A SOLID-LIQUID EXTRACTION PROCESS TO PRODUCE BIODIESEL FROM JATROPHA SEEDS

Soo Ching Soh¹, Mohamed Kheireddine Taieb Aroua², Abdul Aziz Abdul Raman³
¹,²,³ Chemical Engineering Department, University of Malaya, Kuala Lumpur, 50603 Malaysia
Fax: +603-7967-5319
¹sooching525@yahoo.com
²mk_aroua@um.edu.my
³azizraman@um.edu.my

Abstract: The interest of using Jatropha (Jatropha Curcas L.) as a feedstock for biodiesel production has growing rapidly worldwide. In situ transesterification has received much attention recently to reduce the biodiesel production cost. Nevertheless, Jatropha oil contains about 14% of free fatty acids (FFA) which are far beyond the limit of 0.5 % FFA level that can be converted into biodiesel by transesterification using alkaline catalyst. Therefore, this project introduces an integrated procedure, continuous solid-liquid chemical extraction process for converting high FFA% Jatropha oil. This project aims at developing a continuous chemical extraction process to convert Jatropha seeds to biodiesel without prior oil extraction. The oil extraction, esterification and methanol recovery were performed in continuous mode by a laboratory scale soxhlet extraction rig. The important process parameters studied include retention time (1-6 hrs) and methanol-seed ratio (6-12 mL/g). The product (FAME) was then analyzed by Gas Chromatography Mass Spectrometry. Under the constant heating capacity (approximate 75-80 °C) and 20 wt% of acid sulfuric, it found that FAME yield increase as retention time increases or methanol to seed ratio increases. However, FAME yield only increase 6 % from 93 % after 4 hrs retention time; and increase 2 % after 10.5 mL/g methanol-seed ratio. Hence, optimum FAME yield, 93 % could achieve with 20 acid wt% and 10.5 mL/g methanol-seed ratio at 4 hrs time. Furthermore, 6 % FAME yield increases when experiment repeated under optimum condition with grinded seeds without shell. Therefore continuous chemical extraction process can be a potential route for biodiesel production that reduces the processing steps and cost.

Key Words: Acid catalyst; Biodiesel; Continuous solid-liquid chemical extraction; Jatropha

1. INTRODUCTION

More and more people across the country are speaking out about the advantages of biodiesel due to the limitation of traditional fossil resource and concern over the greenhouse gas emissions. Biodiesel, a biodegradable and renewable fuel, has recently been considered as the best candidate for a diesel fuel substitution (Xu & Wu, 2003; Dube et al., 2007) due to its high flash point, high cetane number, low viscosity, high lubricity and fewer emission profiles compared to conventional fossil fuels (Dorodo et al., 2003).

There are many different variety of biodiesel feedstock especially vegetable oil such as, canola (Dalai et al., 2006), sunflower seed (Georgogianni et al., 2008), and palm oil
Presented at the 3rd Regional Conference on Chemical Engineering
EDSA Sangri-la Hotel, Metro Manila, Philippines
January 20 – 21, 2011

(Baroutian et al., 2008). The main concern about biodiesel production is the high cost of vegetable oil compared to that of fossil based diesel fuel. Hence, few studies have been reported on low cost oils like used cooking oil, grease, and tallow (Alcantara et al., 2000; Dorado et al., 2002; Cayli & Kusefoglu, 2008) as well as non-edible tree-based oil seeds such as cotton seed (Qian et al., 2008) and Jatropha seeds (Lu et al., 2009; Kaul et al., 2010).

Jatropha (Jatropha Curcas L.) seed oil is one of the non-edible oil which has a great potential as biodiesel feedstock. Jatropha has been recognized as a powerful source of energy and it yield up to 30-60% of oil content per year. Its various favorable attributes like hardy nature, short gestation period, high oil recovery and quality of oil make it more economic source for biodiesel production and avoid from falling into the controversy of fuel versus food. Table 1 shows the fatty acid composition of Jatropha seeds.

Table 1. Fatty acid composition (%) of Jatropha curcas L. seeds oil

<table>
<thead>
<tr>
<th>Fatty Acid</th>
<th>Jatropha curcas L. seed oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic 18:1</td>
<td>44.7</td>
</tr>
<tr>
<td>Linoleic 18:2</td>
<td>32.8</td>
</tr>
<tr>
<td>Palmitic 16:0</td>
<td>14.2</td>
</tr>
<tr>
<td>Stearic 18:0</td>
<td>7.0</td>
</tr>
<tr>
<td>Others</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Saturated</td>
<td>21.6</td>
</tr>
<tr>
<td>Monounsaturated</td>
<td>45.4</td>
</tr>
<tr>
<td>Polyunsaturated</td>
<td>33</td>
</tr>
</tbody>
</table>

(Edem, 2002)

