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Value-added Utilization of Crude Glycerol from Biodiesel Production: A Survey of Current Research Activities

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Abstract. *Glycerol is a by-product from biodiesel industry. As the biodiesel production is increasing exponentially, the crude glycerol generated from the transesterification of vegetables oils has also been generated in a large quantity. Despite of the wide applications of pure glycerol in food, pharmaceutical, cosmetics, and many other industries, it is too costly to refine the crude glycerol to a high purity, especially for medium and small biodiesel producers. Many research projects and studies have been conducted and innovative utilizations of the crude glycerol are under investigations. It will be beneficial to the research community as well as biodiesel industry in understanding the progress of glycerol for value-added applications and for reference in manipulating their own integrated plans for sustainable and profitable biodiesel production. This report summarizes the currently available studies and possible ways on the utilizations of crude glycerol generated from biodiesel industry.*

Keywords. Biodiesel, Crude glycerol.

Introduction

Biodiesel production in the United States has increased dramatically from 500,000 gallons in 1999 to 70 million gallons in 2005 (National biodiesel Board, 2006). The principal by–product of biodiesel production is the crude glycerol, which is about 10 %wt of vegetable oil (Dasari et al., 2005). For a current biodiesel production of 150 million gallons/year, the glycerol amount is 50 million kg High purity glycerol is a very important industrial feedstock. Its applications are found in food, drug, cosmetic and tobacco industries. In the past decade, industrial glycerol price was in the range of $1.28 to $1.65 (Kirk-Othmer Encyclopedia of Chemical Technology, 2004). However, crude glycerol derived from biodiesel production possesses 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. It is generally treated and refined through filtration, chemical additions, and fractional vacuum distillation to yield various commercial grades. If it used in food, cosmetics, and drugs, further purifications are needed such as bleaching, deodoring, and ion exchange to remove trace properties. Purifying it to that stage, however, is costly and generally out of the range of economic feasibility for the small to medium sized plants. As more and more crude glycerol is continuously generated from the biodiesel industry, it is very important that economical ways of the low-grade glycerol utilization be explored to further defray the cost of biodiesel production in the growing global market.

Basic Glycerol Chemistry

Glycerol, or 1,2,3-propanetriol, is a trihydric alcohol. It is a colorless, odorless, sweet-tasting, syrupy liquid. It melts at 17.8°C, boils with decomposition at 290°C, and is miscible with water and ethanol (Perry and Green, 1997). The chemical formula for glycerol is

$OH\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}OH$

It is hygroscopic; i.e., it absorbs water from the air; this property makes it valuable as a moistener in cosmetics. Glycerol is present in the form of its esters (glycerides) in all animal and vegetable fats and oils.

Glycerol Utilization for Specific Products

For every 9 kg of biodiesel produced, about 1 kg of a crude glycerol by-product is formed (Dasari et al., 2005). The usage of low-grade quality of glycerol obtained from biodiesel production is a big challenge as this glycerol cannot be used for direct food and cosmetic uses. An effective usage or conversion of crude glycerol to specific products will cut down the biodiesel production costs. This paper aims to cover possible conversion of glycerol into useful products. The products are 1,3-propanediol, 1,2-propanediol, dihydroxyacetones, hydrogen, polyglycerols, succinic acid, and polyesters. Glycerol, when used in combination with other compounds yields other useful products. For example glycerol and ethylene glycol together can be used as a solvent for alkaline treatment of poly fabrics (Yang and Tsai, 1997). Glycerol reductions with magnesium synthesize the carbon onions (Du et al., 2005). Glycerol can be used as dielectric medium for compact pulse power systems (Brown et al., 1999). Glycerol acts as a medium in electrodeposition of Indium-Antimony alloys from chloride tartrate solutions (Kochegarov and Belitskaya, 1971). Biomass is converted to liquid fuel using glycerol that can be blended with gasoline as an alternative fuel (Demirbas, 2000). Mixed culture fermentation of glycerol synthesizes short and medium chain polyhydroxyalkanoate blends (Koller et al., 2005).

Products from Glycerol

1,3-propanediol

1,3-propanediol is a simple organic chemical. The high cost and limited availability has restricted its commercial use. 1,3-propanediol has numerous uses. It can be formulated into composites, adhesives, laminates, powder and UV-cured 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 corterra polymers. As the production is limited and costs are higher, glycerol has become an attractive feedstock for production of for 1,3-propanediol. Microbial fermentation is an important technology for the conversion of renewable resources to chemicals. It 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.

