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ABSTRACT

The biodiesel process itself is more than just a chemical reaction. The practical aspects of how to turn an ordinary reaction into a large full-scale industrial plant are of utmost importance. It has been proven that bench top reactions and equipment often do not properly scale up to full processing plant size, and biodiesel is no exception.

Concerns for the feedstock such as fatty acid content, fatty acid profile, phosphorus, sulfur, moisture, and other various qualities are evaluated along with the overall cost of not taking time to tightly control these specifications.

Biodiesel product specifications are also discussed, along with the variances in specifications from location to location and the significant differences of each. The importance of how to label or market the biodiesel is also a concern for all involved, as the media can quickly turn a small error into a worldwide embarrassment for the biodiesel community.

Although the intent of making biodiesel is not to make glycerine, the glycerine component and its treatment are an important economic decision that will affect the overall profitability of the facility.

This paper includes information learned during the recent construction of the largest US plant dedicated to biodiesel production.

INTRODUCTION

The processes and production of biodiesel (methyl ester) from vegetable oil and animal fat feedstocks remain a strong growth market in the United States and Canada as well as the European Union. Currently, the U.S. and Canada methyl ester capacity is 200 million GPY (US gallons per year), or 700,000 MTPY (metric tons per year), and the Europeans are nearing 573 million GPY (2 million MTPY) of dedicated capacity. Expected market demand and production incentives suggest that volumes in these industrial markets could exceed 1.1 billion GPY (3.8 million MTPY) by 2007. Currently, 24 countries worldwide produce biodiesel, mostly in Europe, followed by the U.S. Other related oleochemical plant capacity and production data are confidential in nature; many existing oleochemical companies periodically divert methyl ester production to fuel markets. Current volumes consumed in Europe are approximately 345 million GPY (1.2 million MTPY) and the North American market reached only 20 million GPY (70,000 MTPY). These capacity and consumption numbers are generalized due to lack of formal reporting in some national markets, confidential plant capacity and production by companies, and the moving target nature of pinning these down over the last few years. (Austrian Biofuels Institute, 2002 and Bockey, 2002, U.S. Department of Energy, 2003).

<table>
<thead>
<tr>
<th></th>
<th>2001</th>
<th>2016</th>
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<tbody>
<tr>
<td>Diesel</td>
<td>33,129</td>
<td>100%</td>
</tr>
<tr>
<td>B100</td>
<td>1,644</td>
<td>5%</td>
</tr>
<tr>
<td>B5</td>
<td>32,870</td>
<td>99.20%</td>
</tr>
</tbody>
</table>

It is expected that U.S. market could reach 2.7 billion gallons (95 million metric tons) in 2016 based upon theoretical limits for all feedstocks and land usage as presented in TABLE 1. The DOE data is based upon full biomass feedstock utilization.

Scale up from lab and pilot plants requires significant effort in both theoretical calculations and practical engineering from equipment design through to start up. This paper reviews the practical experience Crown learned in building a 12 million GPY (40,000 MTPY) biodiesel plant, the largest dedicated to biodiesel in the U.S. It is expected that technology development will provide significantly lower costs of feedstock and high unit processing capability from world-scale plants.

CHEMICAL REACTION FOR BIODIESEL

Production of methyl esters using vegetable oil or animal fat feedstock requires selective catalysis and controlled process conditions to meet customer driven product specifications. The key issue is the purity of the feedstock. The resulting reaction is called “transesterification” where the catalyst speeds the exchange of glycerol with three methanols creating methyl esters of fatty acids as noted in Figure 1.

**Figure 1. Schematic of the Transesterification Process**
Effectively, the resulting glycerine separates from the fatty acid methyl esters by gravity. Many proprietary and patented processes govern the many aspects in these chemical reactions, separations, and subsequent purification steps.

**FEEDSTOCK ISSUES**

The purity and composition of the feedstock affect the yield of the final products. Generally, the higher content of free fatty acids (FFA), water, phosphorus, sulfur, and other contaminants, the more expensive or difficult the process becomes.

**FFA**

FFA presence leads to the use of an increased amount of catalyst and thus other chemical usage as well. An increase in catalyst will result in higher salt and water concentration in the crude glycerine because an increase in catalyst will increase the amount of acid needed to be neutralize the catalyst. Aside from the increased cost of these chemicals, the presence of FFA causes a larger potential for soap formation and all the production issues associated with soap, including more difficult phase separations and more frequent cleaning of process vessels for removal of the soap.