Transesterification reaction is the most commonly used reaction to produce biodiesel. In this reaction, triglycerides in oil will react with an alcohol with the assist of catalyst to produce ester and glycerol (Marchetti et al., 2007). Conventional method of biodiesel production in industry from oil seed must go though several steps. This multi processing stages including oil extraction (expelling); pretreatment (degumming, dewaxing, deacidification, dephosphorization, dehydration etc); follow by esterification/transesterification and separation/purification of biodiesel. The oil extraction and pretreatment process constitute more than 70% of the total biodiesel production cost (Zeng et al., 2009). Hence in situ extraction or in situ esterification/transesterification, also called as reactive extraction has been introduced to cut the processing cost. In situ extraction is direct production of biodiesel with omitting the expelling or extruding step where the oil-bearing material contacts with alcohol directly instead of reacting with pre-extracted oil. In other words, reactive extraction eliminates the requirement of costly hexane oil extraction process and thus reducing processing time and production cost (Shuit et al., 2010b).

Current alkaline base reactive transesterification require a very strict feedstock condition, an anhydrous condition (total water content must be 0.1-0.3 wt % or less) and a very low free fatty acid (FFA, must not exceed 0.5 %) level (Lotero et al., 2005; Marchetti et al., 2007). Jatropha oil contains about 14% of free fatty acids (FFAs) which are far beyond the limit of FFA level that can be converted into biodiesel by transesterification using an alkaline catalyst. As such in order to convert Jatropha oil to biodiesel using in-situ transesterification reactions, two steps are required. The first step uses an acid catalyst to convert the FFAs and the second uses a base as catalyst for the conversion of the triglycerides (Kumartiwari et al., 2007;
Berchman & Hirata, 2008). However, this 2-steps reactive extraction is complicate, require larger amount of chemical used and produce comparable more waste products. Hence, an integrated optimized procedure for converting Jatropha oil, which contains high FFA level into biodiesel, is very much required.

Recent research conducted by final year students in Chemical Engineering Department, Malaya University, showed that it is possible to produce biodiesel directly from Jatropha seeds as feedstock, thus omitting the oil extraction step. The preliminary research was carried using a batch solid-liquid extraction process enhanced with chemical reaction in the liquid phase. Under optimum conditions biodiesel yield of 60 % were achieved. To improve the biodiesel yield, a continuous process with acid catalyst should be used. As such this project aims at developing a continuous solid-liquid chemical extraction process to convert Jatropha seeds to biodiesel where the oil extraction, transesterification and methanol recovery can perform in a continuous mode.

2. METHODOLOGY

Material
Jatropha Curcas L. seeds were obtained from India and used as feedstock for continuous solid-liquid chemical extraction process. Methanol (AR grade, 99.9% purity); n-hexane (GC grade, >99%) and sulphuric acid (H₂SO₄, 95-07% purity) were purchased from Fisher Scientific (M) Sdn. Bhd. The FAME standard mixture (GLC-10) used for GC calibration was obtained from Supelco Analytical, USA.

Measure of Moisture and Oil Content of Jatropha Curcas L. Seeds
Initially, Jatropha seeds were blended into a small size. It was then weighted and dried in an oven at 76 °C repeatedly until a constant weight was achieved (Shuit et al, 2010a). Moisture content was calculated based on the different between the fresh seeds and constant dry seeds’ weight. To determine the amount of oil contained in the Jatropha seeds, a conventional method, Soxhlet extraction was using to extract the oil by excess n-hexane solvent.

Continuous Solid-Liquid Chemical Extraction
The continuous solid-liquid chemical extraction was carried out in a B-811 Buchi Extraction System applying Soxhlet Warm Standard method. The complete extraction process consists of three sequential steps - extraction, rinsing and drying which would run automatically according to the parameter set in the program as shown in Table 2.

| Table 2. Parameter setting of Soxhlet extraction |
|-----------------|-------------|-------------|----------|
| Step | Level Heating Value | Time (hr) |
|      | Lower | Upper |      |
| 1    | Extraction | 12 | 4 |  a |
| 2    | Rinsing | 12 | - | 0.5 |
| 3    | Drying | 5 | - | 0.5 |
| a: extraction time vary according to the manipulated retention time from 1-6 hrs
Figure 1 shows the assembly of soxhlet extraction rig. Initially, a thimble with specified amount of grinded Jatropha seeds was put into the glass sample tube and 150 mL of methanol was put into the solvent beaker. When the extraction, rising and drying process completed, 2 layers of liquid were formed in the beaker where the upper layer in dark yellow color was crude biodiesel while the lower layer in dark brown color was glycerol. The upper volume was recorded and washed with 20% NaCl solution several times until the pH became neutral. After washing, the upper layer was dried over anhydrous sodium sulfate.

The manipulated variables studied include retention time (duration of direct-transesterification 1-6 hrs) and methanol to seeds ratio (6-12 mL/g) at constant heating capacity (75-80 °C) and 20 wt% of H₂SO₄ concentration.