Using Clostridium Butyricum

Himmi et al. (1999) did batch fermentations to produce 1,3-propanediol. To study the glycerol conversion, three types of media were used: a rich medium, a low-nutrient medium (LNM), and when biotin was replaced by yeast extract in the LNM (LNM-YE). To study fermentation at the pilot scale, cultures were carried out using a 20 L reactor with 17 L useful volume. It was equipped with a boiler to produce steam for in situ sterilization of the culture medium and reactor piping. The culture inoculum consisted of 11 (6% vol) of pH-controlled inoculum culture using industrial glycerin equivalent to 50 g/l of pure glycerol. To determine an adequate nitrogen level for glycerol fermentation by Clostridium Butyricum, NH_4CI was added to LNM in various amounts, and pH-controlled cultures were performed with high concentrations of glycerol corresponding to an initial C/N ratio between 60:1 and 112:1. Biotin of 4 µg/L was sufficient to convert 129 g/L of glycerol and 121 g/L of industrial glycerin into a large amount of 1,3-propanediol. In the proposed medium nitrogen constituted a limiting factor for glycerol fermentation, especially when the C/N ratio was less than 81:1. Papanikolaou and Aggelis (2003) simulated the production of 1,3-propanediol by Clostridium Butyricum strain F2b from raw glycerol by a Contois-type model. The production of 1,3-propanediol by Clostridium Butyricum F2b was suitable for this type of bioconversion. It was found that the maximum theoretical 1,3-propanediol productivity was comparable with the highest one achieved during growth of various bacterial strains on pure glycerol in batch and continuous cultures. Papanikolaou et al. (2000) carried out batch and continuous cultures of a newly isolated Clostridium Butyricum strain. The preculture was carried out in 100 mL conical flasks, filled with 50 mL of medium (the carbon source was 30 g/L of pure glycerol), inoculated with the first post-sporal Hungate-tube culture and incubated at 33°C without agitation for 10-14 h. Batch and single-stage continuous cultures were conducted in a 2 L reactor filled with 0.9 L of medium and inoculated with 0.1 L of preculture. In order to ascertain the anaerobiosis during the first fermentation steps of the fermentor culture, nitrogen gas, at a rate of 0.5 vvm, was infused into the culture medium. The agitation speed was 200 rpm and the pH was adjusted to 7±0.05 by automatic addition of 2 N KOH. The incubation temperature was 33°C. A two-stage continuous culture seemed attractive for achieving simultaneously high product concentration and productivity. The first stage presented a high dilution rate in order to obtain an increased 1,3-propanediol volumetric productivity. The second stage with a lower dilution rate, served mainly to further increase the product concentration. Significant cell growth was observed in the first stage of the culture, whereas at the high flow rates significant substrate amounts remained unconsumed in the culture fluid. For both types of cultures, the conversion yield obtained was around 0.55 g of 1,3-propanediol formed per 1 g of glycerol consumed. The highest 1,3-propanediol concentration for single stage process was 35-48 g/L. They found that 1,3-propanediol was associated with cell growth whereas acetate and butyrate seemed non growth-associated products. Low and medium dilution rates up to 0.1/hr favored butyrate production whereas at higher rates acetate production increased. The maximum 1,3-propanediol volumetric productivity obtained was 5.5 g/L·h. In a two-stage continuous fermentation, the first stage presented high 1,3-propanediol volumetric productivity, whereas the second stage (with a lower dilution rate) increased the final product concentration. High 1,3-propanediol concentrations were achieved (41-46 g/L), with a maximum volumetric productivity of 3.4 g/L·h. A cell concentration decrease was reported between the second and the first fermentor. For Batch and Continuous cultures, Zeng (1997) obtained conversion around 0.55 g of 1,3-propanediol formed per 1 g of glycerol consumed. Zeng (1996) calculated theoretical maximum yield of 0.72 mol/mol glycerol without any hydrogen and butyric acid formation. The product concentration and productivity of 1,3-propanediol by Clostridium Butyricum was far below the optimum performance on comparing the experimental results with theoretical calculations using Klebsiella Pneumoniae due to the relatively high formation of butyric acid.

Using Klebsiella Pneumoniae

Another microorganism that ferments glycerol to 1,3-propanediol is Klebsiella Pneumoniae. Xiu et al. (2004) optimized the conditions of batch and continuous fermentations on the basis of volumetric productivity of 1,3-propanediol. Their mathematical model was based on growth kinetics of multiple inhibitions and the metabolic overflow of substrate consumption and product formation. They found the optimal initial glycerol concentration to be 960 mmol/L with a given inoculation of 0.1 g biomass/L, for the batch culture leading to the highest volumetric productivity (52.6 mmol/L·h) of 1,3-propanediol. For continuous fermentations, the optimal dilution rate and initial glycerol concentration in feed were 0.29/h and 731 mmol/L, respectively. The productivity was 114 mmol/ L·h that was more than twice the productivity of an optimal batch culture. They proposed two-stage continuous process in which the first stage was operated at the optimal conditions and the second one was used to consume the residual glycerol in the first one. The dilution rate was higher in the second stage than in the first one. A two-step bioprocess of two bioreactors in series appeared to be more favorable than a single bioreactor system with the same volume in terms of the concentration, yield and productivity of 1,3-propanediol. Chen et al. (2005) study showed that the increment of key enzyme activities is essential to 1,3-Propanediol formation. Fermentation conditions of key enzymes of 1,3-Propanediol production by Klebsiella Pneumoniae were studied under microaerobic condition. Before inoculation, the strain was incubated for 24 h at 37°C in 250 mL shake flasks containing 50 mL of preculture medium with shaker speed 120 rpm under aerobic conditions. Uniform design and genetic algorithms and coupling artificial neural networks were developed for the medium optimization. When the strain grew in the optimized medium under optimal fermentation condition in a 5 L stirred tank bioreactor for batch production, glycerol dehydrogenase (GDH), 1,3-propanediol oxidoreductase (PDOR) and glycerol dehydratase (GDHt) activities were 3700, 3840 and 8.70 U referred to 1 L of fermentation broth after 20 h cultivation and the productivities of GDH, PDOR and GDHt (U/L h) were 185, 192, 0.435 and the maximum concentration of 1,3-Propanediol was 10.5 g/L. Chen et al. (2004) examined different carbon sources, organic nutrients, nitrogen sources and salts for their effects on key enzymes formation for fermentation. According to them the optimal medium ingredients were glycerol 30 g/L, KCl 1.6 g/L, NH_4Cl 6.7 g/L, $CaCl_2$ 0.28 g/L and yeast extract 2.8 g/L. The optimum operating conditions were 37°C, initial pH of 7.0, shaker speed of 200 rpm as well as 5% inoculum. The results suggested that appearance of maximum activities of key enzymes is earlier than that of maximum concentration of 1,3-propanediol. Chen et al. (2003) studied the glycerol metabolism by analyzing according to energy (ATP), reducing equivalent and product balances. Their theoretical analysis showed that a microaerobic condition was more perfect for the production of 1,3-propanediol from glycerol than anaerobic and aerobic conditions. The yields of 1,3-propanediol, biomass and ATP to glycerol under microaerobic conditions depend on the molar fraction of reducing equivalent oxidized completely by molecular oxygen in tricarboxylic acid (TCA) cycle and on the molar fraction of TCA cycle in acetyl-CoA metabolism. Their experimental results of batch cultures demonstrated that microaerobic cultivations were favorable for cell growth, reduction of culture time and ethanol formation, and enhancement of volumetric productivity of 1,3-propanediol. In addition, no aeration could improve the yield of 1,3-propanediol to glycerol in comparison with that of an anaerobic or aerobic culture. Menzel et al. (1997) obtained a final propanediol concentration of 35.2-48.5 g/L in a continuous fermentation of glycerol. A working volume of 2 L was used. The reactor was agitated at 300 rpm and sparged with N_2, at a flow rate of 0.4 vvm. The pH was controlled at 7.0 by addition of 30% KOH. The culture temperature was 37°C. A glycerol solution of 870 g/L was separately fed to the medium reservoir instead of to the bioreactor according to the glycerol concentration required in the feeding medium. At each dilution rate, steady states were obtained at different medium glycerol concentrations. A relatively low glycerol concentration was used at the beginning of each dilution rate, which resulted in substrate limitation. The glycerol concentration was then carefully increased by small steps, which ultimately resulted in glycerol excess in the culture. A final and a volumetric productivity of 4.9-8.8 g/L·h were obtained at dilution rates between 0.1 and 0.25/h. These results corresponded to about 80-96% of the theoretical maxima with no ethanol and hydrogen formation. The highest propanediol concentration achieved was 50-60 g/L in batch and fed-batch cultures. The productivity of the continuous culture was about 2-3.5-fold higher. Wang et al. (2001) studied the conversion of glycerin to 1,3-propanediol with batch and continuous fermentation processes under anaerobic and microaerobic conditions. The 1,3-propanediol conversion rates of both processes were similar, but the productivity of 1,3-propanediol under microaerobic condition was higher than that under anaerobic condition. In the continuous culture at a dilution rate of 0.1/h and glycerin limitation, both yield and productivity of 1,3-propanediol under