Although FFA can be acid catalyzed in a reaction with methanol to form methyl esters, the amount of acid required is much higher than the amount of catalyst used in the transesterification of neutral oil. The reaction also does not go as far to completion as transesterification, which may lead to the resulting biodiesel product to be out of spec on FFA. Acid catalysis of FFA to methyl esters also results in higher salt and water formation.

**Water**

Water presence creates soap and all the problems associated with soap as mentioned above.

**Phosphorus**

Phosphorus presence leads to an increased difficulty in the separation of the biodiesel and glycerine phases. It may also cause a problem with accurate level detection of the interface layer within a decanting vessel. In addition to creating process problems, an increase in phosphorus increases the likelihood of phosphorus in the biodiesel product, causing it to be out of specification.

**Sulfur**

Sulfur is a product specification issue because very little that is present in the feedstock will be removed in the biodiesel process. A feedstock with high sulfur needs to be either blended with a low sulfur feedstock in order to reduce the amount of sulfur in the product or not used at all. One of biodiesel’s positive points is that it can replace the need for sulfur in petroleum diesel. It would be counterintuitive to allow a higher level of sulfur to be in a B100 biodiesel compared to petroleum diesel. Legislating the reduction of sulfur in petroleum diesel is being discussed and mandated in various parts of the world and it
makes sense that biodiesel specifications will likely not be allowed to become less strict than its petroleum diesel counterpart. What may be fine for a high sulfur feedstock now could easily become inappropriate.

The European biodiesel feedstock supply is 84% rapeseed and the U.S. and Canada are driven by soy oil supply as well as programs for soybean and canola planting, similar to Europe. Used oils, sometimes called “recycled frying oils” as well as animal fats are processed in these markets, although the reduced yields and processing costs become critical economic factors. Under normal conditions with low FFA clean feedstocks, the net yield is in excess of 98% with production costs approximately 20% of operations. Most producers report raw material feedstock near to 80% of production costs. Hence, there are strong factors that favor low cost feedstocks. US feedstock supply is 79% virgin soy oil, but significant production potential exists with residual corn oil (maize) from food and ethanol processes. Finally, continued research points the way to high efficiency and yields using waste oil and fats. Additional significant volumes remain a potential should the U.S. and Canadian governments authorize industrial crops such as mustard (Brassica sp.).

Palm oil and palm kernel oil production is the world’s highest yield oilcrop at 5.5 metric tons/hectare compared to the other oilseeds. This offers new opportunities to develop high yield processing in key oil producing regions where biodiesel can replace petroleum diesel, especially helping reduce air pollution in urban areas. We see a solid market developing to use high hectare productivity PO and PKO to produce excellent biodiesel for use in key Asian urban centers where petroleum diesel is currently identified as a major health issue.

**PRODUCT SPECIFICATIONS**

Two specifications currently exist that determine the market and commercial character of biodiesel production. One, the ASTM (D6751) and, two, the CEN (pr EN14214) require purity levels demanded by engine manufacturers and petroleum suppliers. Product specifications are driven by consumers with limited input by producers, unlike petroleum fuel markets. In most cases, the distribution chain from manufacturing to consumption involves a product quality assurance program based upon ISO (BQ9000). The U.S. based National Biodiesel Board (NBB) supported the ASTM specification development and currently is working towards a B20 specification for 20% biodiesel blends with petroleum diesel. Also, the NBB backs the development of BQ9000 programs to assure quality is maintained from production to consumption. Crown is active in the NBB in a variety of roles. The driving force in both the product specifications and the quality programs is to develop confidence in biodiesel amongst the petroleum producers and distributors as well as the diesel engine Original Equipment Manufacturers (OEM). It can not be stressed enough that production to specification and meeting recognized quality programs mean only significant producers with strong capitalization will join this market. Essentially, there is no room for under capitalized manufacturers in the market where world-scale plants will provide both high quality and low unit costs of production.
PLANT DESIGN

FIGURE 3. Typical Biodiesel Plant View

Plant design is a collaborative effort by the design and engineering firm with the plant owners to optimize the yield, mass balance and integration with existing or new feedstock facilities. In most cases, biodiesel plants are designed as part of larger oilseed processing operations. It is unlikely any new plants will be constructed as “stand alone” facilities. This allows optimization of feedstock and product storage and integration with transportation and utilities.

