

Is Biodiesel Ready...

By Rachel Burton

Editor's note – Rachel Burton just completed a two-year United States Department of Energy research project as principal investigator, examining the use of enzymes in biodiesel. She serves as a senior associate at MARC-IV Consulting and founded Piedmont Biofuels.

Renewal of the biodiesel tax credit in December's fiscal cliff legislation has opened up a new window of opportunity for many feedstock and biodiesel producers throughout the United States. Some producers may be looking for new process technologies to improve production efficiencies or increase production capacity to achieve better scale economies. Biodiesel producers looking to increase production volume typically look at less expensive fats and oils as potential feedstocks. Lower quality lipids such as yellow and brown greases or acid distillates, which differ from traditional biodiesel feedstocks by exhibiting substantially higher free fatty acid (FFA) content, offer attractive alternatives. However, they are often underutilized due to the additional processing requirements that accompany a high FFA feedstock.

It is well documented that FFAs are created during the hydrolysis of fats and oils. Alkaline catalysts (e.g., potassium and sodium hydroxide) will react with FFAs to produce soap, an undesirable biodiesel contaminant. FFAs can be converted into methyl or ethyl esters for use as biodiesel by acid-catalyzed esterification, but this increases capital and operating costs as well as process complexity. If acid pretreatment is not used, high levels of soaps are formed during transesterification complicating downstream processing and reducing the yield of biodiesel. While FFA levels can be reduced by using acid pretreatment or other means, some FFA will be present during subsequent alkaline transesterification of the triglycerides and the inevitable soaps must be removed during biodiesel purification to achieve ASTM International standards. Performing esterification using a strong acid as the catalyst will reduce soap formation and improve yields. However, this pretreatment method also generates an acidic methanol waste with subsequent disposal. As a result, each process has its trade-offs between side streams, soap formation, yield, and economics.

As an alternative, enzymes known as lipases can easily catalyze

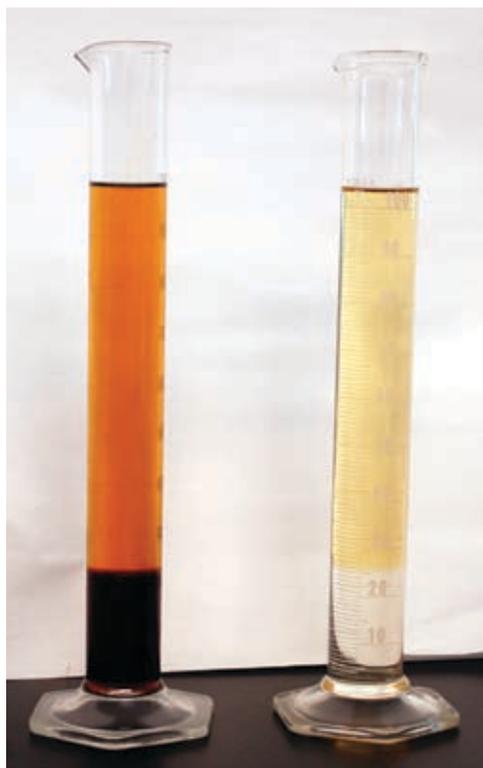
conversion of both triglycerides and FFAs into fuel-grade esters. Enzymatic catalysis does not form soaps, operates at or near room temperature, does not require high pressure, and does not result in unintended side-reactions. Without soaps, water use associated with the typical water wash and water from soap formation is eliminated, significantly improving glycerin quality from 60 percent to more than 97 percent purity. In addition, less energy is used compared to the current process or other catalysts such as metal oxides. The enzymatic process accommodates both low and high quality feedstocks without biodiesel yield loss.

Enzymatic biodiesel production has been heavily researched over the past 15 years, resulting in the publication of nearly 1,000 scientific papers. Despite this intense examination by a number of skilled research groups, the technology has never been sufficiently developed to allow its adoption by the biodiesel industry. This is due primarily to the absence of affordable, commercially available enzymes and the technologies that use them, making the process economically competitive.

A limited number of researchers and companies have now pushed the laboratory research to a level that is commercially viable. Each of these entities has developed various approaches to adopting lipases as catalysts for biodiesel production. One

technique is lipase transesterification as a replacement for traditional alkaline transesterification. This is best suited for high quality feedstocks like virgin vegetable oils or high quality animal fats, which are composed predominantly of triglycerides. This lipase technology enables high degrees of conversion of these triglycerides to fatty acid alkyl esters, typically yielding bound glycerol levels of 0.22 percent by mass or less when measured by ASTM D6584 total and free glycerol protocol. Often, a small amount of residual FFA, two percent or less, may remain in the resulting fatty acid methyl esters from this process. These FFAs can be esterified (by either enzymes or acid) or removed by a caustic treatment.

