Value Added Derivatives Of Glycerol Obtained From Biodiesel Industry: A Review

Saroj.K Padhi [b], * Achyut K. Panda [b], R. K. Singh [a]
[a]National Institute of Technology Rourkela, Odisha,
[b]Centurion University of Technology and Management, Odisha, India

Authors Details

1.   ***Corresponding Author**: Dr. Achyut K. Panda, Assistant Professor, Department of Chemistry, School of Engg. and Technology, Bhubaneswar Campus, Centurion University of Technology and Management, Odisha, India PIN: 752050, India,

2.   Prof. (Dr.) R. K. Singh, Department of Chemical Engineering, National Institute of Technology, Rourkela (Orissa) , India, PIN: 769008,

3.   Dr. S. K. Padhi, Department of Chemical Engineering, School of Engg. and Technology, Parlakhemundi Campus, Centurion University of Technology and Management, Odisha, India,

Abstract

The recent increases in crude oil prices, depletion of fossil fuel and the global concern for the environment have created unprecedented opportunities to displace petroleum-derived materials with renewable energy sources. Bio-energy is as new and eco-friendly source of energy and bio-diesel is one of them. The production of biodiesel from vegetable oils provides numerous local, regional and national economic benefits. To develop biodiesel into an economically viable and significant option across the world, it is required to utilize suitably the byproducts and ensure good prices for it. Glycerol is a by-product from biodiesel industry, which is generated in large amounts during the production of biodiesel from different vegetable oils. The tremendous growth of the biodiesel industry created a glycerol surplus. 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 state. This report presents the currently available studies and possible ways on the

utilizations of crude glycerol generated from biodiesel industry. Conversion of glycerol from biodiesel plants to different value added chemicals like propanediols, acrolein, polyglycerol, tartonic acid etc. has the capability to turn biodiesel production units into economically attractive entities. In the present report, various routes of conversions have been discussed. A few application of different value added chemicals have also been discussed.

Keywords: Vegetable oil, transesterification, Bio diesel and Glycerol, Value added byproducts

Contents

1. Introduction

Our economy and lifestyle rely on the use of fossil resources for the transportation fuels and materials; however there has been rising concern over their cost, sustained availability, and impact on global warming and pollution [1]. This has led to a search for technologies that generate fuels and materials from renewable carbon sources, such as plant biomass. Depending on the component of the biomass used as feedstock and the technology employed to transform component into desired product, at least three general platforms have been envisioned: the sugar [2], syngas (synthesis gas) [3], and oil [4] platforms. The sugar and oil platforms are the best established today, with bioethanol and biodiesel being the examples of their commercial products respectively. Bioethanol is produced through microbial fermentation of sugar derived from corn, sugarcane or sugar beet [5]. Biodiesel is produced by the transesterification of vegetable oils with alcohols to produce esters. [4]

Given the increasing demand for bio-fuels [6], there is an urgent need to investigate new and more efficient alternative ways for their production. For example, the conversion of lignocellulosic biomass to ethanol and the use of oil accumulating algae in the production of biodiesel are being investigated [7, 8]. These approaches are very promising and will provide abundant non food feedstocks for the production of bio-fuels with environmental benefits and large net energy gains. However, an outstanding issue in both current and future bio-fuel production platforms is economic viability. The implementation of bio-refineries has been proposed as a means to increase the economic viability of the bio-fuel industry [9]. In its 'conventional' form, a bio-refinery would make use of a fraction of the feedstock to co-produce different chemicals along with the bio-fuel. The higher revenue

from the co-product, would improve the economics of bio-fuel production. A more economically viable model for a bio-refinery, however should consider the use of byproducts or waste streams generated during the production of bio-fuel. Glycerol-rich streams generated by the bio-fuels industry have the potential to be used in this context. Bio-diesel is a domestically produced, renewable fuel that can be manufactured from vegetable oils, animal fats, or recycled restaurant greases and it can replace fossil fuel [10]. Bio-diesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources [11]. Although short term tests using neat vegetable oil showed promising results, longer tests led to injector coking, more engine deposits, ring sticking and thickening of the engine lubricant. These experiences led to the use of modified vegetable oil as a fuel. Although there are many ways and procedures to convert vegetable oil into a diesel like fuel, the trans-esterification process was found to be the most viable oil modification process [12]. Biodiesel has demonstrated a number of promising characteristics, including reduction of exhaust emissions [13].

There are more than 350 oil bearing crops identified, among which only sunflower, safflower, soybean, cottonseed, rapeseed and peanut oils are considered as potential alternative fuels for diesel engines [14].. Although vegetable oils can be used in diesel engines but due to high viscosity, low volatility and poor cold flow properties it causes many problems [15, 16]. Trans-esterification was well known as early as 1864, when Rochleder described glycerol preparation through ethanolysis of castor oil [17-18]. Trans-esterification is the process of using an alcohol (e.g. methanol, ethanol or butanol), in the presence of a catalyst, such as sodium hydroxide or potassium hydroxide, to break

the molecule of the raw renewable oil chemically into methyl or ethyl esters of the renewable oil, with glycerol as a by product. Glycerol is the major value-added byproduct produced from oil and fat from transesterification reactions performed during biodiesel manufacturing processes. Glycerol is liberated at levels of around 10% of the oil or fat and approximately one ton of glycerin is produced for every ten tons of biodiesel. The global amount of glycerin generated from biodiesel is increasing rapidly.

Absorbing excess glycerin into these markets by replacing petrochemically derived polyols such as ethylene glycol, propylene glycol, and pentaerythritol used in automobile antifreeze, aircraft deicers and alkyd resins may partially alleviate glycerin surpluses. The development of innovative applications for glycerin appears to be the most constructive approach to utilize excess glycerin. Practically, developing glycerol as a primary chemical building block that may be converted into other value added chemicals becomes more attractive as crude glycerin prices drop. Currently, industry and nation is increasing their efforts to develop new and improve existing glycerol chemistry. Present study focused on importance of SVO ,production of biodiesel from oils and the different routes to synthesis of value added chemicals like propylene glycol, propandiols, acrolein, MTBEs fuel oxygenates, epichlorohydrin from glycerol and to analyse the economics of the existing methods of synthesis.

2. Straight vegetable oil (SVO) and Biodiesel

The concept of using vegetable oil as a fuel dates back to 1895 when Dr. Rudolf Diesel developed the first diesel engine to run on vegetable oil. Rudolf Diesel stated: "the use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of the present
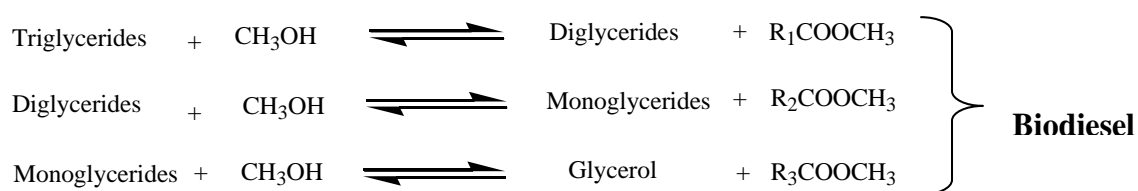
time"[19]. Different sources of vegetable oil are like soybeans, sunflower seeds, rape seeds, palm, Jatropha, Karanja, Rapeseed in different ways like preheating the oil, blending it with diesel and proved that vegetable oils are feasible substitutes for diesel fuel [20-35]. According to Guibet et al. [36], evaluating a SVO as a diesel fuel reduces to focusing on the viscosity, density, and cloud point. The cloud point of SVOs is strongly related to the fatty acids saturation. It has been shown that short-term engine performance is not greatly affected when vegetable oils are used as fuel [37-39]. However, long-term use of straight vegetable oils or in blends with small quantities of diesel fuel has shown some adverse effects on the engine power output, emissions and durability [40-42]. Some of the properties of vegetable oils which influence engine performance have been investigated thoroughly [43-45]. It would be the best way to use vegetable oil in diesel engines in the long term as there is no processing required. If vegetable oil is to be significant as one of the future fuels for compression ignition engines it would be necessary to modify fuel injection equipment and combustion chamber design. These changes would be needed to take into account the effects of properties of vegetable oils on the spray characteristics and the subsequent process. Few researchers have worked with feedstock having higher FFA levels using alternative processes [46]. But there are certain exceptional cases wherein direct trans-esterification cannot be performed. Such cases appear in raw vegetables oils (Non edible oil) like karanja oil, mahua oil, Nim,Jatropha and sal oil, etc because these raw vegetable oils posses higher free fatty acid (FFA). If the acid value is less than 3, then the raw vegetable oil can be directly trans-esterified. If the acid value is greater than 3, then there is slight change in the production process. At first the oil undergoes esterification

