BIODIESEL FOR PUERTO RICO

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ABSTRACT

The University of Puerto Rico, in collaboration with the Department of Energy-National Renewable Energy Laboratory, Panzardi-ERM, Caguas and Isabela Municipal Government, Puerto Rico Senate Energy Committee, and Puerto Rico Energy Affairs Administration, is studying the transesterification process to convert waste greases, used cooking oil, and animal fats into fatty acid methyl esters (FAMEs). This is an alternative diesel fuel known as Biodiesel. In this study (Phase I) the long-term objective is the establishment of a Biodiesel Industry in Puerto Rico. Other supporting objectives include the development of laboratory expertise on Biodiesel process technologies using available raw materials, “Top Down” and “Bottom Up” studies regarding raw material availability and potential customers in Puerto Rico, and conduct engineering analysis for scale-up. The former includes the development of a reaction system utilizing ultrasound mixing which results in very high conversions to biodiesel from used cooking oil and tallow. The latter includes a preliminary process design “tailored” toward the needs, resources and opportunities available in Puerto Rico. In addition, an aggressive demonstration initiative was initiated to develop the customer base. As of July 2002, six demonstrations were on-going participating two municipalities, a state government agency and three companies. In this presentation the most important results from all the Phase I project tasks will be discussed.

Key Words: Biodiesel, Fatty Acid Methyl Esters (FAME), Used Cooking Oil & Renewable Energy

INTRODUCTION

On October 2000 the University of Puerto Rico at Mayagüez (UPRM) obtained a grant from the Department of Energy for the project Grease Biodiesel for Puerto Rico. The key objective is to develop a Center for Biodiesel Expertise in the Caribbean that could lead to and support a biodiesel industry in Puerto Rico using domestic feedstocks such as recycled restaurant greases and other imported feedstocks. The projects include resource assessment (task 1), market assessment (task 2), and engineering designs (task 4) for producing and using biodiesel in Puerto Rico. Also, identifying Industry Partnerships (task 5) for Biodiesel Production and Marketing and Demonstrations is required. Another key component of the Grease Biodiesel for Puerto Rico Initiative is developing laboratory expertise on biodiesel processing (task 3) technologies and develop data for engineering designs. This includes investigating a variety of raw materials, developing analytical methods and reaction engineering expertise. In this presentation the most important results from these tasks will be discussed.
METHODOLOGY AND RESULTS

As mentioned earlier the Biodiesel Initiative at Puerto Rico involves several tasks. These will be discussed in the following subsections:

**Tasks 1 and 2** – The main objectives of these tasks were to develop market data on the supply of biodiesel feedstock, quality, value, composition, current use, and pretreatment. Another objective was to develop market data on the highest and best uses of biodiesel in the power and transportation industries. In addition, an evaluation of potential markets for biodiesel synthesis byproducts such as glycerol and fertilizer was required. In performing the data collection process a “top down” and bottoms up” approach was used. The former refers to obtaining data from government agencies and/or regulating agencies and relevant organizations. The latter involved interviews at the source or “generators” and “collectors”. This approach was used for both raw material suppliers and consumers. In general, as can be seen in figure 1, the information was obtained by municipality. In the figure, the restaurant per capita for Puerto Rico is shown. Several other maps that included fast food restaurants, hospitals and hotels were also generated.

![Puerto Rico Restaurant Density](image)

Figure 1: Puerto Rico Restaurant Density

The most important result in the resource assessment study was that in Puerto Rico there is a collection potential of used cooking oil and greases between 5.0 to 10.0 million gallons per year of which only 1.0 to 1.5 is presently collected. This implies that an alternate raw material source may be required especially for a 10.0 million gallons per year or bigger biodiesel production facility. As will be discussed below, a 10 million gallons per year would be commercially viable in Puerto Rico.

In the market assessment study, the most relevant result was that diesel consumption in Puerto Rico is distributed as follows (millions of gallons per year); Agriculture (3), State Government (17), Services (18), Construction (32), Manufacture (33), Ground Transportation (37), Boats/Ships/Cruises (38), Electric Power Authority (414) and others (21). Based on the surveys and excluding the Electric Power Authority, the market was also divided into three categories of customers (gallons/year); 10,000 – 100,000, 100,000 to 1.0 million and greater than one million. The last group includes Bus Authority (3.4 million gallons/year), Cruise Ships (18.0 million gallons per year) and several pharmaceuticals (boilers). The middle range involves fleets from waste collection companies and other companies and San Juan municipality. Also the Telephone Company is in this range but for their remote location diesel generators. The lower range includes most of the municipalities. Regarding the Electric Power Authority, most of their diesel is utilized in several 10 MW turbines located around the island. They are used during peak periods.