The trend is towards large facilities instead of small. As with almost any process industry, a large plant is more efficient than a small plant due to “economy of scale.” The major holdback facing the biodiesel industry against building larger plants similar to the sizes used for vegetable oil refining (an industry most can relate to considering the feedstocks used for making biodiesel) is consumer demand. As demand increases, there will be little to stop an increase in the size of the average biodiesel processing plant because current biodiesel plants are nowhere near what can be considered “large.”

A modern transesterification plant is continuous instead of batch. A continuous plant leads to better heat economization, better product purity from phase separation by removing only the portion of the layer furthest from the interface, better recovery of excess methanol in order to save on methanol cost and regulatory issues, minimal operator interference in adjusting plant parameters, and lower capital costs per unit of
biodiesel produced. One particular processor that has run both batch and continuous biodiesel plants has vowed never to run a batch plant again.

Feedstock to the biodiesel plant should be as consistent as possible. Although the best feedstock for a biodiesel plant would be RBD vegetable oil, it has been found that an acid degummed soy oil (or equivalent) will be virtually as easy to process. Lower quality feedstocks can be used as starting points, but we have found that the costs associated with pretreating these lesser quality feedstocks are not to be underestimated. It is difficult to quantify the exact cost of pretreating these lower quality feedstocks, as they tend to vary significantly in consistency. A prime example is the collection of waste grease from various locations. Even waste grease from the same location can vary substantially. It is often the unknown component in the feedstock, not an elevated level of FFA or phosphorus, which causes problems with processing.

Another important consideration is wash water discharge. From experience at previous plants, it was determined that reducing or eliminating the wash water discharge would be highly desirable. It has been found that recycling of the wash water creates no side effects that cannot be already handled in the process. A portion of the water eventually makes it to the glycerine phase, but this is also chemically treated along with the glycerine to make the product leaving the plant acceptable as a crude glycerine. This crude glycerine can then be processed along with other spent soap lye or sweetwater sources without the need for additional chemical treatment at the glycerine processing plant.

In general, the process consists of five sections:
1) Two-stage reaction to make biodiesel
2) Separation of the biodiesel layer after each stage in the reaction
3) Water wash of the biodiesel
4) Methanol and water recovery from all products and byproducts
5) Methanol and water purification by distillation for reuse in the process

Although each section could be considered a separate unit operation, they are of course highly dependent on one another. In the design of a continuous plant, the ability to share resources across unit operations is essential. The use of a water wash, as stated previously, is one of these items that needs consideration across the entire biodiesel facility instead of just in the location it is used specifically for washing the biodiesel.

Safety of the process has been somewhat of a challenge not because it is not known how to make the process safer, but because of determining what is actually necessary for designing a safe plant from the processor’s point of view. Crown’s experience in oilseed extraction plants using hexane is relevant, but a major difference is that the oilseed extraction industry has a widely accepted guideline specifically written for it that a processor’s insurance company can use. Biodiesel plants have no such equivalent, and so more time may be necessary to work with and convince an insurance company of a plant’s safety.
Another challenge related to process safety is convincing prospective processors about the need for safety programs that fall outside the scope of engineering the process itself. To own a safe plant is the first step, but maintaining a safe plant, a safe working environment, and the procedures to handle any emergency is a full time job. The relative immaturity of the biodiesel industry attracts more that its share of entrepreneurs that may not have considered the enormous task of dealing with these types of safety concerns.

One important thing learned in a recent biodiesel plant construction phase was the value of having isometric piping drawings. Although Crown does all its oleochemical equipment design and plant drawings in 3D and uses a database system for instant updating of elements across multiple drawings, isometric piping drawings have not always been used. For such a relatively large amount of pipe in such a small building, it was recommended to the customer that isometric piping drawings should be done to save both the time and expense of having an extra person on site and the large amount of rework that may need to be done if not planned out correctly. In the end it was a benefit to the customer, as it likely saved time on what needed to be a quick construction project and also allowed the customer to get a more accurate bid from a subcontractor on the piping installation costs. It was a benefit to both Crown and the customer because it allowed all parties involved to see the entire plant as it would be constructed and make any changes beforehand to vessel design or orientation based on what would create the least amount of installation or operational difficulties.

