ENHANCING BIODIESEL PRODUCTION PROCESS THROUGH MICROWAVE-ASSISTED CATALYSIS: A RESEARCH NOTE

Armando T. Quitain ¹ and Dewoowoogen P. Baclayon²

Abstract

A novel method for producing biodiesel by the combined advantages of microwave irradiation and solid catalysts was investigated. Results of batch experiments showed a remarkable decrease in reaction time to within a minute compared to a minimum of 1 h using the conventional method to achieve above 95% conversion. The mechanism of reaction and the effects of operating conditions are discussed.

Keywords: microwave, solid catalyst, biodiesel, bioenergy, transesterification

1.0 Introduction

With the steady increase in global demand for energy, coupled with recent concerns about climate change, environmentally benign and economically viable alternatives to fossil-derived fuels are seriously being explored. As potential alternatives, biofuels such as ethanol and biodiesel are being pursued (Shinnar and Francesco 2006, Ritter 2007). Biodiesel is produced by transesterification of oils and fats with alcohol. The conventional method for production of biodiesel is based on the use of batch processes, in which a basic homogeneous catalyst is used, and at the end of the reaction, the catalyst is neutralized. This also involves removal of the catalyst in the products by washing with water. The demand for biodiesel is expected to increase, and a more efficient, simple, and continuous process is sought with for the purpose of reducing production costs.

This study investigates a method of producing biodiesel by the combined advantages of microwave irradiation and solid catalysts. Experiments on the effects of operating conditions were also carried out.

2.0 Methodology

Materials and Apparatus

A commercial rapeseed oil from NacalaiTesque (Japan) was mainly used in this study. The average molecular weight of rapeseed oil was assumed to be 806 (Kusdiana and Saka 2001). Methanol (HPLC grade), Ca(OH)2 and CaO (99.9%) were purchased from Wako (Japan), while other catalysts were

¹RIST, Kagawa, Japan
²Southern Leyte State University
purchased from Sigma-Aldrich (Japan). All microwave-assisted experiments were performed using an in-house microwave apparatus, working at 2.45 GHz frequency, with a power programmable from 0 to 700W. Temperature could be controlled, and the reactants could be mixed using a magnetic stirrer.

Experimental Procedures

In a typical run, about 11.5 g methanol and 48.5 g rapeseed oil (MeOH-oil molar ratio = 6) were placed in a three-necked round bottom flask, and heated either in an oil bath or in a microwave apparatus described above. The MeOH-oil ratio was fixed at a commonly used molar ratio of 6, which is also the ratio being employed in industry. The amount of catalyst was varied from 1 to 20 g. The reaction temperature was set at 60°C, unless otherwise specified. In experiments involving constant microwave heating power, the temperature was not controlled. After reaction, the products were centrifuged to separate the catalysts. Afterwards, the unreacted MeOH in the products were removed using a rotary evaporator at 70°C. The products were then analyzed of its composition.

Analysis

The products were analyzed of its composition by a gas chromatography – flame ionization detector (GC-FID) apparatus (Shimadzu GC-14B) connected to a computer for data collection and analysis. Component separation was made in a 50m x 0.25mm CP Sil 88 capillary column (GL Science, Japan), tailor-made for FAME. FAME analysis using helium as a carrier gas. The column, detection and injection temperatures were set to 190, 300 and 270°C, respectively. The sample injection volume was 5 ul and peak identification was made by comparing the retention time between the sample and the standard compound. FAME quantitative mixtures (GL Science, Japan) were used for peak identification and for quantitative analysis.

3.0 Results and Discussion

Evaluation of Catalytic Activities of Various Solid Catalysts

Experiments on the evaluation of catalytic activities of various solid catalysts such as Amberlyst 15, Amberlite-OH, Amberlite-Acid, zeolite, sulfated zirconia (in powder and pellet forms), Ca(OH)$_2$ and CaO. Among the catalysts, Ca(OH)$_2$ showed to be the most effective. CaO also gave fairly good results. The use of these two relatively cheap catalysts shows potential for biodiesel production, thus Ca(OH)$_2$ was used in the succeeding experiments unless otherwise specified.

Comparison of Microwave and Conventional Heating
Microwave was compared with conventional heating. In the case of conventional heating, the oil bath temperature was set at 60°C, and the mixtures of reactants and catalysts were heated for 1 min. Using microwave, the power was set at 700 W. Heating for 1 min, the temperature of the mixtures did not reach above 60°C in all runs.

