A Review on the Production of Glycol from Glycerol
Aznira Alias* and Roila Awang**

ABSTRACT
Crude glycerol is the primary by-product of the biodiesel industry and too costly to purify it into a higher quality product. However, glycerol can be converted into other useful products used in the pharmaceutical and cosmetics industries such as trimethylene glycol (1,3-propanediol), propylene glycol (1,2-propanediol), ethylene glycol and ethanol through the hydrogenation process and the microbial fermentation process. This article reviews factors affecting glycerol conversion, glycol selectivity, concentration and conversion yield through both the hydrogenation and microbial fermentation processes.

INTRODUCTION
Crude glycerol derived from biodiesel production has a very low value because of the impurities. Further refining of the crude glycerol will depend on the economy of production scale and/or the availability of a glycerol purification facility. Larger scale biodiesel producers refine their crude glycerol and move it to markets in other industries.

Keywords: fermentation, hydrogenation, glycerol, glycol.

GLYCOLS FROM GLYCEROL
1,3-Propanediol/Trimethylene Glycol

The 1,3-propanediol is a simple organic chemical. It is produced from petroleum derivatives such as ethylene oxide and acrolein through a chemical route. Its high cost of production and limited availability have restricted its commercial use. The 1,3-propanediol has numerous uses. It can be formulated into composites, adhesives, laminates, powder and UV-coatings, mouldings, novel aliphatic polyesters, co-polyesters, solvents, anti-freeze and other end uses (Shell Chemicals, 2006). One of the most successful applications has been in the formulation of corrrterra polymers. As the production is limited and costs are higher using petroleum derivatives, glycerol has become an attractive feedstock for the production of 1,3-propanediol. Microbial fermentation is an
important technology for the conversion of renewable resources into chemicals. Similarly, 1,3-propanediol can be obtained by microbial fermentation of glycerol. Propanediol-based polymers exhibit better properties than those produced from 1,2-propanediol, butanediol or ethylene glycol.

1,2-Propanediol/Propylene Glycol

The 1,2-propanediol is a three-carbon diol with a stericogenic centre at the central carbon atom. It is a promising chemical with an annual production of over 3.5 billion pounds and a 4% annual growth in market size. Typical uses of propylene glycol are in saturated polyester resin, functional fluid, pharmaceuticals, foods, cosmetics, liquid detergents, flavours and fragrances, paints and animal feed (Martin and Murphy, 1994).

Ethylene Glycol

Ethylene glycol is an odourless, colourless syrupy liquid with a sweet taste. The major use of ethylene glycol is as a coolant or anti-freeze in automobiles. This chemical is also used as a feedstock for the manufacture of polyester fibres and resins including polyethylene terephthalate, which is used to make plastic bottles for soft drinks. The most common method to produce ethylene glycol is by reacting ethylene oxide with water. The base material for ethylene oxide is ethylene which is derived from petroleum or natural liquid gas. Ethylene oxide production is sensitive to the cost of ethylene and energy.

CONVERSION OF GLYCEROL TO GLYCOL VIA THE CHEMICAL ROUTE

There are several routes to produce glycol from renewable feedstock. The most common route of production is through the hydrogenation process at high temperature and pressure in the presence of a metal catalyst (Chopade et al., 2001). Several publications and patents document multiple schemes for hydrogenating glycerol to glycol. Casale and Gomez (1994) described a method of hydrogenating glycerol using a copper and zinc catalyst as well as sulphide ruthenium catalyst at a pressure of 2175 psi and temperature in the range of 240°C-270°C. Che (1987) described a method of converting glycerol to 1,2-propanediol using a homogeneous catalyst containing tungsten and group VIII transition metal at a pressure of 4600 psi and a temperature of 200°C. Schuster and Eggersdorfer (1997) described a preparation process for 1,2-propanediol using a catalyst containing cobalt, copper, manganese, molybdenum and an inorganic polycryl at a pressure of 3600 psi and a temperature of 250°C.

The production of glycol from glycerol is prominently influenced by the presence of a catalyst as a selector for the final product via two routes. The first route is through C-C cleavage (also known as retro-aldol) which produces ethylene glycol, while the second route is through C-O cleavage which produces 1,2-propanediol and 1,3-propanediol (Figure 1) (Montassieur et al., 1998). Erin and Robert (2007) evaluated commercial carbon-supported ruthenium (Ru) and platinum (Pt) catalysts in the batchwise hydrogenation of glycerol in aqueous solution. They found that Ru favoured the production of ethylene glycol over 1,2-propanediol (C-C cleavage) while Pt favoured the production of 1,2-propanediol over ethylene glycol (C-O cleavage). In the catalyst screening conducted by Mohanprasad et al. (2005), it was reported that copper or copper-based catalysts exhibited higher selectivity towards propanediols (C-O cleavage) with little or no selectivity towards ethylene glycol and degradation by-products. On the other hand, a catalyst like ruthenium (Ru) and palladium (Pd) showed low selectivities, less than 50%, due to competitive hydrogenation of the C-C and C-O bonds (Mohanprasad et al., 2005). Recently, a Cu-ZnO catalyst was reported which might produce a higher 1,2-propanediol selectivity (C-O cleavage) than for ethylene glycol in glycerol hydrogenation (Wang and Liu, 2007).

