Production of Diesel Engine Fuel by Ozonation of Sunflower Seed Oil

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Abstract
In the first stage of this project we applied an additional process of ozonation and electroreduction to fatty acid methylester and tried to crack fatty acids with a long carbon chain into low molecular materials. The main purpose of these new treatments was to improve the disadvantages of biodiesel (BDF) like high viscosity, flash point and pour point. This new method was very effective to improve viscosity and flash point, but no improvement was found in pour point. Its flash point became around 25 °C which was not within the regulation of biodiesel standard. Therefore, we decided to employ methyl-transesterification as the basic method for BDF production, and tried to improve its high pour point by using additives. The optimization of reaction and purification process in BD production was done for the establishment of continuous BDF production system. In order to increase the business possibility of BDF, basic studies on the conversion of waste glycerol to 1,3-propandiol and the genetic breeding of sunflower for controlling oil production yield and the fatty acids composition in sunflower oil were conducted. The feasibility study on CDM in Thailand was also conducted, and we submitted its PDD to the UN evaluation committee.

Keywords : biodiesel, pour point, additives, glycerol, genetic breeding

1. Introduction
On February 16, 2005 the Kyoto Protocol came into force representing a global commitment by most of the world’s industrialized countries to reduce carbon emissions. Carbon emission reduction is now a universal goal. Many governments and international development agencies have programs to address rural agricultural development, environment policy and sustainable development. On December 27, 2002 Japanese cabinet also issued the vision named “Comprehensive strategies of Biomass Japan. In European countries and USA much attention has been paid on biodiesel (BDF), which is the methylester of fatty acid from triglycerides of vegetable and plant seeds oil. Owing to the characteristics of carbon neutral the production and use of BDF has been regarded as a countermeasure to curb global warming. The EU has decided to accelerate the application of biomass fuels and its proportion in 2005 was set at 2% of total fuel consumption. The proportion of biomass fuels is targeted to increase to 5.75% (11 million tons) by 2010. The US Department of Energy also plans to implement 30% BDF use for all vehicles by 2010. To be able to produce such huge amount of BDF, the government is closely cooperating with soybean farmers. In the US Congress, a bill has been passed on May 2004 that gives 1 cent tax exemption for every 1% BDF blended with oil. With this, the gap in prices between diesel oil and BDF is
further reduced.

While in Japan even after the issue of the vision the production amount of BDF is very limited (only 5000 kl/year), and any quality standard for BDF is not yet prepared. The purpose for BDF production in Japan was mainly for the preservation of environment and a reuse of waste materials. The uniformity of quality of waste oil is low and it hinders the application of economically effective continuous production process. Also, the output of household used edible oil is only 290,000 kl, pointing the problem of stable supply of raw material. This amount is too small to fight against global warming. More or less 20% of CO$_2$ emission in Japan comes from the transport sector; total of which is 267 M ton. Reducing this has become an urgent topic. Considering the following problems, we have to formulate a strategy to propagate sustainable large-scale production and use of BDF.

1) Large amount of vegetable oil has to be secured at a low price.
2) A reliable process has to be developed for continuous production of biodiesel.
3) Some additives have to develop to improve the fuel properties originated from raw vegetable oils.
4) Conversion technologies (bio-refinery) of waste parts of plant to valuable materials have to develop to make biodiesel business profitable.

2. Experimental

2.1 Selection of suitable vegetable oils for BDF mass production

Using several vegetable oils trial production of biodiesel based on methyl-transesterification was conducted, and their fuel properties were examined. We tried also the genetic breeding of sunflower to control its fatty acid composition.

2.2 Establishment of continuous production process for high quality BDF

We tried to establish a continuous production process of high quality biodiesel which should fit to or exceed the EN14214 standard. Additional processes of ozonation and electrolysis were first introduced into the conventional biodiesel production process. This modification of process was effective for reducing molecular weight of methylester and extremely reduced the viscosity and flash point. However, its flash point of 25 $^\circ$C is out of the regulation of biodiesel and similar to that of kerosene. Therefore, we decided to employ the well known methyl-transestrification and optimize its reaction and purification process by paying the attention to control regulated impurities especially the residual glyceride contents.

2.3 Development of additives to improve the fuel properties originated from raw vegetable oils

Since the fuel properties of low-temperature flow characteristics, oxidation stability and iodine value are highly dependent on fatty acid composition of raw materials, it was very difficult to improve only by modification of production process. We tried first to develop a new additive which can improve pour point of neat BDF and makes it possible to use pure biodiesel (B100) even in winter season. The other fuel properties like oxidation stability and iodine value depend on unsaturated fatty acid content, so that these properties are possible to improve by selecting the variety of sunflower which contains much more oleic acid.