followed by trans-esterification. In the esterification process the excess of the free acid gets reacted and the remaining acid content in the oil undergoes trans-esterification. So this method is effective for oils that contain higher free fatty acid (FFA) content .Trans esterification is a chemical reaction that aims at substituting the glycerol of the glycerides with three molecules of mono alcohols such as methanol thus leading to three molecules of methyl ester of vegetable oil **[10].** Suitable alcohols include: methanol, ethanol, propanol, butanol, and amyl alcohol. Methanol and ethanol are widely used in the trans-esterification process because of low cost **[47]**. This process is widely used to reduce the viscosity of triglycerides, there by enhancing the physical properties of fuel and improve engine performance. However, higher ratio of alcohol to oil is generally employed to obtain biodiesel of low viscosity and high conversion **[48].** Alkali-catalyzed transesterification is very fast compared to acid catalyzed trans-esterification **[18, 49].**

3.0.   Glycerol as by-product of Biodiesel

Glycerol is generated as a by-product during the processes of transesterification (equation 1) of vegetable oil [**50-51**].

Typical reaction to produce biodiesel is given by the following Equation 1;

$$Triglycerides + CH_3OH \rightleftharpoons Diglycerides + R_1COOCH_3$$
$$Diglycerides + CH_3OH \rightleftharpoons Monoglycerides + R_2COOCH_3$$
$$Monoglycerides + CH_3OH \rightleftharpoons Glycerol + R_3COOCH_3$$

Biodiesel

Equation 1 Reactions in biodiesel manufacture

During the transesterification reaction about 10 wt% (of fatty acid) glycerol is produced. Production of glycerol is expected to increase with the increase in production of biodiesel [**52**]**.** Glycerol is a commodity chemical with multifaceted utilities [**53**]. The soap and

cosmetics industry constitutes 28% of glycerol utilization whereas polyglycerols, esters, food and beverages constituted up to 47%. Glycerol is a topic of research recently and the researchers are keen to find out its alternate applications for fuels and chemicals **[54-56].**

4. Conversion of Glycerol into Higher Value Products (Derivatives of Glycerol)

Glycerol can be converted to value-added products by different methods like pyrolysis, steam gasification and catalytic treatment. At lower projected costs, there is a tremendous potential to develop a variety of new processes and product lines from glycerol, taking advantage of its unique structure and properties. Lower cost glycerol could open significant markets in polymers, ethers, and other compounds. The different routes of glycerol utilization to value added derivatives are discussed below.

4.1. Production of oxidation derivatives of glycerol

Selective oxidation of glycerol leads to a very broad family of derivatives such as dihydroxyacetone (DIHA) glyceraldehydes (GLYHYDE), glyceric acid (GLYA), glycolic acid (GLYCA), hydroxypyruvic acid (HPYA), mesoxalic acid (MOXALA), oxalic acid (OXALA) and tartronic acid (TARAC), that would serve as new chemical intermediates, or as components of new branched polyesters or nylons. These products would address very large chemical markets. Technical barriers for production of these materials include the need of development of selective catalytic oxidation technology which can operate on a polyfunctional molecule such as glycerol. In addition, the processes would also need to use simple oxidants, such as oxygen or air, to carry out the required transformations.

In order to control the product selectivity to the desired product, glycerol oxidation has been studied extensively by applying different reaction conditions using different metals

(Au, Pd, Pt, Pt/Bi) supported mainly on carbon. The reaction conditions particularly the pH and the right choice of the metal is reported to tune the selectivity of the desired product and affect significantly the direction of the reaction pathway. Thus, by using acidic conditions, secondary alcoholic groups, dihydroxyacetone **[57]** and hydroxypyruvic acid [58] are formed, whereas at basic conditions, the primary alcoholic groups are preferentially oxidized and glyceric acid is obtained [54]. Depending on the metals employed, Au [59-60] and Pd [54] metals at basic conditions are more selective towards glyceric acid than Pt [61] metal. Doping Pt/C catalyst with Bi is reported to give the highest selectivity to dihydroxyacetone, indicating the change on the direction of the reaction pathway towards to the secondary alcoholic group [62]. Supported gold catalysts can give high selectivity to glyceric acid (>90%) at 100% conversion under alkaline conditions which depend on the methods of preparation [63-64].

The presence of similar reactive hydroxy groups renders its selective oxidation particularly difficult [64]. The oxidation of primary hydroxy groups yields glyceric acid and subsequently tartronic acid, both of which are commercially useful compounds. The aerobic oxidation of glycerol in water over conventional precious-metal-based catalysts such as Au/C and Pt/C yields glyceric acid. Carbon-supported Au catalyzes the oxidation of glycerol to sodium glycerate with 92% selectivity at full conversion, [65] where as Pt/C at $50^{o}C$ yields glyceric acid with a maximum 70% yield at pH 11 [54,66]. Pt supported over CeO_2 catalyzes the oxidation of both primary hydroxyl groups to give tartronic acid in 40% yield [67].

The organic nitroxyl radical TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) is a selective catalyst for both the oxidation of all the hydroxy groups of glycerol and thus affords high yields of ketomalonic acid by using NaOCl as a stoichiometric oxidant [68].
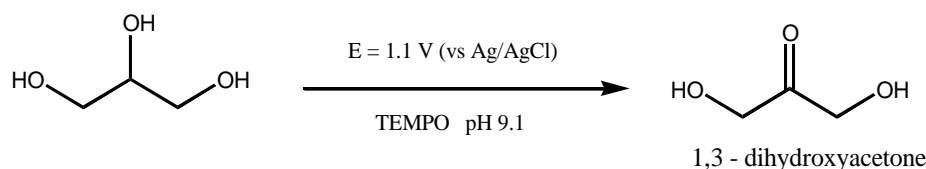
Reaction 2 One step oxidation of glycerol to 1,3 – dihydroxyacetone is achieved simply applying electric potential in presence of catalytic TEMPO

Oxidation of the secondary hydroxy group yields the important fine chemical dihydroxyacetone (DHA), whereas the oxidation of all three hydroxy groups yields the highly functionalized molecule ketomalonic (or mesoxalic) acid. A clean and direct conversion of glycerol into DHA by anodic oxidation in the presence of catalytic TEMPO is recently introduced. One step oxidation of glycerol to 1,3 – dihydroxyacetone is achieved simply applying electric potential in presence of catalytic TEMPO is given in above Equation 2 [69]. The process yield (25%) is comparable to that of the biotechnological process used in industry. However, no stoichiometric chemical oxidant is used throughout the whole process and the radical TEMPO can be entirely recovered at the end of the reaction by simple extraction [70].

