

Biodiesel Tech

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Biodiesel Education Program, University of Idaho
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CONVERTING GLYCEROL TO HIGHER VALUE PRODUCTS

As biodiesel production increases in response to federal and state tax credits and mandates, more and more glycerol (a byproduct of biodiesel production) will be produced as well.

While glycerol (also known as glycerin) is a useful product for the food and pharmaceutical industries, the glycerol that results from biodiesel production is “crude” because it is contaminated with methanol and other impurities. Crude glycerol generally sells for less than 5 cents per pound if a buyer can be found. Purifying the glycerol can be expensive.

Over the past decade, researchers have tried to deal with the glut of crude glycerol by experimenting with composting and burning it, using it as an animal feed, and by converting it via thermochemical or biological processes to value-added products. See “New Uses for Crude Glycerin from Biodiesel Production” for more information on the range of research.

Research done at the University of Idaho shows that a thermochemical process using a metal catalyst can result in a high yield of propylene glycol, which is a high-value product. Propylene glycol is used in the pharmaceutical, cosmetics, automotive, and food industries.

Converting glycerol without added hydrogen
Propylene glycol and glycerol are very similar chemically. Glycerol is converted to propylene glycol when one of the three OH groups in glycerol is replaced by a single hydrogen atom. In the past, other researchers have successfully converted glycerol to propylene glycol by externally supplying hydrogen. The hydrogen (H_2) reacts with one of the OH groups to form water, leaving behind one H.

Researchers wanted to find out if glycerol could be converted into propylene glycol without relying on external hydrogen. They wanted to avoid adding hydrogen for two reasons: to reduce reliance on fossil fuels (since hydrogen is generally derived from fossil-based resources such as methane), and to lower the cost of converting the glycerol, since hydrogen is expensive to buy, transport, and store.

If added hydrogen is avoided, the glycerol conversion process could be carbon-neutral. The process of converting glycerol to other alcohols releases some carbon dioxide into the air. This release of carbon dioxide is not necessarily a problem if glycerol from vegetable oil is used, since the oilseed crops absorbed carbon dioxide from the air as they grew. However, if petroleum derived hydrogen is also added, the process would not be carbon-neutral. Researchers theorized that, by adding water, heat, and pressure, and applying a catalyst, the glycerol could be converted to propylene glycol without adding hydrogen externally.

Methods tried

The glycerol was first mixed with water, which inhibits undesirable reactions. The researchers then applied pressure and heat to the glycerol and water mixture. The researchers did manage to produce a small percentage of methanol, ethanol, and propylene glycol, but much of the glycerol was converted to tar and other undesirable products.



Next, the application of several metal catalysts based on nickel, copper, and iron were tested. Catalysts can decrease the energy required for a chemical reaction. Catalysts can also serve to direct the reaction towards the production of the desired products.

This time, a higher percentage of alcohols was produced within minutes of starting the pressure and temperature treatment. The alcohols included propylene glycol, ethanol, acetol, and propanol.

Raney nickel catalyst method

Of all the catalysts tried, the Raney nickel catalyst worked the best. It converted the glycerol at a lower temperature, saving energy and money. It also worked the fastest, and produced the highest yield of propylene glycol.

When using a Raney nickel catalyst, the researchers found that after 15 minutes of heat and pressure, over 90% of the glycerol was converted to other alcohols or gases. This included about 30% propylene glycol, 6% ethanol, and 4% acetol, as well as carbon dioxide and water. About 9% of the glycerol did not convert. It remained glycerol, and could theoretically be recycled back into the process.

While a longer reaction time resulted in a higher glycerol conversion rate, the percentage of propylene glycol dropped to about 17% after 105 minutes, and the percentage of ethanol increased to about 11%. The researchers theorized that a longer reaction time causes some of the propylene glycol to undergo further reactions to convert to ethanol and gaseous products such as hydrogen, carbon dioxide, and carbon monoxide.

Table 1 shows that the propylene glycol yield was highest when the reaction time was only 15

Table 1. Yields of alcohols based on reaction time and water-to-glycerol ratio

Reaction Time (min)	Water to Glycerol Mass Ratio	Conversion (%mol)	Ethanol yield (%mol)	Propylene glycol yield (%mol)
15	1:1	91.1 ± 2.3	6.11 ± 0.38	30.16 ± 0.74
45	1:1	98.6 ± 0.2	8.52 ± 0.73	28.74 ± 1.96
75	1:1	99.6 ± 0.5	9.69 ± 0.81	22.98 ± 4.06
105	1:1	99.9 ± 0.1	10.37 ± 0.20	17.45 ± 0.72
45	7:3	99.9 ± 0.1	10.91 ± 0.39	15.99 ± 0.84
45	3:7	95.3 ± 0.2	7.25 ± 0.33	24.55 ± 1.28

minutes. Table 1 also shows that an optimum water to glycerol ratio is 1:1. When either more water (7:3) or less water (3:7) was used, the yield of propylene glycol was lower.

Previous research into glycerol conversion has shown a yield of 90% propylene glycol when additional hydrogen is used. Although the yield of propylene glycol is much lower when no additional hydrogen is used, the researchers felt this was an acceptable trade-off because of the lower cost of the process, and the fact that the process was carbon neutral.

Working with crude glycerol

Experiments were started using glycerol that was 99.5% pure. However, experiments using crude glycerol from biodiesel production showed similar results to those using pure glycerol: a yield of about 30% propylene glycol. Researchers did only preliminary tests on converting crude glycerol, and are not sure whether the conversion rate and yields of other alcohols and gases are similar or significantly different when using crude glycerol, compared to purified glycerol.

The main problem with crude glycerol is that the impurities in the glycerol tend to de-activate the catalyst, so the catalyst cannot be separated and re-used without additional regeneration. Researcher suggested that either the crude glycerol should be purified first and then converted, or a more robust catalyst must be found or created that is resistant to the impurities in crude glycerol.

Application to the biodiesel industry

Researchers used a small batch reactor to conduct these experiments. A larger reactor would be needed to process the glycerol from a biodiesel plant, and while this larger reactor would be a major investment for a small biodiesel producer, it may make sense depending on the producer's goals. This method could also be used by large petroleum companies which already have the necessary infrastructure. If petroleum companies get into the business of converting glycerol to propylene glycol, the demand for crude glycerol could cause the price to increase, thus benefiting biodiesel producers.

