Hydrotreating of Algae Oil for Third Generation Biofuels Production

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Recently, algae as a feedstock for biodiesel production have been considered as the most promising substitute for oil crops. Transesterification is currently the primary route for biodiesel production. However, an alternative route for the production of renewable diesel from vegetable oils and fats is hydrotreatment of triglyceride-containing feedstocks. In this work, synthetic algae oil based on Chlorella vulgaris fatty acid composition was hydrotreated in the hydrotreating pilot plant of the Colombian Petroleum Institute. Some properties of biodiesel produced were determined, and it was encountered that biodiesel of synthetic algae oil meets the requirements listed in ASTM Biodiesel Standard D 6751. In order to establish a preliminary criterion of renewability, hydrogenation and transesterification processes were compared in terms of how much methane is required to produce the corresponding amounts of hydrogen and methanol consumed in obtaining renewable diesel. This study is pioneer in Colombia and lays the basis for future research on third-generation renewable diesel production.

1. Introduction

Biodiesel, a diesel compatible biofuel, is produced mainly by transesterification vegetable oils and fats. This process has many benefits; however, new biodiesel plants must be built requiring a large capital investment (Huber et al., 2006). An alternative route for biodiesel synthesis is hydrotreating. In this process triglycerides are converted by olefinic double bond saturation, oxygen elimination through hydrodeoxygenation (HDO), decarboxylation and decarbonylation, and finally hydrocracking of the carbon chain of fatty acid molecules. Figure 1 illustrates the olefinic double bond saturation and the three possible oxygen removing reactions from a trioleic triglyceride. In reaction route I (hydrodeoxygenation, HDO) 1 triglyceride molecule is converted into 3 long chain (as long as the fatty acid chain) n-paraffin, 1 propane and 6 H2O molecules. Decarboxylation and decarbonylations also take place via reaction routes II and III; here the oxygen forms CO2 and CO. In case of II and III, the formed chain’s carbon number is less than that of the fatty acid chain with one (Tóth et al, 2009). This process has been used to produce straight chain alkanes ranging from n-C15–n-C18, from several lipid feedstocks (Sebos et al., 2009; Guzman et al., 2010; Tóth et al., 2010) having water, propane and CO2 gases as byproducts. Also it takes advantage of existing oil refineries
by processing in hydrotreating units the triglyceride-containing materials or blends of them with petroleum-derived feedstocks, such as heavy vacuum oil (Huber et al., 2007). Cold weather properties, heating content and cetane number of the liquid distillate fuel thus obtained are greater than those of first-generation biodiesel. Additionally, propane is preferable over glycerol (Guzman et al., 2010).

Moreover there is currently widespread interest in cultivation of different algae species, whose oil can also be used as feedstock in the production of biodiesel. This algae biodiesel is called third-generation biodiesel. Algae have high growth rates, doubling its population within 24 hours (Rittmann, 2008) and can grow in salty or waste water (Schenk et al., 2008). Additionally, their oil production per unit of cultivated area can be many times greater than that of oil plants (Chisti, 2007).

This paper presents hydroprocessing of synthetic algae oil. This synthetic algae oil simulates the fatty acid composition of *Chlorella vulgaris* oil and was used because of the limitations in obtaining the pure *Chlorella vulgaris* oil in the amounts needed for a complete study. This work was sponsored in the framework of projects supported by the Colombian Agriculture and Rural Development Ministry.

### 2. Materials and methods

#### 2.1 Preparation of the synthetic algae oil

To prepare the synthetic algae oil (SAO), the procedure described by Plata et al. (2010) was followed. The fatty acids in *Chlorella vulgaris* oil reported by Petkov and Garcia (2006) for outdoor cultivation were grouped according to their degree of unsaturation. Thus, 14:0, 16:0 and 18:0 were grouped as saturated fatty acids and their percentage in the mixture was calculated equal to 13 %. Similarly, 16:1 and 18:1 were grouped as mono-unsaturated, 16:2 and 18:2 as di-unsaturated, and 16:3 and α-18:3 as tri-unsaturated. The percentages calculated for each group are 13 % for saturated, 20 % for mono-unsaturated, 28 % for di-unsaturated and 39 % for tri-unsaturated.

Different combinations of oils were tested in order to find a mixture that fulfilled the math requirement expressed by the system of linear equations formed by equations 1, 2, 3 and 4 in figure 2; these equations represent the mass balance of saturated, mono-unsaturated, di-unsaturated and tri-unsaturated fatty acids in an ideal mixing unit, where

\[
\begin{align*}
\text{CH}_2\text{O} & \xrightarrow{+15 \text{H}_2} \text{C-(CH}_2)_2 \xrightarrow{+6 \text{H}_2} \text{CH-CH=CH-(CH}_2)_2 \xrightarrow{+9 \text{H}_2} \text{CH}_3 \xrightarrow{3 \text{n-C}_{18} \text{H}_{33} + \text{C}_3 \text{H}_6 + 6 \text{H}_2 \text{O}} \text{O} \xrightarrow{3 \text{n-C}_{17} \text{H}_{35} + \text{C}_3 \text{H}_6 + 3 \text{CO}_2} \text{O} \xrightarrow{3 \text{n-C}_{17} \text{H}_{35} + \text{C}_3 \text{H}_6 + 3 \text{CO} + 3 \text{H}_2 \text{O}} \text{CHO} \xrightarrow{3 \text{n-C}_{18} \text{H}_{41} + \text{C}_3 \text{H}_6 + 6 \text{H}_2 \text{O}}
\end{align*}
\]