**Task 3** - One of the key components of the Biodiesel for Puerto Rico Initiative is the development of a Center of Expertise (task 3). The procedure that was used in this task can be divided in two main components, Analytical and Conversion. The former emphasizes in developing expertise in critical analyses for both raw materials (oils and greases) and products (biodiesel and glycerol) in order to support a biodiesel industry. The ASTM PS121 (now ASTM 6751) required methods were used for the biodiesel quality analysis. The oil and greases were analyzed with...
standard analytical methods used in the Food Processing Industry. An “analytical matrix” was developed. Also, a Cetane No. and Cloud Point analysis certificate was obtained from a local laboratory.

The Conversion component is subdivided into Mass Balance Closure/Process Design Support, Reaction Engineering, Raw Materials/Catalysts, Patent Invention Disclosure and Dissemination efforts. In addition, the Reaction Engineering studies involved the effects of Agitation (Mechanical versus Ultrasound), Equilibrium (reactants ratio) and Temperature. The Raw Materials/Catalysts efforts included catalyst recovery studies with Ion Selective Electrodes and X-ray Fluorescence. It should be mentioned that Panzardi-ERM (PERM) closely collaborated with UPRM personnel in this task. In addition, so far, more than twenty undergraduate students and two graduate students (Ph.D. and MS) have participated in these studies.

In the Mass Balance Closure/Process Design efforts several Preliminary Process Flow Diagrams (PFDs) were generated using the process design software Superpro Designer 4.5 version. Some of the cases that were considered included virgin oils, tallow and yellow grease based biodiesel synthesis. In addition there were also other process design support activities. This includes determining and providing PERM personnel with chemical and physical properties of raw materials and products. Also several experiments were requested by PERM and performed related to storage, catalyst solution stability and products separation issues.

The major component of the Conversion component was in Reaction Engineering, which included Mixing (see table below), Equilibrium and Temperature effects. These were selected since they are related to biodiesel synthesis inherent limitations during basic transesterification.

Table 1: Ultrasound versus Mechanical mixing comparison

<table>
<thead>
<tr>
<th>Reaction rate constant (k)</th>
<th>Average value</th>
<th>Literature value *</th>
<th>Activation energy (literature value)**</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
<td>40°C</td>
<td>60°C</td>
</tr>
<tr>
<td>T6 → D6</td>
<td>0.0110</td>
<td>0.0402</td>
<td>0.1056</td>
</tr>
<tr>
<td>kT6 [wt.*min]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16 → DG</td>
<td>0.0276</td>
<td>0.1060</td>
<td>0.3200</td>
</tr>
<tr>
<td>kDG [wt.*min]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


In this reaction cooking oil and/or animal grease reacts with alcohol to form esters (biodiesel) and glycerol. A 3:1 stoichiometry alcohol/oil ratio is required to obtained the esters. It is catalyzed by base. The reaction proceeds in steps; triglyceride to diglyceride, then to monoglyceride and in the last step glycerol is formed. A molecule of ester (biodiesel) is released in each step. The oil/grease and alcohols are immiscible thus requiring an effective agitation. The esters and glycerol are also immiscible. Also, the catalyst has more affinity for the alcohol phase (and glycerol). It should be mentioned that a Patent Invention Disclosure was submitted documenting the potential advantages of ultrasound mixing for bulk and polishing reaction conditions. A comparison between ultrasound and mechanical mixing is shown in table 1.

Notice that the estimated values using ultrasound were 3.0 to 4.5 times higher than those reported in the literature using mechanical agitation. Also, the estimated activation energies were consistent with those reported. In the next
figure typical graphs that were obtained to determine the order and reaction rate constant are shown. A differential initial rate method was used in order to be able to neglect reversibility effects. Also, a pseudo order approach was used for the methanol. Its contribution is included in the pseudo rate constant.

\[
TG \xrightarrow{k_{TG}} DG
\]

\[
\ln \left( -\frac{d[TG]}{dt} \right) = \ln k'_{TG} + \beta A \ln [TG]
\]

\[
\frac{1}{[TG]} = k'_{TG} t + \frac{1}{[TG]_0}
\]

**Figure 2: Differential rate method typical results.**

On a related preliminary study the Raleigh-Pesset equation was used to determine the radius of bubbles during their growth and collapse cycles during ultrasound mixing. Notice in the following graph that in a cycle the bubbles grow from 1.0 to 70, 121 and 220 µm for 25, 40 and 60°C reaction conditions, respectively. This compares with bubbles formed during mechanical agitation, which typically are bigger than 100 microns. More studies are been performed in this area.

