catalyst dosages



of 0.0016 and 0.0044, respectively). Thus, when combined with the 16 original runs from Phase I, catalyst dosage was varied to five different values in total. Next, the combined results of Phases I and II were combined and the following polynomial regression model was derived:

$$\text{CONV} = 85.72 + 1.75 x_1 + 1.09 x_1^2 + 0.85 x_1 x_2 + 1.59 x_2 \quad (1)$$

where CONV is the conversion (%), x_1 is the coded value of the catalyst dosage and x_2 is the coded variable indicating the presence of agitation. The analysis of variance (ANOVA) of this empirical model is shown in Table 3, where the P-value of 0.029 indicates that the model is statistically significant at $\alpha = 0.05$.

Table 3. Analysis of Variance of Final Regression Model

Source of Variation	d.o.f.	SS	MS	F	P-value
Model	4	140.55	35.14	3.42	0.029
Error	19	195.23	10.28		
Total	23	335.78			

Such an empirical statistical model makes no attempt to provide a mechanistic explanation of the underlying phenomena (Montgomery, 2005). However, it can be regarded as a statistically sound description of the system, within the range of values of the factors that are included in the experiments. Thus, in this case, the model can make a reasonable prediction of conversion levels provided that, $-1.4 \leq x_1 \leq 1.4$ and $-1 \leq x_2 \leq 1$. Optimization of Eq. 1 using the commercial software LINGO 12.0 shows that using catalyst dosage of 0.0044 g OH/g oil ($x_1 = 1.4$) and with agitation applied ($x_2 = 1$) should result in a conversion level of 93.09% on the average. Furthermore, Eq. 1 suggests that potentially higher conversion levels can be achieved by further increasing both catalyst dosage and agitation intensity. However, the exact extent of such gains can only be ascertained through further tests beyond the experimental region used in this work.

4. CONCLUSIONS

A design of experiment (DOE) approach was used for systematic investigation of experimental factors influencing conversion levels in the microwave-based process intensification of coconut oil transesterification. Specifically, response surface methodology (RSM) was utilized to determine that catalyst dosage and the presence of agitation had statistically significant positive effects on the conversion of coconut oil into methyl esters. Four other factors, namely, methanol-to-oil ratio, reaction temperature, reaction time and type of alkali catalyst, were found to have no significant effects over the ranges of values investigated, which suggests that their values can be set to arbitrary values or to those which are most convenient or economical from a process engineering standpoint. This result is particularly important in the case of methanol-oil ratio, since the separation and recovery of excess methanol accounts for a major portion of downstream processing in typical biodiesel plants.

Future work should thus focus on further optimization of the microwave-intensified reaction to improve product quality, and to investigate interactions of this process with other potential process units within a biodiesel production flowsheet.

5. ACKNOWLEDGMENTS

We would like to acknowledge financial support of Department of Science and Technology (DOST) through Philippine Council for Industry and Energy Research and Development (PCIERD) and Engineering Research and Development for Technology (ERDT) program. Additional support was also received by the last three authors from the University Research Coordination Office (URCO) at



De La Salle University.

6. REFERENCES

- Chen, K. S., Lin, Y.-C., Hsu, K.-H. and Wang, H.-K. (2012) Improving biodiesel yields from waste cooking oil by using sodium methoxide and a microwave heating system. *Energy*, 38, 151 – 156.
- Cross, W. T. and Ramshaw, C. (1986). Process intensification: laminar flow heat transfer. *Chemical Engineering Research and Design* 64: 293 – 301.
- Demirbas, A. (2009). Progress in recent trends in biodiesel fuels. *Energy Conversion and Management* 50: 14 – 34.
- Department of Energy (2012). Oil Supply/Demand Report 2010. (<http://www.doe.gov.ph/DO/OilSupplyDemandReport.htm>, accessed May 2, 2012)
- Hernando, J., Leton, P., Matia, M. P., Novella, J. L. and Alvarez-Builla, J. (2007) Biodiesel and FAME synthesis assisted by microwaves: Homogeneous batch and flow processes. *Fuel*, 86, 1641–1644.
- Kamath, H. V., Regupathi, I. and Saidutta, M. B. (2011). Optimization of two step karanja biodiesel synthesis under microwave irradiation. *Fuel Processing Technology*, 92, 100 – 105.
- Kumar, R., Kumar, G. R. and Chandrashekar, N. (2011). Microwave assisted alkali-catalyzed transesterification of Pongamia pinnata seed oil for biodiesel production. *Bioresource Technology*, 102, 6617 – 6620.
- Leonelli, C and Mason, T.J. (2010). Microwave and ultrasonic processing: Now a realistic option for industry" *Chemical Engineering and Processing: Process Intensification*, 49, 885-900
- Lertsathapornasuk, V., Pairintra, R., Aryusuk, K. and Krisnangkura, K. (2008). Microwave assisted in continuous biodiesel production from waste frying palm oil and its performance in a 100 kW diesel generator. *Fuel Processing Technology*, 89, 1330 – 1336.
- Liu, S., Wang, Y., Oh, J.-H., and Herring, J. L. (2011). Fast biodiesel production from beef tallow with radio frequency heating. *Renewable Energy*, 36, 1003 – 1007.
- Monteiro, M. R., Ambrozin, A. R. P., Liao, L. M. and Ferreira, A. G. (2008) Critical review on analytical methods for biodiesel characterization. *Talanta*, 77, 593 – 605.
- Montgomery, D. C. (2005). *Design and Analysis of Experiments*, 6th ed. Wiley, New York.
- Motasemi, F., Ani, F.N. (2012). A review on microwave-assisted production of biodiesel. *Renewable and Sustainable Energy Reviews*, 16, 4719-4733
- Nascimento, U.M., Vasconcelos, A.C.S., Azevedo, E.B. and Silva, F.C. (2009). Optimization of biodiesel production from babaçu coconut oil with microwave heating. *Ecletica Quimica*, 34, 37 – 48.
- Qiu, Z., Zhao, L., Weatherley, L. (2010). Process intensification technologies in continuous biodiesel production. *Chemical Engineering and Processing: Process Intensification*, 49, 323 – 330.
- Razon, L. F. (2009). Alternative crops for biodiesel feedstock. *CAB Reviews: Perspectives in Agriculture, Veterinary Science, nutrition and Natural Resources* 4: 10.
- Rathana, Y., Roces, S., Bacani, F., Tan, R., Kubouchi, M., Yimsiri, P. (2009). Alkali-catalyzed transesterification of kenaf (*Hibiscus cannabinus* L.) seed oil by microwave irradiation. *International Journal of Chemical Reactor Engineering*, 8, S5.
- Sorda, G., Banse, M. and Kemfert, C. (2010). An overview of biofuel policies across the world. *Energy Policy* 38: 6977 – 6988.