Fig. 1 shows a remarkable increase in the yield of methyl esters using microwave heating compared to the conventional. The yield, corresponding to the amount of methyl esters in the oil phase, reached above 95% using 20g Ca (OH)$_2$.

Even if the bulk temperature did not reach 60°C, it is likely that localized heating above 60°C occurred at the surface of the catalysts, which brought about a significant increase in reaction rate, resulting into high yield. This is advantageous especially from the viewpoint of equipment design as this entails less provision for heat-resisting reactor materials.

![Figure 1. Comparison of microwave and conventional heating for production of biodiesel.](image)

Table 1 summarizes the comparison between the proposed process and the conventional method of producing biodiesel. In the proposed process, the reaction time is reduced to less than 60 sec as compared to 1 to 8 h using the conventional method. In addition, the use of solid catalysts avoids the rigors and complexities of dealing with post-reaction treatments (i.e. neutralization of homogeneous catalysts and washing of the products with water). Furthermore, with short reaction time, development of a continuous process is highly feasible thus reducing equipment costs.
Table 1. Comparison between the conventional and microwave-solid catalyst methods for producing biodiesel.

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>Microwave-Solid Catalyst</th>
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<tbody>
<tr>
<td>Reaction Time</td>
<td>1.8 h</td>
<td>&lt;60 sec</td>
</tr>
<tr>
<td>Reaction Conditions</td>
<td>0.1 MPa</td>
<td>0.1 MPa</td>
</tr>
<tr>
<td>30-65°C≤60°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alcohol-Oil Ratio</td>
<td>6.1</td>
<td>6.1</td>
</tr>
<tr>
<td>Catalysts</td>
<td>homogeneous</td>
<td>non-homogeneous (solid)</td>
</tr>
<tr>
<td>acid or base</td>
<td>ex: CaO, Ca(OH)₂</td>
<td></td>
</tr>
<tr>
<td>By-products</td>
<td>methanol, catalysts, glycerin</td>
<td>methanol, glycerin</td>
</tr>
<tr>
<td>Post-Reaction Treatment</td>
<td>complex</td>
<td>simple</td>
</tr>
</tbody>
</table>

**Effect of Operating Conditions**

Figure 2 shows the effect of microwave irradiation power on the yield. No significant differences were observed at 140 and 350W, but the yields were comparatively high at 700W especially at 10 and 20g Ca(OH)₂. Using 10g Ca(OH)₂, the reaction time was increased to 5 min. Results showed that while the temperature increased sharply above 110°C in just 5 min, the yield decreased to 20%. It is likely that reverse reaction took place brought about by an increase in reaction temperature and subsequent evaporation of MeOH from the reaction zone. The same results were observed in the works of Hernando et al. (2007) on the batch tests performed with microwaves.
Comparison with Other Vegetable Oils

The results for rapeseed oil were compared with soybean and coconut oils. The fatty acid compositions of these oils differ as shown in Table 2. Rapeseed oil is rich in oleic acid, while soybean and coconut oils are rich in linoleic and lauric acids, respectively. Results in Fig. 3 show that almost similar results were obtained even with different kinds of vegetable oils, with the yield for coconut oil a little higher than the two other types of oil. This result suggests that the method is applicable to any type of raw materials (oils or fats) for biodiesel production.

Table 2. Fatty acid composition of various oils.

<table>
<thead>
<tr>
<th>Fats/Oils</th>
<th>Fatty Acid (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Caprylic (C8:0)</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>6</td>
</tr>
<tr>
<td>Soybean</td>
<td>0.3</td>
</tr>
<tr>
<td>Coconut</td>
<td>8</td>
</tr>
</tbody>
</table>

Figure 3. Comparison of the yields obtained from various vegetable oils.
4.0 Conclusion

Microwave-assisted solid catalyzed process for biodiesel production can reduce reaction time to about 1 min to obtain at least 95% yield. This short reaction time can pave the way for the development of a continuous process, thus reducing equipment costs. This adds to the inherent benefits of using solid catalysts to avoid the rigors and complexities of dealing with post-reaction treatment procedures. With the above mentioned advantages, and as the demand for renewable energy increases, the prospect is high for the use of this proposed process for biodiesel production in the near future.

5.0 References Cited