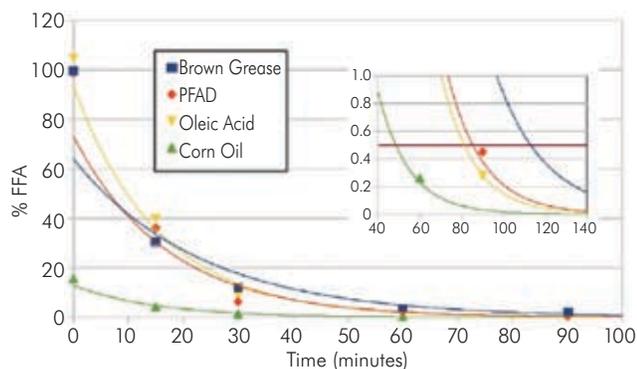
The second application for which enzymes have been developed as catalysts for biodiesel production is in the esterification of high FFA feedstocks; that is, as a replacement for the traditional inorganic acid catalyzed esterification. The tech-



Biodiesel glycerol from chemical catalysis (*left*) and enzyme catalysis.

for a Catalyst Upgrade?

Figure 1. Time course for FFA reduction in various lipid feedstocks by enzymatic esterification.



Reaction conditions: 40-gram lipid sample, four percent wt., immobilized lipase, 13 percent of methanol, shaken at 45 degrees Celsius.

Inset: Expansion of the time course at low FFA levels. The horizontal red line indicates acid value requirement. PFAD – palm fatty acid distillate.

nique can also be utilized as an acid value reduction process for the low amounts of FFAs that may remain after the enzymatic transesterification process. This method helps in-process biodiesel achieve ASTM D664 specification for acid value. In addition, this same technique can reduce the low levels of FFAs found in some high quality fats and oils. Figure 1 displays typical time courses for this esterification technique with varied feedstocks. It is notable that acceptably low levels of residual FFA are achieved, and that this occurs within moderate reaction times.

How does the production process vary when using enzymes? For both esterification and transesterification, temperature is a consideration for the life of the enzyme catalyst. Typically, there are reactor conditions between 30 and 60 degrees Celsius. Alcohol exposure is also a factor for many of these catalysts, when using methanol, and attention must be given to alcohol-to-oil molar ratios to limit enzyme deactivation. Reaction time varies with process techniques; some esterifications can be complete within 30 minutes whereas some transesterification processes may require up to 12 hours. Proper choice of process conditions will determine whether a biodiesel producer can maximize product yield as well as maintain catalyst life.

Some biodiesel process issues can be improved by utilizing enzymes as the catalyst for either the transesterification process or the esterification pre-treatment process. The alkali catalysts used in conventional transesterification processes react with FFAs in the system to create sodium or potassium salts of the FFA, or soap. In contrast, lipase-catalyzed transesterification systems lack alkali and therefore no soap is created. Many biodiesel plants remove the soap generated during conventional alkaline catalysis by washing the biodiesel with water, which produces a soapy wastewater stream. By avoiding the need for

a water wash to remove soaps, enzyme catalysis can reduce process water consumption and its attendant costs while also eliminating the soap waste stream.

Catalyst Availability and Re-use

The lipases produced by a multitude of microbial strains have been evaluated for the production of fatty acid esters, and some are now in the commercial arena. Some of the key strains that have been investigated are *Candida antarctica*, *Thermomyces lanuginosa*, *Pseudomonas fluorescens*, *Pseudomonas cepacia*, *Candida rugosa*, and *Rhizomucor miehei*. Complex plants and animals also produce lipases, but microorganisms are substantially easier to grow and manipulate and are thus the source of lipases used in biodiesel production. Commercial suppliers to the biodiesel industry include Novozymes and TransBiodiesel. Lipases are available in varied preparations, either immobilized on a solid support or dissolved in water (i.e., “free” form). When immobilized, the enzyme is prepared and adhered to a solid support structure, usually approximately 0.3 to 0.7 millimeters in size, to enhance continuous reuse of the catalyst. Immobilized enzymes can be used in either fixed-bed or stirred-tank reactor configurations. The enzyme and support remain in the reactor and should not leach into the feed stream.

Although the immobilized enzymes demonstrate good reusability, the costs of their preparation cause a higher initial investment. Thus, one of the key economic drivers to successful commercial implementation of an enzyme-based technology is the ability to reuse the catalyst. With traditional dissolved or homogeneous chemical catalysts, such as sulfuric acid or sodium hydroxide, producers typically do not have the ability to recapture the catalyst. Furthermore, the low cost of these catalysts imparts little incentive for their recovery, but this is not the case for the “free” or liquid preparation of enzyme catalysts. Though cheaper than immobilized lipases, their costs are sufficiently high to foster interest in their recovery and reuse. Until recently, this has not been reported.