Direct conversion of glycerol into poly (ketomalonate) (PKM) in an oxidative polymerization process using a single multifunctional supported CeBiPt/C catalyst in either under basic [71] or acidic [72] conditions is reported which can be converted to a high-molecular-weight polycarboxylate that is an excellent building block for household detergents.

4.2 Production of fuel oxygenates from glycerol (Esterification)

Although glycerol has comparatively high calorific value, it cannot be added directly to fuel as at high temperatures it polymerizes and thereby chokes the engine and also, it is partly oxidized to toxic acrolein. However, the glycerol derived oxygenates can be used as fuel additive. For example, glycerol tertiary butyl ether (GTBE) is an excellent additive with a large potential for diesel and biodiesel reformulation like oxygenated molecules such as methyl tertiary butyl ether (MTBE) used as valuable additives as a result of their antidetonant and octane-improving properties. In particular, a mixture of 1,3-di-, 1,2-di-, and 1,2,3-tri-tertbutyl glycerol, when incorporated in standard 30–40% aromatic-containing diesel fuel, leads to significantly reduced emissions of particulate matter, hydrocarbons, carbon monoxide, and unregulated aldehydes [73]. Such ethers are easily synthesized from glycerol by treatment with isobutylene in the presence of an acid catalyst, and the yield is enhanced by carrying out the reaction in a two-phase reaction system, with one phase being a glycerol-rich polar phase (containing the acidic catalyst) and the other phase being an olefin-rich hydrocarbon phase from which the product ethers can be readily separated [74]. On the other hand, if the reaction is carried out over an amberlyst resin, methanol in the crude glycerol must be removed to avoid catalyst poisoning. In an aim to replace toxic MTBE, the optimization of glycerol ether formulations based on the results of engine tests is being carried out [75].

5.3 Production of hydrogen and syn-gas from glycerol

The available literature on production of hydrogen and syn-gas from glycerol by pyrolyis and steam gasification is discussed in this section. The production of hydrogen from sorbitol, glycerol and ethylene glycol at temperatures of $225^{o}C$ and $227^{o}C$ and under high

pressure in a single-reactor aqueous-phase reforming process [56]. Platinum supported on - alumina was used as catalyst. Hydrogen yield was reported to be higher using sorbitol, glycerol and ethylene glycol than that of glucose. The hydrogen yields from glycerol reforming were 64.8 mol% and 57 mol% at 225 ^{o}C and 265°C respectively. Liquid products consisted of ethanol, 1,2-propanediol, acetic acid, ethylene glycol, acetaldehyde, 2-propanol, propionic acid, acetone, propionaldehyde and lactic acid. The production of hydrogen and syn-gas from pyrolysis of glycerol in a fixed bed reactor. Pyrolysis was performed with and without a carrier gas (nitrogen). One set of experiments was performed at 400^{0}C and 500^{0}C and glycerol flow rate of 2.0 g/h without using any carrier gas [76]. It was reported that the operation was quite difficult without using carrier gas because of char formation in the feed inlet. Another set of pyrolysis experiments was performed in a fixed bed reactor with the nitrogen flow rate of 50 mL/min over a temperature range from 350 ^{o}C to 700°C and glycerol flow rate from 2.2 to 4.0 g/h. It was reported that complete conversion of glycerol occurred at 700°C. Furthermore, gas yield obtained was 50 wt% but no liquid product was observed. The residue was 6.3 wt% whereas the remaining mass percent was char. Steam gasification of glycerol was performed [76-77]. Results showed that steam gasification of glycerol does not produce liquid product at 600 ^{o}C and 700°C in a fixed bed reactor [76]. It is reported that steam gasification of glycerol produced liquid product consisting of acrolein and acetaldehyde at 600°C to 675°C in a laminar flow reactor [77].

Carbon catalyzed gasification of the organic feed stocks such as glycerol, glucose, whole biomass feed stocks (bagasse liquid extract and sewage sludge) and cellobiose using supercritical water. Catalysts used were spruce wood charcoal, macademia shell charcoal,

coal activated carbon and coconut shell activated carbon. The range of parameters investigated for gasification was temperature from $500\,^{o}$C to 600°C, WHSV 14.6-22.2 h^{-1} and pressure 251-340 MPa. It was reported that glycerol was easily and completely gasified to 54.3 mol% hydrogen rich gas with low (2 mol%) yield of CO. The presence of catalyst had little effect on the gas composition [78]. The production of H_2 from glycerol, sorbitol and ethylene glycol by aqueous phase reforming at temperature near 227^{0}C and pressures of 2.58-5.14 MPa in presence of Sn promoted Raney-Ni catalyst. The feed concentration was 1 to 5 wt% in water. It was reported that addition of tin decreased the rate of methane formation. Gas composition was 66 mol% of H_2 and 32 mol% CO_2, when glycerol was used as feed [79]. It is reported that catalytic steam reforming of bio-oil derived fraction and crude glycerol (a by-product from trans-esterification of vegetable oil with methanol) in a fluidized bed reactor to produce hydrogen [80]. Commercial Ni catalyst was used. Superheated steam was used to fluidize the catalyst. The temperature of crude glycerol was maintained at 60-80 ^{0}C and it was reported that at lower viscosity in this temperature range it was easy to pump and atomize glycerol. Glycerol was fed at 78 g/h with a steam rate of 145 g/h and WHSV of 1600 h^{-1}. Concentration of major gas products was found to be constant but methane production increased from 500 parts per million (ppm) to 2200 ppm when the run time was increased from 0 to 250 min. Hydrogen yield was around 77 wt% and it was suggested that hydrogen yield can be increased if higher amount of steam is used. The conversion of carbon monoxide in the gas through water-gas shift to CO_2 and H_2 would increase the hydrogen yield to 95 wt%.

**4.4 Production of liquid chemicals from glycerol**

In this section the available literature on production of liquid chemicals from glycerol is presented. The production of value added chemical such as methanol, acetalydehyde, acrolein, allyl alcohol, acetone, and ethanol from glycerol under supercritical conditions [55]. The temperature range investigated was 349 to 475 ^{o}C and pressure was maintained at 25, 35 and 45 MPa. The reaction was carried out in tubular reactor with reaction time in the range from 32 to 165 s. It was reported that the decomposition of glycerol primarily followed ionic mechanism at low temperature and high pressure and free radical mechanism at high temperature and low pressure. The amount of acetaldehyde and formaldehyde decreased with increase in temperature whereas amount of allyl alcohol and methanol increased with increase in temperature.