2.4 Development of bio-refinery technologies

With regard to glycerol, we are trying to convert glycerol to 1,3-propanediol which is the raw material of the biomass plastic PTT. The waste glycerol issued from biodiesel production process contains methanol, base catalyst and soap. We have succeeded to remove the methanol by vacuum evaporation and the catalyst and soap by pH control. For the conversion to 1,3-propanediol an electro-reduction had been applied.

3. Results

3.1 Selection of suitable vegetable oils for BDF mass production

Using several vegetable oils trial production of biodiesel based on methyl-transesterification was conducted, and their fuel properties were examined (Table 1). As shown in Table 1, there are no remarkable differences in density, viscosity and flash point. However, low-temperature flow characteristics indexed by pour point clearly showed dissimilarities. Table 2 shows the fatty acid structure of different plants and animals. Usual vegetable oil would include oleic, linolic and linoleic acid, more than 50% of which is unsaturated. Palm and coconut oil, however, have more saturated
fatty acids. The same is true with animal fats like cow and pig oils. These saturated fatty acids content influence the pour point of BDF to a large extent. The fact that the quality of saturated fatty acid, specifically, relative proportions of palmitic acid, lead to a higher pour point is established here. To minimize the pour point problem, the careful selection of raw material should be done. Moreover, we have to identify the substances in BDF which affect pour point and develop the methods for eliminating or limiting their influence.

Rape seed and sunflower oil with low content of saturated fatty acid was highly recommended. Especially, sunflower has many varieties, and not only seed but also other parts of plant can be converted to useful materials like pulps from its stem. Therefore, we decided to use sunflower as the most suitable oil plant for biodiesel production.

Table 1. Fuel properties of BDF prepared several different kinds of vegetable oil.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Rape Seed Oil</th>
<th>Sunflower Oil</th>
<th>Soy Been Oil</th>
<th>Palm Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/ml)</td>
<td>0.871</td>
<td>0.873</td>
<td>0.870</td>
<td>0.842</td>
</tr>
<tr>
<td>Viscosity (cSt)</td>
<td>4.43</td>
<td>4.30</td>
<td>4.12</td>
<td>5.19</td>
</tr>
<tr>
<td>Flash Point (°C)</td>
<td>178</td>
<td>182</td>
<td>186</td>
<td>179</td>
</tr>
<tr>
<td>Pour Point (°C)</td>
<td>-13</td>
<td>-5</td>
<td>-2</td>
<td>12</td>
</tr>
<tr>
<td>Cloud Point (°C)</td>
<td>-4</td>
<td>1</td>
<td>1</td>
<td>18</td>
</tr>
</tbody>
</table>

Table 2. Fatty acid composition of vegetable oils and animal fats.

<table>
<thead>
<tr>
<th>Oil and Fat</th>
<th>Lauric acid</th>
<th>Myristic acid</th>
<th>Palmitic acid</th>
<th>Stearic acid</th>
<th>Oleic acid</th>
<th>Linoleic acid</th>
<th>Linolenic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Number/Double Bond Number</td>
<td>12:0</td>
<td>14:0</td>
<td>16:0</td>
<td>18:0</td>
<td>18:1</td>
<td>18:2</td>
<td>18:3</td>
</tr>
<tr>
<td>Rape Seed</td>
<td>4.0</td>
<td>1.7</td>
<td>58.6</td>
<td>21.8</td>
<td>10.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soy Bean</td>
<td>10.3</td>
<td>3.8</td>
<td>24.3</td>
<td>52.7</td>
<td>7.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sunflower</td>
<td>6.7</td>
<td>3.7</td>
<td>19.6</td>
<td>49.0</td>
<td>7.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corn</td>
<td>11.2</td>
<td>2.1</td>
<td>34.7</td>
<td>50.5</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Olive</td>
<td>9.9</td>
<td>3.2</td>
<td>73.0</td>
<td>10.4</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palm</td>
<td>44.2</td>
<td>4.5</td>
<td>39.3</td>
<td>9.6</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coconuts</td>
<td>47.0</td>
<td>18.0</td>
<td>9.0</td>
<td>7.0</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jacaranda</td>
<td>14.0</td>
<td>8.0</td>
<td>34.0</td>
<td>43.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peanuts</td>
<td>11.4</td>
<td>4.0</td>
<td>41.5</td>
<td>34.9</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Case Fat</td>
<td>3.0</td>
<td>22.6</td>
<td>17.6</td>
<td>43.0</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pig Fat</td>
<td>2.0</td>
<td>20.5</td>
<td>12.1</td>
<td>42.5</td>
<td>9.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3.2 Establishment of continuous production process for high quality BDF

The emphasis of the study was on controlling regulated impurities especially the residual glyceride contents in BDF which are highly affected by the production method and process conditions. Using crude SFO transestrification with methanol was conducted under several different operating conditions: temperature: 25–60 °C, mixing intensity: 300–600 rpm, catalyst amount: 0.1–1.0 %wt. of oil, molar ratio: 6–20 mol-MeOH:mol-oil.