A higher hydrogenation reaction temperature increases glycerol conversion and results in increasing glycol production. Glycerol conversion at 180°C reaction temperature was 24% and 35.1% glycol production while at 200°C reaction temperature, glycerol conversion increased to 54.8% and 85% glycol production (Mohanprasad et al., 2005). Tomohisa et al. (2007a) reported that glycerol conversion increased gradually with increasing reaction temperature from 120°C to 180°C on Ru/C, and the selectivity to 1,2-propanediol was relatively high. Wang and Liu (2007) also reported that increasing reaction temperature in the range 180°C to 220°C increased glycerol conversion from 10.3% to 55.7% and 1,2-propanediol selectivity increased sharply from 16.5% to 81.4%.

A study by Tomohisa et al. (2006) focused on the effect of initial hydrogen pressure on glycerol hydrogenation over Ru/C + Amberlyst. Glycerol conversion increased gradually with increasing hydrogen pressure as well as hydrogenation selectivity to propanediols (Tomohisa et al., 2006). In another work, Mohanprasad et al. (2005) carried out glycerol hydrogenation at various
hydrogen pressures and a constant temperature of 200°C to determine the effect of hydrogen pressure. As expected the conversion of glycerol and 1,2-propanediol selectivity increased as the hydrogen pressure increased from 50 psi to 300 psi.

Conversion of glycerol in basic conditions affects glycol selectivity. According to Erin and Robert (2007), the addition of a base (8.0 M NaOH) to a reaction over ruthenium-supported carbon (Ru/C) switched the glycol selectivity to favour 1,2-propanediol (37%) over ethylene glycol (12%). Without base addition, Ru/C catalyzed glycerol to 32% 1,2-propanediol selectivity and 68% ethylene glycol selectivity. This situation implies that a base-catalyzed reaction has higher selectivity to 1,2-propanediol over ethylene glycol. A study on the effect of initial pH value on glycerol hydrogenation conversion and glycol selectivity at 200°C on CuZnO showed that increasing the pH value from 2 to 7 led to an increase in glycol conversion from 10.4% to 21.1%, which further increased to 33.9% at pH 12. 1,2-propanediol selectivity slightly changed (from 27.9% to 29.4%) in the pH range of 2-7, while it reached as high as 77.5% at pH of 12 (Wang and Liu, 2007). In another work, Chiu et al. (2006) reported that the yield of 1,2-propanediol from glycerol hydrogenation was increased with increasing pH from 14.3% at pH 7.5 to 32.2% at pH 10.5.

The addition of an acid catalyst in the hydrogenation process results in higher glycerol conversion as well as glycol selectivity. The glycerol hydrogenation process which was catalyzed by Ru/C + acid catalyst (Amberlyst) increased glycerol conversion (38.8%) and glycol selectivity (37.4%) (Tomohisa et al., 2006). Performance comparison of various acid catalysts was carried out in a study conducted by Yohei et al. (2006). They found that Amberlyst was the most effective additive to enhance glycerol conversion and to inhibit the cracking by-reaction due to the higher acid strength of Amberlyst (Yohei et al., 2006). Furthermore, for acid strength evaluation, Tomohisa et al. (2007b) carried out the hydrolysis of metal acetate over Amberlyst 70 and Amberlyst 15. Amberlyst 70 showed a higher hydrolysis activity than Amberlyst 15. As a result, the addition of Amberlyst 70 to Ru/C catalyst resulted in higher glycols selectivity and lower selectivity to decomposition products (Tomohisa et al., 2007b).

However, the increasing concerns over green chemistry claim that the hydrogenation process is not environmental-friendly when using a catalyst like copper chrome because of the toxicity associated with chromium (Wang and Liu, 2007). Furthermore, the high temperature and high pressure hydrogenation process requires an expensive reactor and high cost to operate. Therefore, scientists tried to find other economic ways such as microbial fermentation to produce glycol from glycerol.