Oxidation of glycerol was carried out using hydrogen peroxide in liquid phase reaction at temperature of 20 and 70 ^{o}C [65]. Products from this process included, formic acid esters of glycerol and mixture of acetals. In addition to that trace amounts of hydroxyacetone, glyceraldehyde and glyceric acid were also identified. The oxidation of aqueous solution of glycerol at 60°C under atmospheric pressure and p^H of 2, 7 and 11 [54]. The catalysts used in the study were Pd and Pt promoted with Bi on active charcoal. The glyceric acid yield of 30, 55 and 77 wt% was obtained at p^H of 7, 9 and 11, respectively using Pd catalyst. 70 wt% yield of glyceric acid was obtained at 90-100 wt% conversion of glycerol under basic conditions. It was reported that the selectivity towards oxidation of secondary alcohol group was improved by promoting Pt with metals such as Bi and resulted in dihydroxyacetone yield of 30 wt% at 60 wt% conversion. The oxidation of glyceric acid to hydroxypyruvic and tartronic acids at 50 oC and atmospheric pressure. Pt promoted with Bi, supported on activated carbon, was used as catalyst. It was reported

that oxidation of primary and secondary alcohol group resulted in formation of tartonic and hydroxypyruvic acid, respectively [63]. The maximum yield of 83 wt% at 90 wt% conversion of glyceric acid was obtained for tartonic acid at pH of 9-11.

### 4.5 Production of Glycerol carbonates from glycerol

Glycerol carbonate (4-hydroxymethyl-1,3-dioxolan-2-one) is a relatively new material in the chemical industry with a large potential as a novel component of gas-separation membranes, a solvent for several types of materials, and biolubricant owing to its adhesion to metallic surfaces and resistance to oxidation, hydrolysis, and pressure. It can be prepared directly and in high yield from renewable glycerol and dimethyl carbonate in a reaction catalyzed by lipases (Reaction 3).

glycerol carbonate
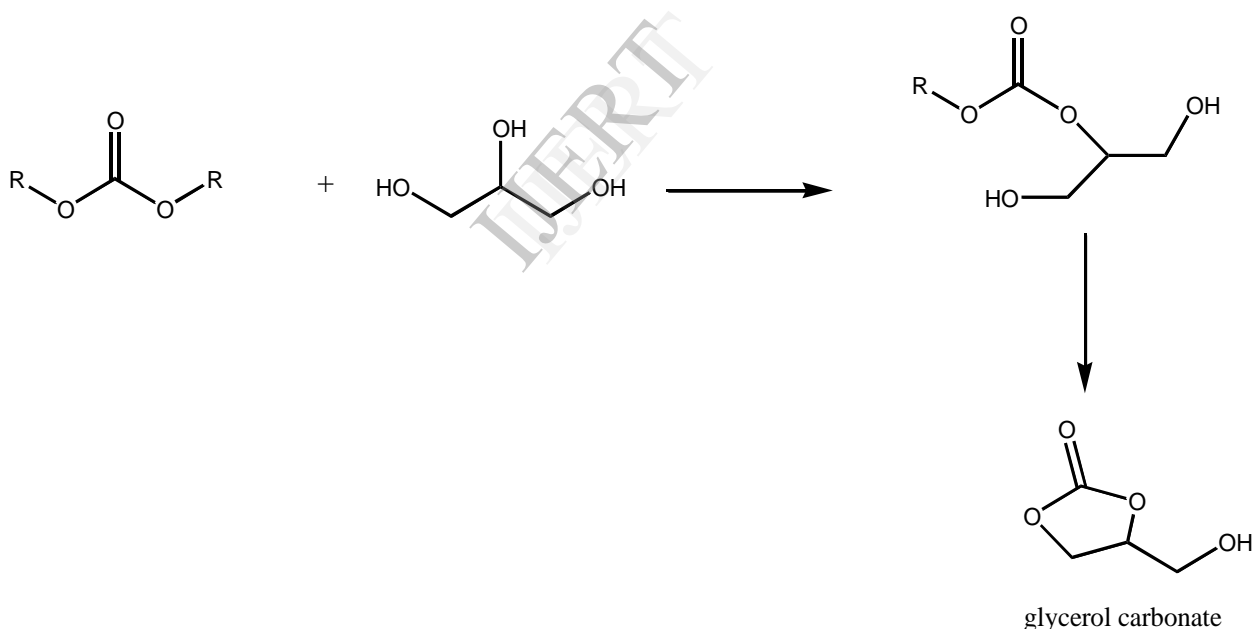
Reaction 3 Glycerol Carbonate from the reaction of a dialkyl carbonate with glycerol, with an intermediate that undergoes a second esterification

Glycerol carbonate could be synthesized from glycerol in supercritical carbon dioxide medium. It is found that an organic carbonate such as ethylene carbonate is required as

starting material under the conditions employed here. It is possible that the carbonatation of glycerol in the presence of ethylene carbonate is enhanced with carbon dioxide as co-source of carbonate for synthesis of glycerol carbonate. The zeolite Purosiv or 13X as well as a strongly basic resin catalyst such as Amberlyst A26 in the hydroxyl form effectively enhanced the reactivity of glycerol adsorbed onto the solid catalyst and the ethylene carbonate dissolved in SC-CO_2. The reaction is explained as per the Reaction 4 [81].

Glycerol (G)   Ethylene carbonate (EC)   Glycerol carbonate (GC)   Ethylene glycol (EG)
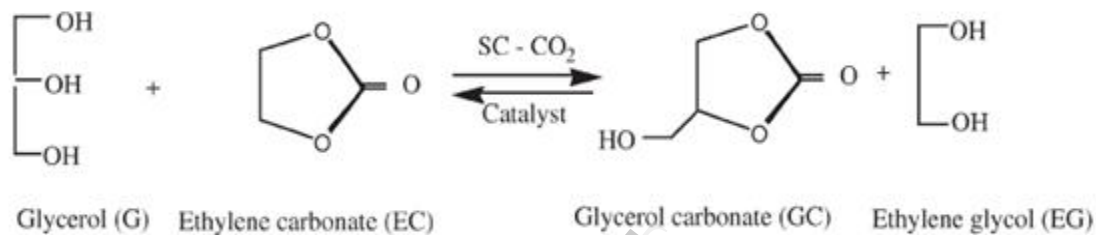
Reaction 4 Glycerol adsorbed onto the solid catalyst and the ethylene carbonate

Glycerol carbonate is prepared by carbonation of glycerol in the presence of ethylene carbonate catalyzed by the resin Ambersep A26 HCO_3^- at moderate temperature. The Reaction 5 shows the root of synthesis of glycerol carbonate [82].

Glycerol (G)   Ethylene carbonate (EC)   Glycerol carbonate (GC)   Ethylene glycol (EG)
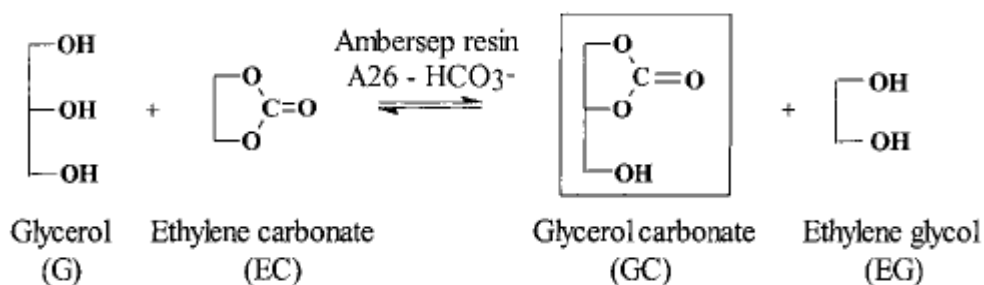
Reaction 5 Synthesis of glycerol carbonate from ethylene carbonate using Ambersep A26 HCO_3^- as catalyst.