microaerobic condition were higher than that under anaerobic condition. Cheng et al. (2005) proposed a kinetic model based on the logistic and Luedeking-Piret equations of cell growth, product formation and substrate consumption with glycerol as substrate in batch system. Based on this model they determined a feeding strategy for glycerol to maximize the final 1,3-propanediol concentrations. The experimental results showed that the feeding mode with nonlinear optimization could improve the 1,3-propanediol productivity and concentration compared with other feeding strategies, such as pulse feeding and constant glycerol concentration feeding. Zeng (1993) analyzed the fermentation of glycerol to 1,3-propanediol by Klebsiella Pneumoniae DSM 2026, with emphasis on the regulation of hydrogen formation and balance of reducing equivalents ($NADH_2$). Under conditions of glycerol limitation, H_2 formation was found to be higher than the maximum amount that could be generated from the splitting of pyruvate to acetyl-CoA. Under conditions of glycerol excess, formation of H_2 was drastically reduced and a surplus of $NADH_2$ was generated for the formation of 1,3-propanediol. Their findings indicated the existence of enzymes in Klebsiella Pneumoniae that transfer reducing equivalents from $NADH_2$ to H_2 and 1,3-propanediol flexibly. Wang et al. (2003) used the selective hydroxylation technique. The idea was to selectively transform the middle hydroxyl group of glycerol into a tosyloxyl group and then remove the transformed group by catalytic hydrogenolysis. With this approach, the conversion of glycerol to 1,3-propanediol was completed in three steps, namely, Acetalization, Tosylation, and Detosylation. The acetalization of glycerol with benzaldehyde was conducted in benzene. The setup included a round-bottomed reaction flask, a condenser, and a Dean-Stark trap. By using a Dean-Stark trap, the water formed in the reaction could be boiled off from the reaction flask as an azeotrope with benzene, and the reaction could be driven to completion. In this experiment, 100 g of glycerol, 120 g of benzaldehyde (6% excess), and 300 mL of benzene, together with 1 g of *p*-toluenesulfonic acid catalyst, were placed in the reaction flask. The reaction was initiated by bringing the reaction solution to a boiling state, and the volume of the water formed in the reaction monitored the progress of the reaction. Tosylation was carried out in pyridine. The reaction flask was placed in a refrigerator at 5°C to allow the reaction to continue for about 12 h. The progress of this reaction was monitored by the formation of needle-shaped (pyridine-hydrochloride complex) crystals. The final step of the conversion was detosyloxylation reaction followed by a hydrolysis reaction. The detosyloxylation reaction removes the tosylated middle hydroxyl group, while the hydrolysis reaction removes the protection on the first and third hydroxyl groups. This last step yields the conversion target, 1,3-Propanediol. It also regenerates the group protection reagent benzaldehyde, which can be recycled back to the acetalization reactor for reuse in the first-step conversion. Lin et al. (2005) enhanced the 1,3-propanediol production by Klebsiella Pneumoniae with fumarate addition. Flask fermentations were carried out for 4 h with an initial concentration of 20 g glycerol/L, and fumarate was added in a range from 0 to 25 mM. The cell grew faster with fumarate addition. They proposed two reasons for this increase. Firstly, fumarate addition may speed up the metabolic flux of 1,3-Propanediol production by increasing the activities of the key enzymes: glycerol dehydrogenase, glycerol dehydrogenase and 1,3-propanediol oxidoreductase. Secondly, the NAD+/NADH ratio was decreased by fumarate addition, so that more reduced power was now available for converting 3-hydroxypropionaldehyde into 1,3-Propanediol.

1,2 propanediol

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 (Dasari et al., 2005). Perosa and Tundo (2005) converted glycerol selectively to 1,2 propanediol. When glycerol and Raney Ni were heated at 150°C for 20 h in a steel autoclave with 10 atm of hydrogen, conversion reached 12%, with 93% selectivity toward 1,2 propanediol, plus small amounts of ethanol and CO_2. At 190°C, the reaction proceeded faster, with selectivity toward 1,2 propanediol in the range of 70-80% and ethanol and CO_2 as the sole by-products. At 210°C, the reaction was still faster, but selectivity toward 1,2 propanediol dropped to 48%. The selectivity and rate towards 1,2 propanediol was found to be improved with addition of a phosphonium salt. Dasari et al. (2005) carried out reactions in a specially designed stainless steel multi-clave reactor capable of performing eight reactions simultaneously. Each reactor with a capacity of 150 mL was equipped with stirrer, heater and a sample port for liquid sampling. The reactors were flushed several times with nitrogen followed by hydrogen. Then the system was pressurized with hydrogen to the necessary pressure and heated to the desired reaction temperature.