**CONVERSION OF GLYCEROL TO GLYCOL VIA MICROBIAL FERMENTATION**

The development of environmental-friendly processes for the production of chemicals has increased as non-renewable resources are depleted and the world population keeps growing. Microbial fermentation processes are particularly attractive because they typically use renewable feedstocks
and do not generate toxic by-products. However, they also have several limitations, such as: (i) the yield and productivity are low, (ii) the recovery and purification of products from aqueous solution is often difficult, and (iii) the range of products is relatively small.

Although there are no simple solutions to overcome all these limitations, they can be reduced significantly. For example, to increase the range of microbial products, new bacterial metabolic pathways have been developed through bacteria engineering. Yield can be improved by the elimination of pathways leading to byproducts. If byproducts are inhibitory, their elimination may lead to increased product titers. Finally, increased titers and reduced byproduct levels may simplify product recovery and purification (Cameron et al., 1998).

Fermentation of glycerol to glycol may be affected by various factors such as bacteria type, fermentation conditions (aerobic or anaerobic) as well as the medium used. Previous research shows that bacteria type is the most important factor affecting glycol production from glycerol. Glycerol can be converted to 1,3-propanediol by several microorganisms including Clostridia, Citrobactor, Lactobacillus and also Klebsiella (Reimann et al., 1996; Biebl et al., 1999). Among these, Klebsiella pneumoniae ferments glycerol to 1,3-propanediol at a high yield and productivity, while Cooper and Anderson (1970) reported that 1,2-propanediol could be obtained from glycerol fermentation by dihydroxyacetone phosphate as an intermediate using Escherichia coli. Fermentation of glycerol with E. coli was carried out in a similar way as with fermentation using aldose but the 1,2-propanediol production was slightly higher with (R)-1,2-propanediol as a major product.

The fermentation process can be carried out under two different conditions - aerobic (with oxygen) and anaerobic (without oxygen). Commonly, the biosynthesis of 1,3-propanediol is always done under anaerobic conditions. According to a recent report, the conversion of glycerol to 1,3-propanediol with batch and continuous fermentation processes was conducted under both anaerobic and microaerobic conditions (Wang et al., 2001). The 1,3-propanediol conversion rates of the processes were similar but the productivity of 1,3-propanediol under microaerobic conditions was higher than under anaerobic conditions. Both fermentation conditions affected glycol concentration and productivity. In another work, Ma et al. (2008) conducted a study on the effect of aerobic conditions on 1,3-propanediol production by K. pneumoniae in batch culture. Results showed that higher 1,3-propanediol concentration (13.44 g litre\(^{-1}\)) and productivity (1.12 g litre\(^{-1}\)) were obtained under anaerobic conditions rather than aerobic conditions where 1,3-propanediol concentration was 8.73 g litre\(^{-1}\) and selectivity was 0.72. However, this aeration technique can only apply to facultative anaerobic bacteria (bacteria that can grow in both aerobic and anaerobic conditions) like K. pneumoniae and E. coli. A study by Chen et al. (2005) showed the increment of key enzymes in 1,3-propanediol production by K. pneumoniae under microaerobic conditions.

Higher bacteria growth is believed to increase glycerol conversion resulting in increasing glycol production. Himmi et al. (1999) studied the use of biotin and yeast extract as the source of the bacteria growth factor in the production of 1,3-propanediol from glycerol by Clostridium butyricum. It was found that 2 g litre\(^{-1}\) of yeast extract and 200 ug litre\(^{-1}\) of biotin were able to produce 0.59 mol mol\(^{-1}\) and 0.62 mol mol\(^{-1}\) of 1,3-propanediol. Furthermore, the lag period (period growth of bacteria) for biotin was longer (30 hr) than for yeast extract (6 hr). These data clearly show that biotin alone could replace yeast extract in the medium without affecting bacteria growth performance. Production of 1,3-propanediol also relies on both iron and phosphate content in the medium growth. When both FeCl\(_3\) and NaHPO\(_4\) of the defined medium were reduced stepwise, the 1,3-propanediol productivity increased by decreasing the H\(_2\) released (Reimann et al., 1996).

CONCLUSION

Conversion of glycerol to glycol can be achieved in two ways, i.e. by hydrogenation and by the microbial fermentation process. Current state-of-art technology shows that hydrogenation is preferred because it is able to convert bulk glycerol to glycol in a short period with high glycol selectivity and productivity, while the microbial fermentation process needs a lot of time to convert bulk glycerol to glycol which produces low glycol selectivity and productivity. This shows that the microbial fermentation process needs further research and development to be commercially viable.

REFERENCES


TOMOHISA, M; SHUICHI, K; KIMIO, K and KEICII, T (2007b). Glycerol hydrogenolysis to 1,2-propanediol catalyzed by a heat resistant ion-exchange resin combined with Ru/C. Catalyst Communication, 329: 30-35.