Unique filtration technology available now can enable a biodiesel producer to reuse the liquid enzymes as well as the immobilized enzyme platform. This technology utilizes a type of membrane filtration called tangential flow filtration (TFF). One company who specializes in TFF, SmartFlow, leverages a patented cartridge technology that greatly improves flow rates by routing retentates through optimized flow-paths that significantly reduce fouling of the membrane surface, greatly increasing permeation rates. This technology allows filtration of the free enzyme from the aqueous phase while maintaining enzyme activity levels. By utilizing the TFF system, producers may be able to increase annual total plant throughput by reducing the volume of aqueous inputs, including the

Continued on page 16

free enzyme that must be returned to the reactor for subsequent runs. This reduced liquid volume may help producers increase the total operating capacity of their plants. It is possible that other ultra-filtration designs will also work in this application.

Co-product Quality

An enzyme-based process converts a waste product of the biodiesel process, crude glycerin, into a true co-product of the process since no further significant post-processing is required. Crude glycerin directly from an alkali-catalyzed transesterification reaction vessel has few direct uses due to the high levels of soap, water, and methanol contamination. It must be acidulated to break the soaps into salts and FFAs by the addition of a strong acid, then neutralized back to a pH of 7.0 with sodium or potassium hydroxide after the FFAs are removed, followed by distillation or methanol removal using heat and vacuum. If the FFAs are removed, the glycerin purity approaches 80 percent, with water as a residual contaminant. If the salts remain, the glycerol concentration can be as low as 50 to 60 percent. Crude glycerin with this quality has a low value and is used primarily in low-grade applications or sold to companies that further upgrade and refine the glycerin to higher grades that are more commonly used in commercial products.

However, since enzymatic catalysis avoids the use of alkali, it produces no soaps. Consequently, the biodiesel producer realizes a reduced investment in glycerol cleanup while still obtaining a high value glycerol product. There is a significant value proposition in the capability of manufacturing a high value, refined glycerin product versus a crude glycerin product. Samples from the enzymatic facility deployed at Piedmont Biofuels have shown a 96.3 percent glycerin content for soy-based biodiesel while the yellow grease esters tested at 97.5 percent glycerin. This quality is sufficient to sell into the technical grade market at prices three to four times higher than crude biodiesel glycerin and 15 times higher than unrefined bottoms. Additional purification is needed to remove minute amounts of moisture and methanol, and some producers may want to

Table 1. Comparison of glycerol products from an enzymatic process and a chemical catalysis.

Test	Unit	Method	Enzymatic Glycerol	Chemical Glycerol
Glycerol content	% mass	AOCS Ea 6-94	97.55	55.78
Ash	% mass	IUPAC 3.A.4	0.00	12.87
Methanol	% volume	EN 14110	0.14	0.45
MONG	% mass	IUPAC 3.A.6	0.40	29.17
Moisture	ppm	ASTM D6304	20500	22900

Note: AOCS – American Oil Chemists’ Society; IUPAC – International Union of Pure and Applied Chemistry; EN – European standard; MONG – Material organic non-glycerol.

treat for color bodies, depending on the parent feedstock.

Table 1 compares glycerol products from an enzymatic process and a chemical catalysis. In the enzymatic glycerol sample analysis, there is a higher glycerol content in the preparation, which is accompanied by profoundly reduced levels of contaminating “matter organic non-glycerin,” such as methyl esters, monoglycerides/diglycerides/triglycerides, or other organics. Methanol is easier to remove and thus lower in the enzymatic product. Due to the absence of alkaline earth metals from the enzymatic process, the ash content of the resulting glycerol is greatly reduced compared to that with conventional alkaline catalysis.

Summary

Currently available feedstocks like yellow and brown grease are five to 100 percent FFA and are significantly less expensive than virgin oils. Feedstocks such as distiller’s corn oil from dry grind ethanol operations that have been growing significantly in use as well as up-and-coming feedstocks like algae and jatropha oil all have FFA levels typically above five percent. With these new sources of biomass becoming available, biodiesel producers now have the opportunity to implement a reusable enzymatic catalyst technology that can fully process all feedstocks regardless of FFA content and without significant yield loss. A substantial increase in the quality of the glycerol co-product is an added benefit that can easily offset the capital investment for catalyst and process technology outlay.

With a one-dollar per gallon tax credit available to biodiesel producers in 2013, this may be the year for a catalyst and co-product upgrade. Are you ready? **R**