The speed of the stirrer was set constant at 100 rpm throughout the reaction. All the catalysts used in this study were reduced prior to the reaction in the same reactor by passing a stream of hydrogen over the catalyst bed at 300°C for 4 h. Copper-chromite catalyst was the most effective catalyst for the hydrogenolysis of glycerol to. The yield of 73% was achieved.

Dihydroxyacetone

Dihydroxyacetone is a simple three-carbon sugar, non-toxic in nature. It is used in cosmetics industries as a tanning agent (Bauer et al., 2005). Garcia et al. (1994) investigated the liquid-phase oxidation of glycerol with air on platinum catalysts at different pH. Oxidation of aqueous solutions of glycerol were carried out at atmospheric pressure in a thermostated glass reactor of 500 mL equipped with a stirrer, a gas supply system, an oxygen electrode and a pH electrode. The catalyst was suspended in 300 mL of water under a nitrogen atmosphere and the suspension was heated to 333 K whilst stirring continuously at 1200 rpm. Glycerol was then added and, following a delay of 10 min, air was bubbled through the slurry at 0.75 mL/min. The initial concentration of the aqueous glycerol solution was 1 mol/L. The reaction medium was maintained at a constant pH by addition a 30% sodium hydroxide solution using a pump controlled by a pH meter. The selectivity to glyceric acid was 70% at 100% conversion on Pd/C at pH 11. On Pt/C catalyst, glyceric acid was the main product with 55% selectivity. They found that deposition of bismuth on platinum particles orientates the selectivity towards the oxidation of the secondary hydroxyl group to yield dihydroxyacetone with a selectivity of 50% at 70% conversion. Kimura (2001) catalytically prepared dihydroxyacetone by selective oxidation of glycerol. Using bismuth in platinum with weight ratio of 0.2 gave dihydroxyacetone selectivity to 80%. Bismuth adatoms controlled the glycerol orientation towards dihydroxyacetone formation functioning as site blockers on Pt (111). They found that the use of fixed-bed reactor increases the conversion and yield. Moreover the catalytic method had higher productivity than the conventional fermentation process. Svitel and Sturdík. (1994) produced dihydroxyacetone by the strain gluconobacter oxydans CCM 1783 in batch cultures with gassing by air/oxygen. They studied the influence of the oxygen concentration and pH of the fermentation medium on product yield. According to them the product yield decreases at acidic pH and below oxygen concentrations of 4×10^{-4} mol/L. The yields of 87-94% were obtained. Usage of air decreased yield by 7 % due to the formation of glycerate as a by-product in fermentation medium. Boriesa et al. (1991) determined kinetic parameters during dihydroxyacetone production by Gluconobacter oxydans in batch culture with different glycerol concentrations with mannitol as a substrate. The fed-batch culture converted more glycerol than batch culture performed with initial substrate concentration of 100 g/L making the kinetic parameters more optimal. They found that presence of dihydroxyacetone exerts an inhibitory effect on G. oxydans. The rate of growth decreases with increasing dihydroxyacetone concentration, and ceases at a dihydroxyacetone concentration of 61 g/L. Glycerol oxidation into dihydroxyacetone is not affected during this period suggesting a decoupling of growth and production. At dihydroxyacetone concentration of 108 g/L, the glycerol conversion ceases. Batch growth followed by fed-batch on glycerol avoids the inhibitory effects and leads to an optimized dihydroxyacetone production process. Bauer et al. (2005) investigated the influence of the product inhibition by dihydroxyacetone on gluconobacter oxydans for a semi-continuous two-stage repeated-fed-batch process. The bioreactor system was a combination of a laboratory scale bubble column with a height of 300 mm and an inner diameter of 100 mm and a laboratory-scale stirred reactor having the same dimensions. The total volume of each reactor was 2 L. The reaction volumes were 1.5 L and 1.47 L for reactor stage 1 and reactor stage 2, respectively. Both reaction volumes were kept nearly constant during the repeated-fed-batch experiments by a correctly set concentration of the glycerol feed in order to compensate the loss of broth volume due to evaporation. The pH in reactor 1 was controlled at 5.3. The pH in reactor 2 was not controlled. The temperature was controlled at 30°C. A dihydroxyacetone concentration of 80 kg/m^3 was achieved without any influence of product inhibition. The regeneration capability of the reversibly product inhibited culture from a laboratory-scale bioreactor system was observed up to a dihydroxyacetone concentration of about 160 kg/m^3. At higher dihydroxyacetone concentrations, the culture was irreversibly product inhibited. The reachable maximum final dihydroxyacetone concentration was as high as 220 kg/m^3. Adlercreutz (1986) studied reaction kinetics for one-step reactions catalyzed by cells immobilized in calcium alginate spherical beads. He assumed Michaelis-Menten kinetics for a one-substrate reaction taking into account the external and internal mass transfer of the substrate for the immobilized preparations. The reaction rate was limited by oxygen when glycerol was in excess. Use of p-

benzoquinone increased the production rates compared with oxygen. Chevalier et al. (1990) reported two distinct pathways for the anaerobic and aerobic metabolism of glycerol used by Klebsiella Pneumoniae. During anaerobic growth, glycerol is first converted to dihydroxyacetone by glycerol dehydrogenase and its phosphorylation yields dihydroxyacetone phosphate. During aerobic growth, glycerol is initially phosphorylated to yield glycerol 3-phosphate and its subsequent reduction gives dihydroxyacetone phosphate. When anaerobically growing cells are switched to aerobic conditions, synthesis of glycerol dehydrogenase is repressed, glycerol dehydrogenase is inactivated, and the protein is degraded. Exposure of cells to oxygen inactivates ethanol dehydrogenase and propanediol oxidoreductase. Exposure of anaerobically growing cells to hydrogen peroxide inactivate enzymes and leads to rapid degradation of glycerol dehydrogenase. Chloramphenicol can prevent the inactivation and degradation of glycerol dehydrogenase caused by exposure to oxygen but did not block that caused by hydrogen peroxide.