Support infrastructure dictates feedstock oil storage and processing, product storage and transportation. Crown plant performance data is noted in TABLE 2. QA and QC, based upon the ASTM or CEN specifications, is mandated by the NBB and the EBB and determined by process monitoring and on-site lab testing. Further, plant engineering requires integration with distribution channels as superior product quality can be reduced by poor handling and storage. A typical marketing program developed before the plant is constructed assures ready markets with leading petroleum fuel distributors. Brand names for biodiesel are emerging from both the producers (Procter & Gamble, Cargill, ADM) and the multinational fuel suppliers (Petronas, Shell, Esso, BP, OMV, Agip, TotalFinaElf), so that customers can recognize and use products from established companies. Traders exist to supply some regional areas, but brand recognition will play a role in these early days before biodiesel becomes a commodity, like petroleum diesel.
**TABLE 2.** Plant Performance Data – Crown Plant

**MINIMUM FEEDSTOCK QUALITY – VEGETABLE OIL**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture and Volatiles</td>
<td>0.05% max</td>
</tr>
<tr>
<td>Acidity</td>
<td>0.5% max</td>
</tr>
<tr>
<td>Phosphorus Total</td>
<td>20 ppm max</td>
</tr>
<tr>
<td>Soap</td>
<td>50 ppm max</td>
</tr>
<tr>
<td>Unsaponifiables</td>
<td>1.0% max</td>
</tr>
</tbody>
</table>

**CONSUMPTION:** Typical figures per metric ton of biodiesel product when feed is supplied at 50C, and plant operating at full capacity, unless otherwise noted.

- **Heating Steam, 10 barg:** 340 kg
- **Cooling Water, 30C:** 60 m³, recirculated at 3C DeltaT
- **Chilled Fluid, 2C**
  - (14% glycol in water): 5 m³, recirculated at 3C DeltaT
- **Seal water for Vacuum Pump:** 0.2 m³, recirculated at 3C DeltaT
- **Electric Power:** 17 kWh (based on connected power), not including utilities
- **Instrument Air:** 50-100 Nm³/h, regardless of plant operating rate
- **Nitrogen, 5-6 barg, 99.9%:** as needed for blanketing
- **Methanol (99.9% min. purity):** 78 kg
- **Sodium methoxide solution**
  - (25% solution in methanol, 0.05% max water): 40 kg
- **Hydrochloric Acid solution**
  - (35% solution in water): 25 kg
- **Caustic Soda solution**
  - (50% solution in water): less than 5 kg

**PRODUCT INFORMATION:**

- **Biodiesel yield*:** greater than 98%
- **Untreated Crude Glycerine:** approximately 130 kg of 75-80% glycerine per metric ton of product
- **Fatty matter:** less than 10 kg
- **Methanol stream:** 99.9% methanol (recycled)
- **Water stream (0.2% methanol):** nil

*Yield based on available triglyceride content after subtraction of moisture, unsaponifiables and FFA. Biodiesel product will conform to ASTM D 6751 or equivalent standard. It should be noted that other feedstock qualities can be accommodated, but this will affect capital and utility costs.
Plant construction takes approximately one year from release of funding and operations requires a team of two-three persons per shift. However, existing plants are integrated into larger oilseed processing plants and both management and operations staff share duties. Calculations for a continuous flow plant use 24 hour days with 330 days per year of production. Maintenance requirements are minimal with process monitoring indicating reliability cycles correlated with turnaround planning. Process Safety Management are typical of any oleochemical plant from start up, lab procedures, training, and product/process certifications.

CONCLUSION

Today’s biodiesel processor has to be concerned with many issues, the least of which may be the cost of the capital investment. Knowledge of how to run a successful chemical plant is essential. There are practical aspects to the successful operation of a large full-scale industrial plant that cannot be ignored. Major concerns will be with the feedstock specifications, product specifications, lab analysis, storage and transportation, safety, and construction. The prospective processor should feel as though all vendors or contractors involved are selling a partnership and the commitment that goes along with it.

REFERENCES
2. Bockey, D., 2002, Situation and Development Potential for the Production of Biodiesel – An International Study. Union zur Förderung von Oel- und Proteinflanzen e. V., Germany