Glycerol is converted into glycerol carbonate by reaction with CO_2 (5MPa) in presence of Sn-catalysts (*n*-$Bu_2Sn(OMe)_2$ at 450K using either glycerol or tetraethylene glycol

dimethyl ether as reaction medium. In the former conditions, glycerol carbonate (crude product) was formed in a 1.14:1 molar ratio with respect to Sn within 15 h (isolated yield 95% with respect to Sn) and the reaction preceded, but with a much lower rate, for several hours afterwards. The reaction is proposed to follow as per the Reaction 6 [83].
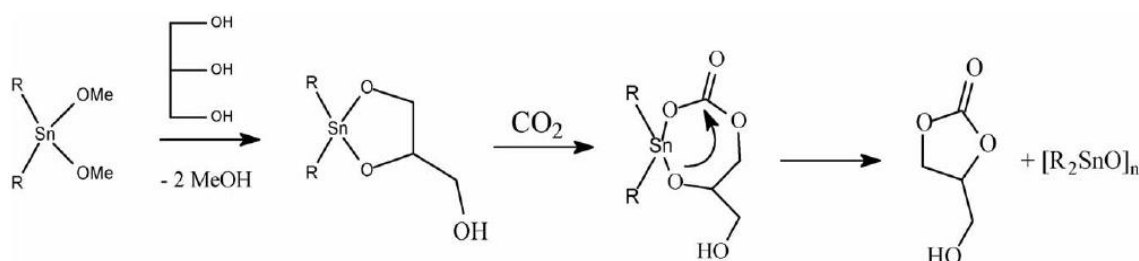
Reaction 6 proposed reaction for Glycerol converted into glycerol carbonate

Inexpensive glycerol carbonate could serve as a source of new polymeric materials such as glycidol, a high-value component in the production of a number of polymers. Glycidol is easily obtained in high yield (86% and 99% purity at 35 mbar and $180^{o}C$) from glycerol carbonate by catalytic reaction, involving rapid contraction of the five-membered cyclic carbonate unit into the three-membered cyclic epoxy unit, within the pores of zeolite.

Besides it being a high-value component in the production of epoxy resins and polyurethanes, glycidol can be polymerized into a polyether polyol called polyglycerol [84]. Its high functionality, together with the versatile and well-investigated reactivity of its hydroxy functions, is the basis for a variety of derivatives. Indeed, a variety of polyglycerols were eventually commercialized for applications that range from cosmetics to controlled drug release.

4.6 Production of Epichlorohydrin from glycerol

Epichlorohydrin, a chemical employed in the production of epoxy resins, is now commercially synthesized from glycerol by a catalytic reaction with HCl followed by

dehydrochlorination with NaOH. The glycerol-based process (named Epicerol) involves the direct synthesis of dichloropropanol, an intermediate product, from glycerine and hydrochloric acid. Thus, natural glycerol is used as a substitute for the propylene feedstock employed in the traditional epichlorohyrin production process, involving formation of allyl chloride by reaction of propylene with Cl_2. Overall, the Epicerol process uses a combination of undisclosed metal catalysts and requires a lower specific consumption of chlorine and water, thereby reducing chlorinated effluents.

4.7 Production of propanediols from Glycerol (Hydrogenolysis)

New bond breaking (hydrogenolysis) technology will lead to the formation of a number of valuable intermediates. Propylene glycol and 1,3-propanediol are promising potential derivatives that could be produced from glycerol by development of appropriate catalytic systems. 1,3-propanediol can be produced through aerobic fermentation, however, a direct route from glucose to 1,3-propanediol (Dupont) is likely to be more cost effective. The conversion to propylene glycol would be via chemical catalysis.

1,2 – propanediol and 1,3 – propandiols are generally obtained from petroleum derivatives. They can also be obtained conveniently by hydrogenolysis of glycerol. Several routes to propanediol can be traced from renewable feedstocks; the most common route is conversion of sugar or sugar alcohols at high temperatures and pressures in the presence of metal catalyst to produce propanediols and other lower polyols.

4.7.1 Production of 1,2 – propanediols from glycerol

1,2-propanediol is a is a three-carbon diol with a steriogenic center at the central carbon atom, a nontoxic and high-demand chemical, which is extensively used for polyester resins, food products, antifreeze, liquid detergents, pharmaceuticals, etc. Currently, the

commercial production of 1,2-propanediol is mainly through the route of propylene oxide hydration. Glycerol hydrogenolysis to 1,2-propanediol represents a sustainable process with valuable potential applications. 1,2-propanediol can be produced with high yields via the vapor phase hydrogenolysis of glycerol over $Cu/ZnO/Al_2O_3$. Furthermore, the mechanism of 1,2-propanediol formation is suggested to proceed mainly through an acetol route over $Cu/ZnO/Al_2O_3$ [85]. The production of 1,2-propanediol was favored at higher hydrogen pressure. At 190 ^{o}C and 0.64 MPa, near complete conversion of glycerol was achieved with 1,2-propanediol selectivity up to 92%.

Perosa and Tundo [86] 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. [87] carried out hydrogenolysis of glycerol to 1,2 propanediol reaction 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 1,2 propanediol. The yield of 73% was achieved.

Hydrogenolysis of biomass-derived glycerol is also a route for the production of propylene glycol. Cu–ZnO catalysts were prepared and examined in glycerol hydrogenolysis to propylene glycol at 453–513 K and 4.2 MPa H_2. Glycerol hydrogenolysis conversions and selectivities depend on Cu and ZnO particle sizes. Smaller ZnO and Cu domains led to higher conversions and propylene glycol selectivities, respectively. Reaction temperature effects showed that optimal temperatures (e.g. 493 K) are required for high propylene glycol selectivity's, Probably as a result of optimized adsorption and transformation of the reaction intermediates on the catalyst surfaces. These preliminary results provide guidance for the synthesis of more efficient Cu–ZnO catalysts and for the optimization of reaction parameters for selective glycerol hydrogenolysis to produce propylene glycol [88].

The combination of Ru/C + Amberlyst was effective to the hydrogenolysis of glycerol to 1,2-propanediol, It was demonstrated that the Ru/C with the heat resistant Amberlyst70, whose highest operating temperature is 463K, exhibited high conversion, selectivity to 1,2-propanediol, and stability in the hydrogenolysis of glycerol [89].

Copper-chromite catalyst was identified as the most effective catalyst for the hydrogenolysis of glycerol to propylene glycol [90]. This studies give the process based on copper-chromite catalyst distinctive competitive advantages over traditional process using severe conditions of temperature and pressure. A novel mechanism to produce

propylene glycol from glycerol via an acetol intermediate was proposed and validated. In a two-step reaction process, the first step of forming acetol can be performed at atmospheric pressure while the second requires a hydrogen partial pressure. Propylene glycol yields >73% were achieved at moderate reaction conditions. The proposed reaction mechanism is is given in Reaction 7.
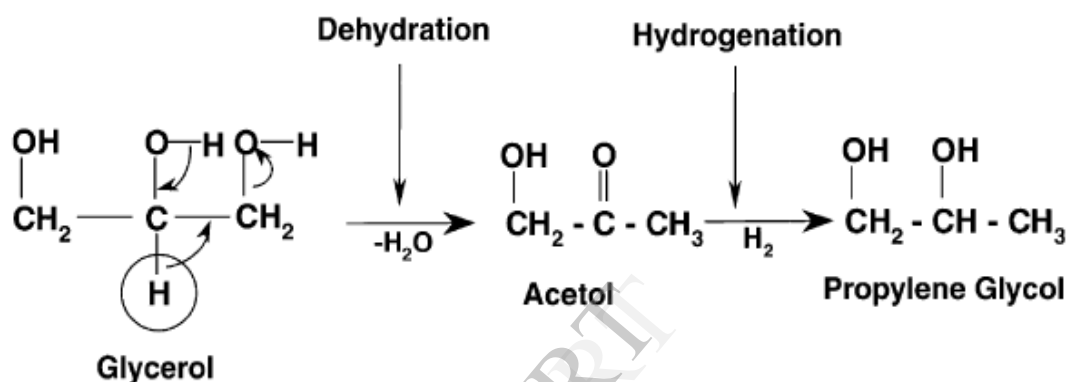
Reaction 7 Mechanism to produce propylene glycol from glycerol via an acetol intermediate

4.7.2 Production of 1,3 – propanediols from glycerol

4.7.2.1 Chemical Route

1,3-propanediol is a simple organic chemical and 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. However, high cost and limited availability has restricted its commercial use. Thus, glycerol has become an attractive feedstock for

production of for 1,3-propanediol. 1,3-Propanediol-based polymers exhibit better properties than those produced from 1,2-propanediol, butanediol or ethylene glycol.