Succinic Acid

Succinic acid is a dicarboxylic acid produced as an intermediate of the tricarboxylic acid cycle and also as one of the fermentation products of anaerobic metabolism (Gottschalk, 1986). It can be used for the manufacture of synthetic resins and biodegradable polymers and as an intermediate for chemical synthesis (Zeikus, 1980). Lee et al. (2001) has reported the method of production of succinic acid by fermentation of glycerol by using Anaerobiospirillum succiniciproducens. Cells were grown in sealed anaerobic bottles containing 100 mL minimal salts medium containing 5 g/L glucose, 2.5 g/L yeast extract and 5 g/L polypeptone with CO_2 as the gas phase. The medium was heat sterilized (15 min at 121°C) in anaerobic bottle with nitrogen headspace. To the sterile medium, concentrated H_2SO_4 was added to adjust the pH to 6.5. They cultured cells in a medium containing 6.5 g/L glycerol to give a high yield (133%) of succinic acid thus avoiding the formation of acetic acid as by-product. The gram ratio of succinic acid to acetic acid obtained was 25.8:1, which was 6.5 times higher than that obtained using glucose as a carbon source. When glucose and glycerol were co-fermented with the increasing ratio of glucose to glycerol, the succinic acid yield decreased, suggesting that glucose enhanced acetic acid formation irrespective of the presence of glycerol. The consumption of glycerol was strongly dependent on the amount of yeast extract added to culture medium.

Hydrogen

Hydrogen is proposed to be the next generation renewable fuel. (US Department of Energy, 2006) plans to spend $ 1.2 Billion in research and development for its possible implementation as future automobile fuel. It might prove an indispensable energy career providing energy security forever. It has excellent environmental compatibility. Ito et al. (2005) did H_2 and ethanol production from glycerol using Enterobacter Aerogenes HU-101. They produced H_2 in continuous culture of self-immobilized cells with a packed-bed reactor. Cultures were maintained at - 80°C with 15% glycerol. A cylindrical glass column reactor diameter of 2.7cm and height of 17cm with a working volume of 60 mL was used for the continuous culture. Fresh medium was supplied from the bottom by a peristaltic pump and evolved gas and effluent liquid were discharged from the top of the reactor. Two mL of the seed culture was transferred into the reactor. After 12 h of incubation in the batch mode, continuous cultivation was initiated by feeding the sterilized medium at a dilution rate of 0.1/h with the peristaltic pump. The cells were cultivated anaerobically at 37°C without controlling pH. The glycerol was diluted with a synthetic medium to increase the rate of glycerol utilization and the addition of yeast extract and tryptone to the synthetic medium accelerated the production of H_2 and ethanol. They reported that yield of H_2 and ethanol decrease with an increase in the concentrations of biodiesel wastes and commercially available glycerol. Moreover, due to a high salt content in biodiesel wastes, the rates of H_2 and ethanol production were much lower than those at the same concentration of pure glycerol. The maximum rate of H_2 production obtained was 30 mmol/L·h. Giving a porous ceramics material support to fix cells in the reactor increased H_2 production rate to 63 mmol /L·h with a corresponding ethanol yield of 0.85 mol/mol-glycerol. Wood (2002) reported that chemical engineers from the University of Wisconsin (Madison) have developed a platinum-based catalytic reforming process operating at moderate temperatures and pressures for hydrogen production from simple biomass-derived molecules glucose and glycerol. The process prevents any steam formation to produce hydrogen only. CO_2 is a by-product. Hirai et al. (2005) did steam

reforming of glycerol in the gas phase with catalysts loaded with Group 8-10 metals. The catalysts were prepared via a conventional impregnation method, using Y_2O_3, ZrO_2, CeO_2, LaO_3, SiO_2, MgO, and Al_2O_3 as supports. A fixed-bed, flow-type reactor made of stainless steel was operated at atmospheric pressure. An aqueous solution of glycerin was fed by a micropump for high-performance liquid chromatography. Alumina balls were placed above a catalyst bed to preheat the glycerine mixture using fixed amount of catalyst for each run. According to them loading of 3 %wt ruthenium on Y_2O_3 at 500°C is optimal for the steam reforming of glycerin gave the best results. The following is the chemistry of the reactions.

Steam reforming of glycerin:

$$C_3H_8O_3 \xrightarrow{H_2O} 3CO + 4H_2 \quad (1)$$

Water-gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (2)$$

Overall reaction:

$$C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \quad (3)$$

Methanation reaction:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (4)$$

Huber et al. (2003) did aqueous-phase reforming of biomass-derived oxygenated hydrocarbons over a tin-promoted Raney-nickel catalyst. The temperatures were around 500 K. The desired catalytic pathway for the production of H_2 and CO_2 by aqueous-phase reforming of oxygenated hydrocarbons involves cleavage of C-C bonds as well as C-H and/or O-H bonds to form adsorbed species on the catalyst surface. Cleavage of these bonds occurs readily over group-8 metals, such as Pd and Rh. The performance was comparable with relatively costly platinum-based catalysts for production of hydrogen from ethylene glycol, glycerol, and sorbitol. The optimal Sn-promoted Raney-Ni catalyst was prepared by decomposition of tributyl tin acetate and had a bulk Sn/Ni atomic ratio of 0.075. They found a decrease of methanol formation with addition of tin to nickel. Another process reported for hydrogen production is the pyrolysis and steam gasification of glycerol. Valliyappan (2004) carried out reactions in an inconel, tubular, fixed bed down-flow reactor at atmospheric pressure. He studied the effects of carrier gas flow rate, temperature and different particle diameter of different packing material on the product yield, product gas volume, composition and calorific value. According to him increase in carrier gas flow rate showed insignificant effect on synthesis gas production at 800ºC with quartz chips diameter of 3-4 mm. This increased gas yield from 65 to 72 %wt while liquid yield decreased from 30.7 to 19.3 %wt when carrier gas flow rate decreased from 70 to 30 mL/min. Reaction temperature showed linear response for the hydrogen yield increasing from 17 to 48.6 mol% and synthesis gas production increasing from 70 to 93 mol%. Pyrolysis reaction at 800°C, 50 /min of nitrogen and quartz particle diameter of 0.21-0.35 mm maximized the gas product yield (71 %wt), hydrogen yield (55.4 %mol), synthesis gas yield (93 %mol) and volume of product gas (1.32 L/g of glycerol). The steam gasification of glycerol was carried with two different packing materials quartz and silicon carbide by changing the steam to glycerol weight ratio from 0:100 to 50:50. The addition of steam to glycerol increased the hydrogen yield from 55.4 to 64 mol% and volume of the product gas from 1.32 L/g for pyrolysis to 1.71 L/g of glycerol. Synthesis gas yield and calorific value of the product gas at this condition was 92 mol% and 13.5MJ/m^3, respectively. The net energy recovered at this condition was 117.19 kJ/mol of glycerol fed.