Figure 1: Reaction pathways for hydrodeoxygenation, decarboxylation and decarbonylation of trioleic triglyceride
the oils are entering and the mixture is leaving. \( W \) is the mass of oil; \( C_{ij} \) the weight percentage in the oil \( i \) of the fatty acid \( j \); A synthetic algae oil; B, C, D and E are oils to mix; 1 saturated; 2 mono-unsaturated; 3 di-unsaturated and 4 tri-unsaturated fatty acids. All oils employed in the preparation of SAO were supplied by Santandereana de Aceites–SACEITES Company (Bucaramanga, Santander).

![Figure 2: An ideal mixing unit to produce SAO](image)

### 2.2 Analysis of the synthetic algae oil
Fatty acid composition analysis of the SAO was carried out by Gas Chromatography (GC) with Flame Ionization Detector (FID). The column employed was a DB-23 (50% cyanopropyl-poly(methylsiloxane), 60 m x 0.25 mm x 0.25 mm) with helium at 1 mL/min as the carrier gas and a split ratio of 10:1. Injector and detector temperatures were 250 °C. Oven temperature started at 120 °C for 2 min, increased to 230 °C at a rate of 5 °C/min, and held at this temperature for 5 min. The reference standards for fatty acid methyl esters were purchased from Supelco.

### 2.3 Hydroprocessing of the synthetic algae oil
Hydrogenation of the SAO was performed employing a conventional hydrotreating catalyst (NiMo/\( \gamma \)Al\(_2\)O\(_3\)), which was previously activated by using straight-run gas oil containing 3 wt % dimethyl disulfide. All experiments were conducted in a trickled-bed reactor and reaction conditions were adjusted in 350 °C, LHSV of 2 h\(^{-1}\), feed flow 120 mL/h and hydrogen flow 472 mL/h. The process variable investigated, i.e., hydrogen pressure was varied from 40-90 bar.

Product samples were collected and analyzed for cetane index (ASTM D-4737), kinematic viscosity at 40 °C (ASTM D-445), acidity number (ASTM D-664), thermal stability (ASTM D-6468), bromine number (ASTM D-1159) and simulated distillation (ASTM D-7213) employing an Agilent 6890 gas chromatograph equipped with a fused silica 10 m x 0.53 mm x 0.9 mm column and a calibration mixture from C\(_3\) to C\(_{60}\).

After, reaction products were separated in a biphasic separator where the reaction pressure was reduced to almost atmospheric pressure. Liquid products were collected in the separator and gases are collected in a stainless steel container. The liquid products, i.e., aqueous phase and the less dense organic phase (hydroprocessed product) were then separated by decantation.
3. Results and discussion

3.1 Preparation and analysis of SAO
After testing different combinations of oils, it was found that the mixture of 729.33 g of linseed oil, 240.09 g of sunflower oil, 8.76 g of olive oil and 21.92 g of palm superstearin are required to prepare 1 kg of SAO. The fatty acid profile of this SAO grouped according to their degree of unsaturation, is reported in Table 1. It can be observed that this profile is close to that of the Chlorella vulgaris oil.

Table 1: Fatty acid composition of Chlorella vulgaris oil and SAO according to their unsaturation degree (wt %)

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>Chlorella vulgaris oil</th>
<th>Synthetic algae oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated</td>
<td>13</td>
<td>12.5</td>
</tr>
<tr>
<td>Mono–unsaturated</td>
<td>20</td>
<td>24.6</td>
</tr>
<tr>
<td>Di–unsaturated</td>
<td>28</td>
<td>27.6</td>
</tr>
<tr>
<td>Tri–unsaturated</td>
<td>39</td>
<td>35.3</td>
</tr>
</tbody>
</table>

3.2 Hydrotreating of SAO
Table 2 shows the properties of renewable diesel obtained from synthetic Chlorella vulgaris oil (RDSCV). These properties were compared to those of renewable diesel produced from crude palm oil, which is registered in Colombia by the mark Biocetano®. It can be noted that, at 40 bar, RDSCV has a lower cetane number and higher kinematic viscosity than Biocetano®. This is due to a decrease in the selectivity to normal paraffins C15, C16, C17 and C18 for hydrotreating of the SAO, as can be observed from the simulated distillation cuts of hydrogenation products showed in table 3. RDSCV presents a higher volume % of products with boiling points in the range between 344 ºC and FBP than Biocetano®.