The most common route of conversion of glycerol to 1,2-propanediol and 1,3-propanediol is from petroleum derivatives [91]. Propanediol can also be prepared from renewable feedstocks; the most common route is conversion of sugar or sugar alcohols at high temperatures and pressures in the presence of a metal catalyst to produce propanediol and other lower polyols [87]. This route suggest that propanediol can be a target compound produced from renewable feedstocks; it has been reported that propanediol can be produced through the catalytic conversion of polyols [92] and glycerol. The effect of various catalysts and other suitable conditions for production of propanediole from glycerol given by different researchers are summarized below.

Using copper and zinc catalysts along with a sulfided Ru catalyst, the reaction of glycerol has been carried out at 15 MPa and 513–543 K [93] and [94]. Investigations on Raney Cu [95] and [96], Cu/C [97], and Cu–Pt and Cu–Ru bimetallic catalysts [98] at 1.0–4.0 MPa and 493–513 K have also been reported. Using catalysts containing Co, Cu, Mn, Mo, and an inorganic polyacid, the reaction conditions were 25 MPa and 523 K [99]; using homogeneous catalysts containing W and group VIII transition metals, the reaction conditions were 32 MPa and 473 K [100]. In addition, dehydroxylation in an aqueous solution of polyols catalyzed by Ru homogeneous complexes has been reported [101], and Schlaf et al. reported dehydroxylation of glycerol in sulfolane catalyzed by homogeneous complexes of ruthenium under rather mild conditions (∽5 MPa, 383 K); however, that activity was low [102]. Hydrogen pressures of around 6–10 MPa and reaction temperatures of 453–513 K have been applied to supported metal catalysts [103],

[104], [105] and [106]. Recently, the reaction of glycerol was conducted at 1.4 MPa and 473 K[91].

The conversion of glycerol to propandiols proceeds by the combination of dehydration with subsequent hydrogenation over metal catalysts. This dehydration followed by hydrogenation reaction is called hydrogenolysis. Among various solid acid catalysts, including zeolites, sulfated zirconia, tungstic acid, and an ion exchange resin, the combination of Ru/C with Amberlyst (ion exchange resin) exhibited the highest activity. In particular, this reaction take place at much milder reaction conditions (393 K, 4 MPa H_2) than those for the catalysts reported above.
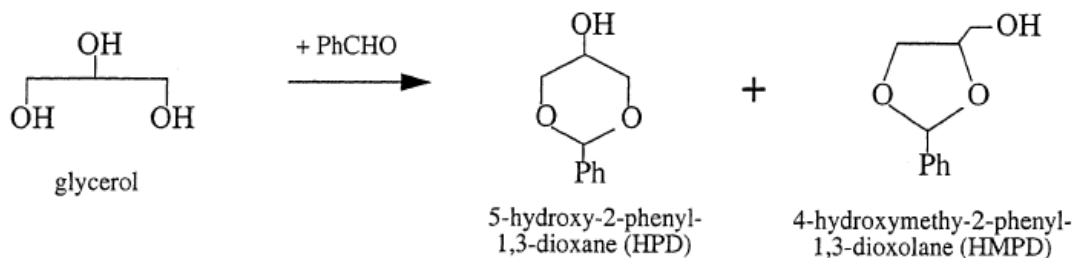
Among the various supported noble metal catalysts, Rh/SiO_2 (G-6) catalyst is effective in the reaction of glycerol under H_2[107]. It is characteristic that Rh/SiO_2 exhibited higher activity and selectivity to hydrogenolysis products (1,2-PD+1,3-PD+1-PO+2-PD) in the reaction of glycerol than Ru/C, which can be regarded as a conventional catalyst. In particular, under the higher H_2 pressure and higher concentration of glycerol, Rh/SiO_2 was more effective catalyst than Ru/C. By the addition of Amberlyst, glycerol conversion on the Rh/SiO_2 increased as well as on Ru/C. In addition, the reaction route of glycerol on Rh/SiO_2 can be different from that on Ru/C. The consecutive hydrogenolysis of propanediols to propanols in the glycerol reaction can proceed mainly via 1,3-propanediol on Ru/C, while the consecutive reactions can proceed mainly via 1,2-propanediol on Rh/SiO_2.

A new approach to the production of 1,3-propanediol from glycerol is proposed by Wang et al. The idea is to selectively transform the middle hydroxyl group of glycerol into a tosyloxyl group and then remove the transformed group by catalytic hydrogenolysis.
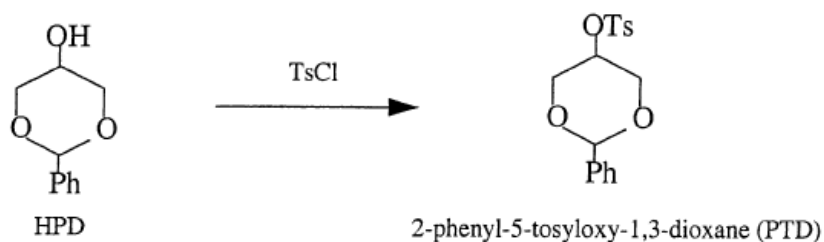
With this new approach, the conversion of glycerol to 1,3-propanediol is completed in three steps, namely, acetalization, tosylation, and detosyloxylation. The acetalization of glycerol with benzaldehyde was conducted in benzene. The setup included a round bottomed reaction flask, a condenser, and a 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, 100g of glycerol, 120 g of benzaldehyde (6% excess), and 300 mL of benzene, together with 1g of *p*-toluene sulfonic 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 (pyridinehydrochloride 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. All of these steps are experimentally examined in the current work to verify the feasibility of the new conversion approach. The mechanism of this reaction is also established and presented in Reaction 8 [108].