Polyglycerols

Polyglycerol esters find their utilization as antifogging and antistatic additives, lubricants, or plasticizers. Clacens et al. (2002) studied the selective etherification of glycerol. Etherification was carried out at 533 K in a batch reactor at atmospheric pressure under N_2 in the presence of 2 %wt of catalyst, water being eliminated and collected using a Dean-Stark system. They studied impregnation of mesoporous solids with different basic elements in order to make them active, selective and stable for the target reaction. Impregnated mesoporous mixture were prepared and agitated at ambient temperature for 2 h. The solvent (methanol) was then rapidly evaporated under vacuum and the solid was calcined under air at 723 K overnight at a heating rate of 1 K/min. The best value to glycerol was obtained over solids prepared by caesium impregnation. The re-use of these caesium-impregnated catalysts did not affect the selectivity to the glycerol fraction. In the presence of lanthanum or magnesium containing catalysts, the glycerol dehydration to acrolein was very significant whereas this unwanted product is not formed when caesium was used as impregnation promoter.

Polyesters

Stumbe and Bruchmann (2004) prepared hyperbranched polyesters by reacting glycerol and adipic acid without any solvents in the presence of tin catalysts. Adipic acid and glycerol were charged into a three necked glass reactor equipped with a gas-inlet pipe for N_2 addition and a claisen condenser with vacuum adapter. The mixture was melted at 100°C under N_2 atmosphere with constant stirring. The temperature was then elevated to 150°C and 0.15 %wt dibutyltin oxide was added to the reaction mixture in order to initiate the polycondensation reaction reducing pressure to 100 mbar. Hyperbranched polyesters obtained had molecular weight of 23,370 g /mol. Pramanick et al. (1988) prepared cross-linked co-polyesters of citric acid and glycerol from different mole ratios. The acid to glycerol mole ratios 0.83 and 0.88 produced maximum cross-link density. Microbial degradation of the polymer samples in aqueous suspension was studied using the fungus Aspergillus niger and the bacterium E. coli. All the polymer samples were degraded by Aspergillus niger and E. coli. More the cross-linking, more was the degradation. Kulshrestha et al. (2005) carried out bulk polycondensations at 70°C for 42 h catalyzed by Immobilized Lipase B from Candida antartica. Hundred mL round-bottom flask was transferred with 2.93 g adipic acid and a mixture totaling 20 mmol of 1,8-octanediol and glycerol. It was heated with stirring at 70°C to form a liquid with two distinct phases. Dried Novozyme 435 beads were then added to the reaction mixture. The polymerization was terminated after 42 h by dissolving the reaction mixture in chloroform, removing the enzyme by filtration, and stripping off the solvent. The polyesters had octanediol-adipate and glycerol-adipate repeat units. Variation of glycerol in the monomer feed gave copolymers with degree of branching from 9 to 58%. Villeneuve et al. (1998) carried out enzymatic esterification of glycerol with dicarboxylic acids to produce mono- and/or diesterified glycerol adducts. Reaction of glycerol supported on silica with dimethyl adipate gave a 40% yield of glycerol-monomethyl adipate ester. Best yields of glycerol-mono- and diesters (70% and 10%, respectively) were obtained by direct esterification of free glycerol with a diester in a solvent-free system with less than 4 % water present. Nagata et al. (1996) prepared aliphatic polyesters from glycerol and aliphatic dicarboxylic acids. Prepolymers prepared by melt polycondensation were cast from dimethylformamide solution and post-polymerized for various times to form a network. A mixture of 0.06 mol of dicarboxylic acid and 0.04 mol of glycerol was heated in a stream of nitrogen near 200°C. The degree of reaction increased with increasing post-polymerization time and length of the methylene chain. The heat distortion temperature also increased with increasing post-polymerization time. Density, water absorption and weight loss by alkali hydrolysis decreased with increasing methylene chain length. Alksnis et al. (1976) did the polycondensation of oxalic acid and glycerol. Polycondensation was carried out in the presence of compounds that did not dissolve oxalic acid and glycerol, but form an azeotropic mixture with water below 100°C. Anhydrous oxalic acid and oxalic acid dihydrate was used for the synthesis of oligoesters. The decarboxylation proceeded parallel with polycondensation of oxalic acid and glycerol. Decarboxylation of carboxyl groups of glycerol monooxalate was found to be accelerated by the arrangement of primary and secondary hydroxyl groups in the glycerol molecule in the 1,2-position. Zhang et al. (2005) synthesized branched polyesteramides (PEAs) from adipic acid, hexamethylene diamine, 1,4-butanediol and caprolactam using glycerol as branching agent by melt polycondensation. Under nitrogen atmosphere predetermined amounts of glycerol were added into a 150 mL reactor equipped with a mechanical stirrer, thermometer and condensation column. The mixture was heated and refluxed for 1 h at 140°C. Then it was heated up to 200°C gradually over 15 min. After about 9 mL of water evaporated, titanium tetrabutoxide catalyst was charged into the reactor. The reaction was kept for another 1 h at 230°C. Then it was continued under vacuum for several hours until the paddle hardly stirred because of the increase in melt viscosity. At the end, the resultant melt was poured onto a steel plate. Thus aliphatic PEA was obtained. The obtained copolymers showed that the melting and crystallization temperatures decrease with increasing glycerol content. The PEAs degraded quickly in alkali and the degradation rate increased with the medium temperature. The branching substantially enhanced the degradation.