The reaction rate and conversion became higher by increasing the reaction temperature. But even when methanolysis was carried out at 60 °C, the unconverted triglyceride in the BDF (0.6%) is much higher than the 0.24 wt% limit imposed by EN 14214 standard. The oil:methanol molar ratio was found to be the most important parameter to improve the contents of unconverted triglyceride. Until now the molar ratio of 1:6 was believed to be the optimum and the use of higher molar ratios was uncommon. As shown in Fig 1, however a molar ratio higher than 10 is necessary to make a total glyceride content lower than 0.24 wt%.
The refining process consists of glycerol separation from crude methylester, recovery of residual methanol, removal of residual base catalyst, soap and free glycerol by washing with water. Although much of the soaps formed will collect in the glycerol phase, a small amount will stay in the biodiesel. The washing process, however, tends to become a delicate operation due to the likelihood of the formation of an emulsion of soap-ester-water mixture especially when employing bulk mixing for washing. This condition should be avoided as recovery of the biodiesel would be very difficult and, in extreme cases, impossible. By deactivating the catalyst and soap with a neutralizing acid, bulk washing can be carried out without any difficulty even under vigorous stirring. In the absence of a neutralizing acid, the washing process can easily emulsify the mixture which lowers recovery of the biodiesel. The use of a mild acetic acid solution as the first washing medium proved to be a better alternative with no occurrence of an emulsion layer such that the water phase would easily separate from the biodiesel. Also, since its boiling point (119°C) is near that of water, it can be co-distilled in the drying step of the process which further limits the acid value of the end product.

Based on the above mentioned studies done on the process, a flow-sheet that will be adopted for the pilot-scale production of sunflower BDF was prepared as shown in Fig. 2. The detail design of pilot-scale process with a production capacity of 2000 l/day has been completed. Laboratory-scale production of sunflower esters was done based on this process flow-sheet and samples were sent to Idemitsu Techno Research Center (Chiba, Japan) for analysis of important quality parameters.

3.3 Development of additives to improve the fuel properties originated from raw vegetable oils

1) Improvement in pour point

The low-temperature flow properties of BDF are mainly dictated by the fatty acid profile of the feedstock material rather than production methods. As shown Table 3, we revealed that the product prepared by ozonation of vegetable oil can act as pour point depressant for BDF by altering its crystallization behavior when subjected to low temperatures (process in the subject of current patent application). Significant decrease in pour points of samples added with the additive was observed in SFO, SBO and RSO biodiesel even with the addition of only 1%. In these samples however, cloud points were not affected. In the case of PMO biodiesel, any improvement on pour point was not observed. The high pour point of PMO biodiesel makes the additive ineffective as pour point depressant. The mechanisms of action of pour point depressants occur in the solid phase. In the case of PMO biodiesel, the pour and cloud points of the neat samples are 12.0 and 18.0 °C, respectively, higher.
Table 3. Effects of new additive on pour point of BDF prepared from different vegetable oils.

<table>
<thead>
<tr>
<th>BDF</th>
<th>RSO-BDF</th>
<th>SFO-BDF</th>
<th>SBO-BDF</th>
<th>PMO-BDF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Properties</td>
<td>Neat</td>
<td>1%</td>
<td>Neat</td>
<td>1%</td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>0.871</td>
<td>0.866</td>
<td>0.873</td>
<td>0.878</td>
</tr>
<tr>
<td>Viscosity (cSt)</td>
<td>4.43</td>
<td>4.68</td>
<td>4.30</td>
<td>4.45</td>
</tr>
<tr>
<td>Flash point (oC)</td>
<td>178</td>
<td>155</td>
<td>182</td>
<td>162</td>
</tr>
<tr>
<td>Pour point (oC)</td>
<td>-13</td>
<td>-30</td>
<td>-5</td>
<td>-24</td>
</tr>
<tr>
<td>Cloud point (oC)</td>
<td>-4</td>
<td>-6</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4. Improvement in pour point of BDF mixed diesel oil by new additive.