**Figure 3: Ultrasound mixing bubble growth**
Regarding equilibrium, esterification reactions are highly reversible. This normally translates into high reactant concentrations in the “crude” product. However, equilibrium behavior can be used as a processing tool to improve the conversion especially varying the reactants ratio. The effect of temperature was also studied due to its strong influence on both reaction rates and equilibrium concentrations. High reaction rates are favored at high temperatures. However, for exothermic reactions, such as transesterification, reactants equilibrium concentrations increase at high temperatures.

The Raw Materials/Catalyst efforts emphasized basic transesterification with KOH as catalyst. Ion exchange resins were also investigated with limited success. Also, extensive studies with tallow were performed due to the commercial potential of this reactant in the Caribbean. Commercial Virgin Oils were also tested as references in addition to recovered trap grease. Regarding alcohols, methanol was preferred, since it is readily available pure and in waste streams in Puerto Rico. Other alcohols were also studied such as ethanol, butanol and isopropanol. In the area of catalyst recovery, two analytical methods are being investigated, Potassium Ion Selective Electrode (Orion 13-620-532) and X-Ray Fluorescence (Asoma Model 200). The latter detected potassium in the Glycerol phase where it accumulates due to the polar nature of both compounds. The ion selective electrode studies are in progress.

In the Patent Invention Disclosure and Dissemination efforts, several presentations and demonstrations were given including Conventions, Companies/Agencies, Workshops, and Schools. Also, a patent invention disclosure was submitted to the UPR Patent and Trademark office. Based on his initial evaluation and literature review, it seems that the proposed concept is novel.

**Task 4** – This task was performed mainly by Panzardi-ERM in collaboration with UPRM personnel. The main objective was developing a conceptual design for a biodiesel manufacturing facility in Puerto Rico. This facility should be able to process a wide variety of raw materials including tallow, used and virgin cooking oils. The study included turnkey units from Energea (Austria) and Química Nova (Argentina) and a “criollo” facility designed utilizing experimental data from the University of Puerto Rico. The main result from the study was that the investment for a facility that could produce between 10 to 15 million gallons per year of biodiesel would be approximately 6.0 to 10 million dollars. A preliminary process flow diagram is shown in the next figure. The facility is divided into four sections including raw material handling and pretreatment, reaction, alcohol separation and products purification.

In addition to the design, a financial analysis was performed to determine the economic viability of the facility. A sensitivity analysis was performed utilizing sales volume growth (2 – 5%), raw material cost (0.10 – 0.15 $/lb), investment (1.5 – 2.0 $/gal) and biodiesel sales value (1.30 – 1.50 $/gal). In most cases, net present values higher than 10.0 million dollars were obtained. Breakeven analyses were also performed. In both cases, as reported in the literature, the raw material cost is the controlling variable contributing to more than 75% of the expenses.

**Task 5** - Another key component of the Biodiesel for Puerto Rico Initiative are the Demonstrations (Task 5). As shown in the following figure this was also very successful.

As of July 2002, six demonstrations were ongoing participating two municipalities, a state government agency, and three companies. The number of participants is expected to triple within this year. Several areas will be tested including Generators, Diesel trucks and boats and boilers. Some of the comments and observations from the demonstrations participants are that diesel emissions smell disappeared and a reduction of the typical sound of diesel engines. Also, an acceleration improvement has been observed.

**Acknowledgements** – Other collaborators that participated in this project are Drs. Edna Negrón, Arturo Portnoy and Lionel Orama, Professors David Muñoz, Jaime Sepúlveda and Edgar Soto and Graduate Students Ernesto Borrero and Fabio Alape from UPRM. In addition, over thirty undergraduate students participated. Panzardi-ERM Collaborators include Engineers Edwin Ayala, Angel Acosta, Félix Colón, Carlos Amado & Nelson Reyes.
Figure 4: Biodiesel Production Facility Preliminary Process Flow diagram

Puerto Rico Biodiesel (B100) Consumption Yardstick

Biodiesel Demos in Puerto Rico
- T - Transportation
- G - Generator
- B - Boiler

- On-going
- April Start-up
- Pending

- 100+ Drums, Phase 2 Target
- 45 Drums, Phase 1 Goal, July 2002
- 10 Drums, April 2, 2002
- 3 Drums, March 18, 2002

Figure 5: Biodiesel Demonstrations location