Polyhydroxyalkonates

Koller et al. (2005) studied fermentations for polyhydroxyalkonates production in bioreactors on hydrolyzed whey permeate and glycerol liquid phase using a highly osmophilic organism. Without any precursor, the organism produced a poly [3(hydroxybutyrate-co-hydroxyvalerate)] co-polyester on both carbon sources. During the accumulation phases, a constant 3-hydroxyvalerate content of 8-10% was obtained at a total PHA concentration of 5.5 g/L (on hydrolyzed whey permeate) and 16.2 g/L (glycerol

liquid phase). In an additional fermentation, an expensive nitrogen source was substituted by meat and bone meal beside the glycerol liquid phase as a carbon source resulting in a final PHA concentration of 5.9 g/L. Ashby (2005) reported the synthesisation for polyhydroxyalkanoates by mixed culture fermentation of glycerol. P. oleovorans and P. corrugata grew and synthesized poly (3-hydroxybutyrate) (P3HB) and medium-chain-length PHA from glycerol at concentrations up to 5%vol. P. oleovorans (1.5 mL from overnight LB broth culture) was inoculated 24 h prior to P. corrugata (1.5 mL) and the flasks allowed to incubate as described above for a total of either 48 or 72 h. Cellular productivity maximized at 40% for P. oleovorans in 5%vol glycerol and 20% for P. corrugata in 2%vol glycerol after 72 h. Increasing the glycerol media concentration from 1% to 5%vol caused a 61% and 72% reduction in the molar mass of the P3HB and mcl-PHA polymers, respectively. The growth patterns of P. oleovorans and P. corrugata on glycerol permitted their use as mixed cultures to produce natural blends of P3HB and mcl-PHA. By incorporating a staggered inoculation pattern and varying the duration of the fermentations, P3HB/mcl-PHA ratios were achieved that varied from 34:66 to 96:4.

Glycerol Processing by Different Processes and

Other Uses

Demirbas (1998) delignified wood and agricultural materials in glycerol at atmospheric pressure, for the production of pulps. Air-dried wood discs were reduced in size before chemical treatments. Each chipped ground wood sample was mixed to facilitate homogeneity and stored in polyethylene containers at 253 K before delignification assay. The wood powder or the chips were loaded into a 250 mL autoclave. In this experiment 9 g of wood were treated in 45-75%wt glycerol, using a charge ratio of wood/solvent of 9/70-9/100(g/g) and 0.5-1.0%wt NaOH or Na_2CO_3 as catalyst, or without catalyst. The maximum delignification temperature was 498 K, with or without mechanical stirring, and 3-9 h of cooking time. At the end of the delignification, fractions were separated from unreacted wood by filtration. The optimization of the aqueous glycerol delignification conditions of Ailanthus wood chips at 440-500 K temperatures, long cooking times, and using a catalyst was carried out. The best results were obtained with 72% glycerol using a ratio of wood/solvent of 9/100 (g/g), 1%wt NaOH as catalyst, 0.3 mm chip thickness, 498 K temperature, and a cooking time of 9 h. Under these conditions about 94% of the initial wood lignin was removed. Pulps obtained under these conditions gave pulp yield, Kappa number, and Klason lignin in the range of 53%, 16 and 8%, respectively. Aqueous glycerol showed a better effect than non-aqueous glycerol on the pulp fiber-length and pulp yield. Xu et al. (1996) reported that gasification of feedstocks like glycerol in super critical water could be catalyzed by varieties of charcoal and activated carbon to produce hydrogen-rich synthesis gas. The reactor used was made of Inconel 625 tubing with 9.53 mm (outer diameter) and 4.75 mm (internal diameter). It was maintained at isothermal conditions by a furnace and a downstream heater. Glycerol completely decomposed in supercritical water (without a catalyst) to a hydrogen rich synthesis gas after 44 s at 600°C and 34.5 MPa. Pressures above about 25 MPa were adequate to realize high gasification efficiencies. Yang and Tsai (1997) reported that Poly (ethylene terephthalate) fabrics could be treated with sodium hydroxide using glycerol as the solvent. Du et al. (2005) reported the process for synthesisation of carbon onions via thermal reduction of glycerol. In their experiment, 0.45 g of magnesium powder (99%) and 5 mL of glycerin were mixed in a stainless steel autoclave of 25 mL. The autoclave was sealed and maintained at 650 °C for 12 h, then cooled to room temperature naturally. The following reaction occurred.

$$3Mg + C_3H_8O_3 \xrightarrow{650\,^{\circ}C} 3MgO + 3C + 4H_2$$

A portion of the black product was directly characterized by X-ray diffraction. The yield of carbon onions was about 60%. The obtained carbon onions had diameters ranging from 60 to 90 nm. Brown et al. (1999) showed that glycerol could be used as a dielectric medium for compact pulse power systems. The high intrinsic time constant (10.7 ms at 0°C) and high dielectric constant (42.5 at 25°C) makes it suitable for repetitive systems operating with charge times in excess of 1ms. Kochegarov and Belitskaya (1971) reported that glycerol could be used for Indium-Antimony alloys deposition from indium and antimony chloride-tartrate solutions in glycerol. The electrolysis conditions were cathodic current density 0.25 to 0.5-amp d/m^2 and the temperature being 85°C. The indium content in the alloy increased with increase of current density and with decrease of antimony concentration in solution. Stirring raised the antimony

