Glycerin to Propylene Glycol: An Introduction

Over the past couple of decades, fatty acid methyl esters derived from vegetable oil and animal fat have assumed importance as a potential diesel fuel extender known as "biodiesel."[i, ii, iii] Worldwide production is approaching a billion gallons per year. The production of biodiesel utilizes surplus vegetable oils, fats and waste restaurant greases while reducing the US dependence on foreign crude oil. Biodiesel is a renewable, alternative fuel that reduces particulate matter and hydrocarbon emissions. For every 9 kilograms of biodiesel produced, about 1 kilogram of a crude glycerin by-product is formed; and today, biodiesel production plants are in need of methods to realize increased income from this glycerin.

The U.S. production of biodiesel is 30-40 million gallons, which is expected to grow at a rate of 50-80% per year, with a target of 400 million gallons of production by the year 2012. However, the major drawback on its commercialization is its high cost when compared to diesel. The production cost for biodiesel range from $0.65- $1.50 per gallon.[iv] At this production capacity, ~3.5 million gallons of crude glycerin is produced every year. This crude glycerin can be purified by several steps including vacuum distillation to produce USP grade glycerin. However, refining the crude glycerin which contains residual catalysts, water and other organic impurities is too complex and expensive to handle for small scale producers in their available limited facilities. Hence, 50% of the total crude glycerin by-product that is generated is disposed of and the remaining is sold at a very minimal price.

Another problem that results from refining this crude glycerin to refined glycerin is that the glycerin market cannot absorb it. In 1998, refined glycerin was abundant and production was declining. But by the end of 1999 and into 2000, the glycerin market was again tight. Today, with plenty of glycerin available to the world market, prices and U.S. exports have declined. Prices in the glycerin market will continue to drop with an over saturated market and new supplies of glycerin coming into the market from the burgeoning biodiesel industry.

Today, biodiesel production plants are in need of methods to realize increased income from this glycerol. If crude natural glycerol could be converted to propylene glycol, this technology could be used in biodiesel production plants to increase profitability. The preferred technology would convert crude natural glycerol at moderate temperatures and pressures.

Propylene glycol, i.e. 1,2 propanediol, is a three-carbon diol with a steriogenic center at the central carbon atom. Propylene glycol is a major commodity chemical with an annual production of over 1 billion pounds in the United States and sells for about $0.81 per pound with a 4% growth in the market size annually. The commercial route to produce propylene glycol is by the hydration of propylene oxide derived from propylene by either the chlorohydrin process or the hydroperoxide process. Some typical uses of propylene glycol are in unsaturated polyester resins, functional fluids (antifreeze, de-icing, and heat transfer), pharmaceuticals, foods, cosmetics, liquid detergents, tobacco humectants, flavors and fragrances, personal care, paints and animal feed.

There are several routes to propylene glycol from renewable feedstocks. The most common route of production is through hydrogenolysis of sugars or sugar alcohols at high temperatures and pressures in the presence of a metal catalyst producing propylene glycol and other lower polyols. In spite of several research efforts, this potentially important reaction is limited to a laboratory scale production because of common drawbacks of existing technologies. One drawback is the use of high temperatures and pressures that would necessitate expensive high pressure equipment, thereby increasing the capital cost of the process. Typical hydrogen pressures anywhere between 1450 and 4700 psi and temperatures in the range 200–350°C were being used for this reaction. An additional drawback is the use of dilute solutions of glycerol for this reaction. Typically, 10–30 wt.% glycerol solutions were predominantly used which will be further diluted through the water from the reaction. This will reduce the average space–time yield of the reaction, increasing the energy consumption of the process and in turn decreasing the process profitability. However, not much has been reported about the positive effect of using dilute glycerol solutions instead of 100% glycerol. A final drawback is the low selectivity towards propylene glycol. Most of the literature reports high selectivity towards ethylene glycol and other by-products like lactic acid, acetol, acrolein, and degradation products like propanol, methanol, carbon dioxide, methane, etc.

In an effort to overcome these drawbacks, our research focuses at developing a technology to perform the reaction at lower temperatures and pressures using concentrated glycerol while simultaneously achieving high selectivity towards propylene glycol and little or no selectivity towards ethylene glycol or other by-products. We are currently able to obtain greater than 90% of the theoretical conversion of glycerol to propylene glycol at only 200 psi and 200 °C. These pressures and temperatures are significantly lower than those reported in the literature while maintaining high selectivity and good conversions

References

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