Step 1: Acetalization

glycerol

+ PhCHO

5-hydroxy-2-phenyl-
1,3-dioxane (HPD)

+

4-hydroxymethy-2-phenyl-
1,3-dioxolane (HMPD)

Step 2: Tosylation

HPD

TsCl

2-phenyl-5-tosyloxy-1,3-dioxane (PTD)

Step 3: Detosyloxylation

PTD

+ H$_2$O
- PhCHO

2-tosyloxy-
1,3-propanediol (TPD)

+ H$_2$
- TsOH

1,3-propanediol

or

PTD

+ H$_2$
- TsOH

2-phenyl-1,3-dioxane

+ H$_2$O
- PhCHO
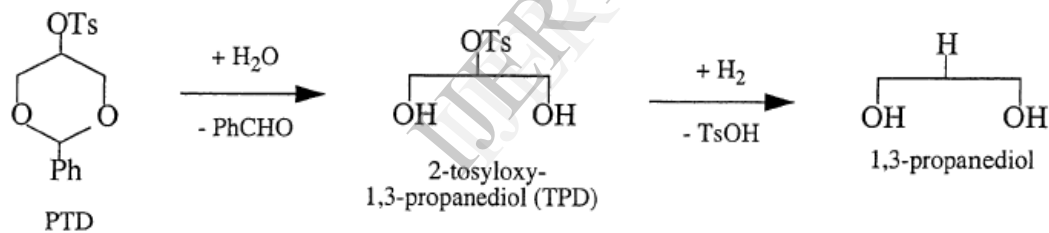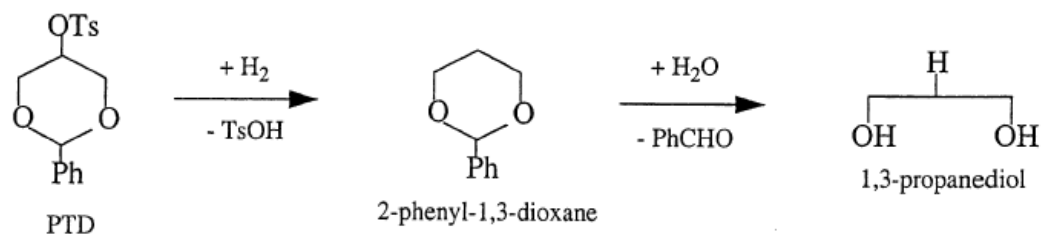
1,3-propanediol

Reaction 8 Proposed mechanism for the production of 1,3-propanediol from glycerol .

4.7.2.2 Biochemical route

Microbial fermentation is an important technology for the conversion of renewable resources to chemicals. 1,3-propanediol can be obtained by microbial fermentation of

glycerol using a great amount of species such as *Klebsiella pneumoniae [109-115]*

Enterobacter agglomerans[116-117], *Citrobacter freundii* [118] and *Clostridium*

butyricum [117-120], among others [121]*, tested 1123 microorganisms that represent*

126 types of bacterial species and was reduced their study at 8 of these species].

Furthermore some that can be obtained by genetic modifications as for example

Clostridium acetobutylicum [120]. From all these bacteria, *Klebsiella pneumoniae* in its

wild form is the most interesting because of their yield, productivity and resistance to

both reagents and products. Also operative and economic aspects of all the alternatives

were analyzed, such as operation conditions, separation equipment, yields of reactions,

and demand of products, finding that the most appropriate of all possibilities is the

glycerol bioconversion toward 1,3-propanediol,

For Batch and Continuous cultures, Zeng [122] obtained conversion around 0.55 g of 1,3-

propanediol formed per 1 g of glycerol consumed. Zeng [123] 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.

Another microorganism that ferments glycerol to 1,3-propanediol is *Klebsiella*

Pneumoniae. Xiu et al. [124] 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.

Cheng et al. [125] 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. This 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. [126] 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 p^H 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. [127] 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. [128] 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. [129] 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.

Zeng et al. [130] 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 w as 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.

Lin et al. [131] 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. Firs tly, 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.

4.8 Production of succinic acid from glycerol

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 [132]. It can be used for the manufacture of synthetic resins and biodegradable polymers and as an intermediate for chemical synthesis [133]. Lee et al. [134] 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.

5. Industrial applications of some value added chemicals obtained from glycerol

5.1   Uses of 1,2 – propandiol

The new engine components especially exhaust gas recirculation (EGR) devices; generate much greater thermal stresses on the engine coolant. The oxidation of ethylene glycol and propylene glycol may accelerate dramatically, resulting in coolant unsuitable for continued use in as little as few months. EGR devices, as the name implies, pass part of

the exhaust gas back to the combustion chamber to lower target emissions. Therefore, exhaust gases, especially those produced by a diesel engine, are much hotter than regular intake air. The EGR gases, therefore, must be cooled by existing engine coolant system before they reach the combustion chamber. Ethylene glycol and propylene glycol have offered the lowest – cost chemical bases for engine antifreezes/coolant for many decades [135].

5.2 Uses of 1,3 – Propanediol

Carboxyl functional polyesters have been prepared from 1,3 – propanediol (PDO), neopentyl glycol (NPG), and an 80/20 terephthalic/isothalic acid (TPA/IPA) combination. These polyesters were formulated with epoxy resins for evaluaton as powder coatings. Increasing the concentration of PDO, i.e. 0, 15, 30 and 50%, slightly reduced the glass transition temperature of he polyesters with all T_g's greater than 50^oC. Powder coating formulation based on these polyesters and epoxy crosslinking agent has been shown to be easily processed in an extruder. The viscosity of the polyester decreased as the level of PDO increased, hence improved flowability resulted.Polyesters containing up to 50 percent PDO in polyol mixture has good storage stability due to their high Tg. Coatings properties indicates that replacing NPG with PDO significantly improved both impact resistance and flexibility. Other properties including hardness, adhesion, solvent resistant and chemical resistance are retained over a broad range of PDO concentrations.

CORTERRA[136] Polymer is an aromatic polyester known generically as PTT, (polytrimethylene terephthalate). PTT is produced by the polycondensation reaction of PTA (purified terephthalic acid) and PDO (1,3-propanediol) and has unique properties as

compared to the other aromatic polyesters, PET (polyethylene terephthalate) and PBT (polybutylene terephthalate).CORTERRA Polymers are now commercially available for use in carpet and textile fibers monofilament, film, nonwoven fabric, and engineering thermoplastic applications. CORTERRA 200 can be used by itself, as the base polymer for compounds, or as a polymer modifier for many engineering thermoplastic applications. Compounded engineering resins based on CORTERRA PTT polymer provide physical properties that are equivalent to or better than those of similar PBT compounds. Extrusion and injection molding conditions, and processing characteristics are very similar to those established for PBT. PTT compounds generally exhibit higher tensile strength, flexural modulus and heat deflection temperatures but with slightly lower impact strength than the PBT counterparts.

Hot melt adhesives (HMAs) are used for a number of applications in automotive, industrial and consumer markets where prolonged bonding quality and durability are essential requirements. As hot melt adhesives form a bond very quickly and dry rapidly after application, they speed up production and improve efficiency. In many cases, hot melt adhesives have successfully replaced solvent-based adhesives to produce better products at lower cost in a continuous process. Hot melt adhesives have no solvent or water to lose and form bonds by hydrogen bonding and crystallization. A small amount of molten adhesive applied to a relatively large area will cool rapidly and solidify to form a bond almost instantaneously. As a result, the production efficiency is drastically improved. As HMAs have no VOCs, the fact that HMAs do not use solvents results in both environmental and economic benefits.Hot Melt Adhesives based on 1,3-PDO prepared from either PAPDO (1,3 – PDO/adipate polyester polyol) or

PTMG(Poly(oxytetramethylene)glycol) exhibited higher tensile strength, modulus and lap shear strength but lower elongation and 180ºpeel strength as compared to HMAs based on 1,4-BD at the same concentrations of hard segments [137].