content in the deposits. Villeneuve (1998) studied the enzymatic esterification of glycerol with dicarboxylic acids to produce mono- and/or diesterified glycerol adducts. The reaction of isopropylidene glycerol with dimethyl sebacate gave a yield greater than 95% of isopropylidene glycerol-monomethyl sebacate ester. Reaction of glycerol supported on silica with dimethyl adipate gave a 40% yield of glycerol-monomethyl adipate ester. Demirbas (2000) reported that the ground biomass samples could be converted completely into water insoluble and soluble chemicals in anhydrous glycerin in the presence of KOH. The biomass samples were dried, chipped and then grounded in a Wiley mill to pass a screen of 1 mm aperture. The ground sample and anhydrous glycerin containing the appropriate amount of alkali (KOH and Na_2CO_3) were put into a round bottom distilling flask with two cylindrical standard ground joint necks attached to a Liebig condenser. Gaseous products from the liquefaction passing into the condenser were collected in a beaker at ambient pressure. The reaction time for the liquefaction was 15–20 min. The products obtained dissolved completely in the aqueous alkaline solution. The content of the distilling flask and the collecting beaker were combined, and extracted with benzene. The combined benzene extracts were washed with distilled water. The solution was dried over anhydrous magnesium sulfate and filtered. Kimuro and Tsuto (1993) reported the synthesization of DL-serine, glycine, serinol and related compounds catalytically from glycerol. Reductive lamination over a Ru-Pd/C catalyst of glyceric acid (one of the oxidation products of glycerol) was effective for DL-Ser synthesis. Glycine was catalytically formed from DL-Serine by dehydrogenation and decarbonylation in hydrogen atmosphere. Catalytic oxidation of Serinol prepared by reductive amination over an Rh-Pd/C catalyst of dihydroxyacetone, another oxidation product of glycerol was also effective for DL-Ser synthesis. Stein et al. (1983) did the pyrolysis of glycerol in steam in a laminar flow reactor at 650-700°C. The products of decomposition were carbon monoxide, acetaldehyde and acrolein. Acetaldehyde and acrolein further decomposed to produce primarily carbon monoxide, ethylene, methane and hydrogen.

Glycerol-water mixture can be used as organic brine (Zoller, 1924) for the refrigeration purposes. The qualities which make it suitable for refrigeration are 1). Less ionizing in aqueous solution,2). Low oxidation of metals, 3). Easy to handle, and 4). The weights of the alcohol-water mixtures are much less per unit volume of brine. The mixture vapor pressures are extremely low at the ordinary commercial refrigeration temperatures, so much so that the loss through volatilization is negligible. Their refrigeration capacities are about equal to that of the inorganic brines. Glycerol being a glucogenic substance can be used as feed additives for ruminants (Hajney, 1981). It is effective to prevent ketosis in high yielding dairy cows.

Summary

Biodiesel production in the United States is increasing dramatically. The by–product of biodiesel production is the crude glycerol, which is 10 %wt of vegetable oil. Crude glycerol possesses low value due to the presence of impurities. To make it of commercial grade, it should be treated and refined through filtration, chemical additions, and fractional vacuum distillation. The refining of the crude glycerol may be a costly affair depending on the economy of production scale and/or the availability of a glycerol purification facility. This paper is an attempt to report the possible alternate technologies for the huge amount of crude glycerol generated annually. It is quiet evident that there can be many possible ways of converting crude glycerol to various useful compounds. For a quick understanding that what can be done with this crude glycerol,derivative products along with their corresponding methods/processes are summarized in a tabular form. This may be helpful for the Biodiesel technocrats giving them a choice for which compound they want to go for from crude glycerol.

Product Name	Process Method/Nature	Researchers/Scientists
1,3-propanediol	Continuous and Batch Microbial Fermentations mainly by the microorganisms Clostridium Butyricum and Klebsiella Pneumoniae. The cultures are specificied by nutrient, microbial and glycerol concentrations. The key parameters are Temperature, pH, Time, and Agitation speed. The target is to maximize the yield and productivity of 1,3-propanediol.	Himmi et al. (1999) Papanikolaou and Aggelis (2003) Zeng (1997) Xiu et al. (2004) Menzel et al. (1997) Wang et al. (2001)
	Selective Hydroxylation Technique involving three stages of Acetalization, Tosylation, and Detosylation.	Wang et al. (2003)
Hydrogen	Continuous Microbial Fermentation by Enterobacter Aerogenes HU-101.	Ito et al. (2005)
	Catalytic reforming operating at moderate temperatures and pressures.	Wood (2002)
	Steam reforming of glycerol in the gas phase with Group 8-10 metals catalysts.	Hirai et al. (2005)
	Aqueous-phase reforming over a tin-promoted Raney-nickel catalyst.	Huber et al. (2003)
	Pyrolysis and steam gasification of glycerol.	Valliyappan (2001)
Succinic Acid	Microbial Fermentation by Anaerobiospirillum succiniciproducens.	Lee et al. (2001)
1,2-propanediol	Low-pressure hydrogenolysis in multi-clave reactor pressurized with hydrogen.	Dasari et al (2005)
	Selective hydrogenolysis with raney nickel catalyst in an autoclave with hydrogen.	Perosa and Tundo (2005)
Dihydroxyacetone	Chemoselective catalytic oxidation with platinum metals.	Garcia et al. (1994)
	Selective oxidation of glycerol with platinum-bismuth catalyst.	Kimura (2001)
	Microbial fermentations by Gluconobacter oxydans in a Batch/Semi-continuous process.	Bauer et al. (2005)
Polyesters	Reacting glycerol and adipic acid in the presence of tin catalysts. Reacting citric acid and glycerol at different mole ratios. Polycondensation of oxalic acid and glycerol. Reacting glycerol and aliphatic dicarboxylic acids.	Stumbe and Bruchmann (2004) Pramanick et al. (1988) Alksnis et al. (1976) Nagata et al. (1996)
Polyglycerols	Selective etherification of glycerol.	Clacens et al. (2002)
Polyhydroxyalkanoates	Fermentation of hydrolyzed whey permeate and glycerol liquid phase by osmophilic organism.	Koller et al. (2005)

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