**Sample Analysis**

The fatty acid methyl ester (FAME) yield in biodiesel samples were analysis by the Agilent 6890 Gas Chromatogram (GC) equipped with Agilent 5973 MSD detector and DB23 capillary column (60 m x 0.25 mm id x 0.15 µm). The analysis method was conducted based on the methodology proposed by Agilent (David et al, 2003) and external standard calibration curves. Table 3 show the detail analysis conditions.

<table>
<thead>
<tr>
<th>Table 3. Analysis Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet temperature: 250 °C</td>
</tr>
<tr>
<td>Injection volume: 1 µL</td>
</tr>
<tr>
<td>Split ratio: 1/50</td>
</tr>
<tr>
<td>Carrier gas: Helium gas</td>
</tr>
<tr>
<td>Solvent: n-Hexane</td>
</tr>
<tr>
<td>Head pressure: Constant pressure mode (pressure approximately 230 kPa at 50 °C, 33 cm/s at 50 °C)</td>
</tr>
<tr>
<td>Oven pressure: 50 °C, 1 min, 25 °C/min to 175 °C, 4 °C/min to 230 °C, 5 min</td>
</tr>
<tr>
<td>Transfer line: 250 °C</td>
</tr>
<tr>
<td>MSD parameter: Scan (40-500 amu), threshold 100</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>MS quad 150 °C, MS source 230 °C</td>
</tr>
</tbody>
</table>

The yield of biodiesel (FAME) was calculated based on equation below (Shuit et al, 2010b):

\[
Yield \, (\%) = \left( \sum \frac{\text{concentration of each component}}{\text{total weight of oil in the sample}} \right) \times (\text{volume of upper layer}) \times 100\% \quad \text{(Eq. 1)}
\]
3. RESULTS AND DISCUSSION

Moisture and Oil Content of Jatropha Curcas L. Seeds
The moisture content of Jatropha Curcas L. Seeds was 4.9% while the average oil content was about 34 wt% which is within the 30-60 wt% range reported in the literature for Jatropha Curcas seeds.

Continuous Solid-Liquid Chemical Extraction
Figure 3 shows the effect of different methanol-seeds ratio range from 6 to 12 mL/g on the percentage of biodiesel (FAME) yield. This effect was studied under a constant heating capacity at 12 heating value (75-80 °C), 20 wt% of H₂SO₄ concentration and 4 hours reaction time. It was found that the FAME yield increase gradually from 65% to 93% when the ratio increase from 6 to 11 mL of methanol per gram of grinded seeds. The role of methanol in a reactive extraction such as continuous solid-liquid chemical extraction is not only as an extraction solvent but also as a transesterification reagent. Therefore, the amount of methanol require will be higher than conventional transesterification process. The FAME yield increase as ratio increase is easily justified as higher amount of methanol used giving a higher concentration gradient to extract the oil from the seeds. In addiction, excess methanol will forward the transesterification reaction to form the FAME. However, it was found that the FAME yield only increase 2% when the methanol-seeds ratio was increase from 11 mL/g to 12 mL/g that may probably due to the difficulties in glycerol separation (Liu et al., 2007).

Figure 2. Percentage of FAME yield at different methanol-seed ratio

Figure 3 shows the effect of retention time on FAME yield at constant heating capacity, 20 wt % of H₂SO₄ concentration and 10.5 mL/g methanol-seeds ratio. Initially, the FAME yield increased rapid and linearly up to 3.5 hours retention time and the then become gradually from 4 to 6 hours. According to Shuit, the limiting factor of reactive extraction is the leaching of oil from the seeds, they found that as long as 10 hours time was required to extract the oil
and subsequently be transesterified to FAME by using 22 wt% of H₂SO₄ catalyst. However, in this study, only 4 hours of reaction time was sufficient to achieve the optimum condition, 93% of FAME yield.

![Figure 3. Percentage of FAME yield at different retention time](image)

Furthermore, 6% of FAME yield increase when experiment repeated under optimum condition with grinded seeds without shell. This is because it can avoid the loss of FAME when some portion of the biodiesel remains on the shell. Therefore, under the optimum condition, 99% of FAME yield was achieved by using 10.5 mL/g methanol-seeds ratio, 20 wt% of H₂SO₄ acid concentration at 4 hours reaction period.

4. CONCLUSIONS

The project proved that acid-catalyzed continuous solid-liquid chemical extraction process can be a potential route for biodiesel production. The analysis shows that both independent variables, methanol-seeds ratio and acid sulfuric concentration are significant and has a great effect on the FAME yield where 99% of yield can be achieve in 4 hours time. Furthermore, the time require to complete the whole production process is much more shorter than two-steps method, or even normal reactive extraction process because it combine the reactive extraction and methanol recovery in a continuous mode rather than run the recovery process separately in rotary evaporator. Hence, continuous solid-liquid chemical extraction process can be a breakthrough technology in direct-seed biodiesel production that reduces the processing steps and cost.
REFERENCES