RDSCV acid number is higher than of Biocetano®. This is because there is a greater presence of free fatty acids formed from the synthetic Chlorella vulgaris oil that cannot be fully deoxyhydrogenated. It has been demonstrated that the presence of oxygen-containing compounds of high molecular weight, like esters, in the reaction mixture causes the deactivation of the sulphide active phase of the catalyst during deoxyhydrogenation (Senol et al., 2005). Esters can be produced simultaneously by esterification of those free fatty acid and some alcohols assigned to reaction intermediates catalyzed by the acid sites of the alumina used as support in this type of catalysts (Guzman et al., 2010).

It can be also seen from table 2 that an increase in hydrogen pressure positively affects the properties of RDSCV, especially bromine and acid number which decreased from 6.4 to 0.4 and 3.75 to less than 0.1. Additionally, from table 3, selectivity to diesel range hydrocarbons 221–344 ºC is improved in 1.3 %, while light paraffinic products (<221 ºC) remains approximately constant. Finally, as can be inferred from table 2, RDSCV fulfills most of the specifications required for a diesel, i.e., high cetane number and thermal stability, low viscosity and low acid number.
Table 2: Properties of renewable diesel obtained from SAO and crude palm oil

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Limits</th>
<th>Biocetano® 40 bar</th>
<th>RDSCV 40 bar</th>
<th>RDSCV 90 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane number</td>
<td>min</td>
<td>45</td>
<td>92.50</td>
<td>79.13</td>
<td>79.90</td>
</tr>
<tr>
<td>Kinematic viscosity at 40 ºC</td>
<td>mm²/s</td>
<td>1.9-6.0</td>
<td>3.692</td>
<td>4.822</td>
<td>4.589</td>
</tr>
<tr>
<td>Bromine number</td>
<td>g Br₂/g</td>
<td>5.75</td>
<td>6.40</td>
<td>0.40</td>
<td>&lt; 0.10</td>
</tr>
<tr>
<td>Acid number</td>
<td>mg KOH/g</td>
<td>0.5 max</td>
<td>1.50</td>
<td>3.75</td>
<td>&lt; 0.10</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>% refraction</td>
<td>70 min</td>
<td>99</td>
<td>99</td>
<td>99</td>
</tr>
</tbody>
</table>

Table 3: Simulated distillation cuts of hydrogenation products obtained at different hydrogen pressure

<table>
<thead>
<tr>
<th>Distillation cuts</th>
<th>Biocetano® 40 bar</th>
<th>RDSCV 40 bar</th>
<th>RDSCV 90 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP – 221 ºC</td>
<td>0.9</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>221 – 344 ºC</td>
<td>89.9</td>
<td>77.1</td>
<td>78.4</td>
</tr>
<tr>
<td>344 ºC – FBP</td>
<td>8.2</td>
<td>19.6</td>
<td>18.3</td>
</tr>
</tbody>
</table>

3.3 Comparison between renewable diesel production by hydrotreating and transesterification of SAO

The amount of hydrogen employed in hydroprocessing of SAO was determined by analyzing of flue gases emitted at 90 bar. 327.4 normal L of hydrogen are needed to process 1 L of SAO. Considering the steam reforming of gas natural reaction showed in Equation 1, 78.178 g of methane are required. Moreover, to transesterify the same quantity of SAO using the best reaction conditions reported by Plata et al. (2010) and taking into account the reaction scheme to produce methanol showed in Equation 2, 140.55 g of methane are needed, almost twice the amount required to produce the hydrogen consumed in hydrotreating. Thus, this process appears as more renewable. However, further studies on catalyst and process optimization are still required, as conventional hydrotreating catalysts are deactivated during deoxyhydrogenation and hydroprocessing of pure vegetable oils involves extreme pressure and temperature conditions.

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (1)
\]

\[
3\text{CO} + \text{CO}_2 + 9\text{H}_2 \rightarrow 4\text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (2)
\]

4. Conclusions

The use of a synthetic algae oil based on *Chlorella vulgaris* fatty acid composition enabled to investigate the effect of the hydrogen pressure on the production and properties of renewable diesel obtained by hydroprocessing. It was found that the greater the hydrogen pressure, the greater the selectivity to diesel range hydrocarbons. Compared to Biocetano®, renewable diesel from synthetic algae oil had a less cetane number and higher viscosity and bromine and acid number. However, these properties fulfilled most of the specifications required for a diesel compatible biofuel. Moreover,
an increasing in hydrogen pressure improved those properties. Thus, synthesis of renewable diesel from algae oil by hydrotreating represents not only a way to deploy the competitive advantages of Colombia derived from its strategic geographic location and biodiversity, but also an approach to meet the demand for diesel compatible biofuels using the existing petroleum refinery infrastructure. Nevertheless, as discussed previously, further studies on catalyst and process optimization are still required.

Acknowledgments

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References

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