<table>
<thead>
<tr>
<th>BDF</th>
<th>Diesel</th>
<th>B10</th>
<th>B20</th>
<th>B30</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>w/o</td>
<td>w/</td>
<td>w/o</td>
<td>w/</td>
</tr>
<tr>
<td>Density (15°C)</td>
<td>0.825</td>
<td>0.837</td>
<td>0.83</td>
<td>0.835</td>
</tr>
<tr>
<td>K. Viscosity (40°C)</td>
<td>2.48</td>
<td>3.17</td>
<td>2.66</td>
<td>2.87</td>
</tr>
<tr>
<td>Pour point (oC)</td>
<td>-10</td>
<td>-25</td>
<td>-9</td>
<td>-25</td>
</tr>
<tr>
<td>Cloud point (oC)</td>
<td>-1</td>
<td>-2</td>
<td>-1</td>
<td>-2</td>
</tr>
<tr>
<td>Flash point (oC)</td>
<td>61</td>
<td>68</td>
<td>64</td>
<td>68</td>
</tr>
</tbody>
</table>

2) Improvement in torque
The other advantage of this novel additive is the function to improve the torque of diesel engine.
As shown in Fig. 3, when B100 of SFO-BDF employed as the fuel the torque was about 10% lower compared to diesel oil especially under a low revolution speed. However, once the additive was mixed BDF at 1%, the torque was completely recovered. This characteristic is very important in the application of BDF as a fuel for buses which frequently repeats stop and start. It will contribute to save fuel consumption.

![Fig. 3. Effect of additive on torque of BDF.](image)

3.4 Genetic breeding of sunflower

Since any practical method for formation of sunflower transformant has not yet known, we conducted basic research works to establish the transformation system of sunflower. With regard to the transfer of foreign genes into sunflower, transgenic hairy roots could be induced from cotyledon explants of sunflower at high frequency by the infection with *Agrobacterium rhizogenes* strain R1000 harboring *rol* genes. In advance to the detail experiments four varieties (Hybrid sunflower, Pacino, Sonja and Valentine) were selected from the view points of high shoot regeneration potential. Using these varieties we tried to establish transformation system consisted from three steps shown in Fig. 4; 1) Gene introduction, 2) Shoot regeneration and 3) Plant regeneration and seed formation.

![Figures 5 shows the protocol for shoot regeneration and gene introduction.](image)

Figures 5 shows the protocol for shoot regeneration and gene introduction. Plant regeneration through adventitious shoots formed on the shoot apical meristem explants was rather easy in Pacino and hybrid sunflower. In these varieties, the regenerated plants grow normally and form many seeds under a culture room condition. Shoot regeneration after transformation by *Agrobacterium* was easier in branching-type sunflowers (Pacino, Sonja and Valentine). In addition, transformed tissue area was larger in these branching varieties. From these results, we selected Pacino as a most useful sunflower variety for the production of transgenic sunflower. It shows dwarf phenotype and very easy to cultivate in cultivation.
We expect that Pacino becomes a model sunflower for future molecular genetic experiments.

Fig. 5. Protocol for shoot regeneration and gene introduction.

Using the GUS assay which specifically stains transformed cells we have confirmed that external gene was successfully introduced. Especially, in branching type sunflower, Pacino and Sonja a broad region of shoot was stained in blue color.

The final step is the induction of roots from the shoots into which some external gene was transferred, and the regeneration of whole plants. Using the protocol for root induction (see Fig 9) we could induce the roots and culture the regenerated plants. The regenerated Pacino made flower and seeds. We have confirmed that the branching sunflower, Pacino is suitable for preparation of transgenic sunflower. Using this transformants it is now very promising to establish a F1 strain which is suitable for BDF production.

Fig. 6. Confirmation of transformed cells by GUS assay.
4. Conclusions

Though the three years NEDO project we got the following fruitful results:

1) Due to the optimization of transestrification process and refinery process we could establish a very practical continuous BDF production process. Since the detail plant design has also been completed, we are ready to start a pilot-scale production of high quality BDF.

2) We develop a novel pour point depressant which can drop the pour point of sunflower BDF to $-24^\circ$C. This additive is effective not only pure biodiesel but also to biodiesel mixed with fossil diesel oil. Furthermore, this additive has a function to improve the torque of diesel engine. This additive gives us a big chance to propagate the application of biodiesel.

3) The practical genetic breeding method of sunflower has been established. In future we can freely produce sunflowers with some special characteristics which required for construction of sunflower plantation under different climate and soil conditions.

Acknowledgement

Owing to the great support of we succeeded to get the above mentioned fruitful developments. These results will be very useful to repress green house effects.

The list of the most important papers and patents from the project

Papers (Total 8)


Presentations (Total 19)

Patents (Total 3)