5.3 Uses of polyglycerols

If water or moist air is trapped in a closed system, condensation droplets (fog) form on the inner surfaces when the temperature cools down below the dew point. This phenomenon is a big issue in fresh food packaging and in greenhouses. For this reason, the development of plastic films with improved antifogging properties is of growing importance. This can be achieved either by spraying an antifogging agent on the surface of the film, or by incorporating an antifogging additive in the polymer matrix. Compared to surface treatment, the use of additive technology is usually preferred as it provides a longer lasting antifogging performance, and reduces significantly the amount of antifogging agent that is in contact with the packaged food or cultivated plants. In food packaging, films with good antifogging properties offer a more attractive display of the packaged products and enhance their shelf life. Antifogging films are also used in greenhouses where they allow better light penetration, enhancing photosynthesis that improves yields. Antifogging additives are typically surface-active products made of two main parts: a hydrophilic head and a lipophilic tail. Examples include sorbitan esters, polyoxyethylene esters, glycerol esters, and more recently, polyglycerol esters. When incorporated in a polymer film, the antifogging additive migrates from the matrix to its surface, decreasing the interfacial tension between the polymer and the water droplets. As a result, the droplets spread across the surface of the film. Therefore, the role of the

additive is not preventing water deposition on the film, but condensing it in an invisible continuous thin layer [138].

Compared to glycerol esters, polyglycerol esters are less volatile, which reduces the evaporation of the additive during extrusion. Polyglycerol esters also exhibit a higher thermal stability than glycerol esters, sorbitan esters or polysorbates, which lowers the possibility of discoloration during film processing.

As with many other antifogging agents, polyglycerol esters also have antistatic properties because the water film that forms on the polymer surface reduces its resistivity. Polyglycerols as such (not esterified) are used as plasticizers in starch based biodegradable thermoplastic compositions. Their lower volatility and higher thermal stability, compared to glycerol or sorbitol, allows easier processing (less evaporation and higher processing temperatures). Polyglycerols or blends of glycerol and polyglycerols are claimed to have better plasticizer properties than glycerol alone in polyvinyl alcohol films (PVA). Diglycerol esters, such as diglycerol tetraacetate, have been described as good plasticizers for cellulose acetate and, more recently, for polyester resin compositions based on polylactic acid. Due to their amphiphilic character and their high thermal stability, polyglycerol esters can also be used as lubricants. This is particularly suitable for food handling equipment since many polyglycerol esters are allowed for food use in many countries.

6. Conclusion

Biodiesel is a renewable biofuel that has environmental and lubricity advantages and provides a degree of energy independence and the associated economic advantages. Although the cost of biodiesel can be lowered a small amount by process improvements

and the economies of scale obtained by producing it in larger, more automated plants, the cost of biodiesel is primarily limited by the cost of the feedstock. The increasing over-supply of glycerol in the market has forced the biodiesel industry to look for new avenues of glycerol utilization. The idea to use glycerol as a primary building block is gaining momentum and continued innovation to develop new reactions of glycerol is critical to the economic well being of the global oleo chemical industry.

8. References

[1]   Hansen AC, Zhange Q, Lyne PWL . Ethanol – diesel fuel blends – a review. Bioresour Technol 2005; 96: 227 – 285.

[2]   Service R, Cellulose ethanol Biofuel researchers prepare to reap a new harvest. Science 2007; 315: 1488 – 1491.

[3]   Henstra A, Sipma J, Rinzema A, Stams A: Microbiology of synthesis gas fermentation for biofuel production. Curr Opin Biotechnol 2007 ; 315:1488 – 1491.

[4]   Marchetti JM, Miguel VU, Errazu AF, Possible methods for biodiesel production. Renewale and Sustain Energy Review 2007; 11: 1300 – 1311.

[5]   Gray KA, Zhao L, Emptage M. Bioethanol. Curr Opin Chem Biol 2006 ; 10: 141 – 146.

[6]   Odling – Smee L . Biofuels bandwagon hits a rut. Nature 2007; 446 : 483.

[7]   Scubert C . Can biofuels finally take center stage? Nat Biotechnol 2006; 24:777 – 784.

[8]   Xu H, Miao X, Wu Q. High quality biodiesel production from a microalgae Chlorella protothecodies by heterotrophic growth in fermenters. J Biotechnol 2006 ; 126: 499 – 507.

[9]   Kamm B. Kamm M. Biorefineries – multi – product processes. Adv. Biochem Engg Biotechnol 2007 ; 105: 175 – 204.

[10]   Sihna S, Bhardwaj D, Gupta PK. Study of Different Parameters of transesterification process for the preparation of sunflower oil based biodiesel. Biomass and Bio energy 2004 ; 13 : 501-505.

[11]   Saucedo E. Biodiesel Ingeniera Quimica 2001 ; 20 : 19–29.

[12]   Ma F, Hanna MA. Biodiesel production: a review. Biores Technol 1999 ;70 : 1–15.

[13]   Altin R, Cetinkaya S, Yucesu HS. The potential of using vegetable oil fuels as fuel for Diesel engines. Energy Convers Manage 2001;42:529–38.

[14]   Pryor RW, Hanna MA, Schinstock JL, Bashford LL. Soybean oil fuel in a small Diesel engine. Trans ASAE 1982 ;26 : 333–338.

[15]   Dunn RO. Alternative jet fuels from vegetable-oils. Trans ASAE 2001;44:1151–757.

[16]   Tiwari S, Saxena M, Tiwari SK. Mahua-oil-based resins for the high-temperature curing of fly ash coatings. Journal of applied polymer Science 2003; 87(2):110-120.

[17]   Bailey S Industrial oil and fat products.Vol. 1.New York: John Wiley and Sons; 1979.

[18] Ghadge SV, Reheman H. Biodiesel production from mahua (madhuca indica) oil having high free fatty acids. Biomass and bio energy 2005; 28:601-605.

[19] Knothe G. Historical Perspectives on Vegetable Oil-Based Diesel Fuels, Inform 2001 ;12: 1103-1107.

[20] Rakopoulos CD, Antonopoulos KA, Rakopoulos DC, Hountalas DT, Giakoumis EG. Comparative performance and emissions study of a direct injection diesel engine using blends of diesel fuel with vegetable oils or bio-diesels of various origins. Energy Conversion Management 2006; 47 : 3272–87.

[21] Engelman HW, Guenther DA, Silvis TW. Vegetable oil as a diesel fuel. Diesel and Gas Engine Power Division of ASME paper no. 78-DGP-19. New York: ASME; 1978.

[22] Masjuki H, Abdulmunin MZ. Investigations on preheated palm oil methyl esters in the diesel engine. In: Proceedings of the Institute of Mechanical Engineers, London, UK.1996 ; 210 : 131–137.

[23] Bari S, Lim TH, Yu CW. Effects of preheating crude palm oil (CPO) on injection system, Performance and emission of a diesel engine. Renewable Energy 2002;27:171–181.

[24] Shaheed A, Swain E. Combustion analysis of coconut oil and its methyl esters in a diesel engine. Proceedings of the Institute of Mechanical Engineers, London, UK. 1999; 213 : 417– 425.

[25] Senthil KM, Ramesh A, Nagalingam B. An experimental comparison of methods to use methanol and Jatropha oil in a compression ignition engine. Biomass and Bioenergy 2003;25:309–318.

[26] Demirbas A. Progress and recent trends in biofuels. Progress in Energy and Combustion Science 2007 ; 33: 1–18.

[27] Narayan CM. Vegetable oil as engine fuels—prospect and retrospect. Proceedings on recent trends in automotive fuels, Nagpur, India; 2002.

[28] Almeida SCAD, Belchior CR, Nascimento MVG, Vieira LDSR,Fleury G. Performance of a diesel generator fuelled with palm oil. Fuel 2002;81:2097–102.

[29] Nwafor OMI. The effect of elevated fuel inlet temperature on performance of diesel engine running on neat vegetable oil at constant speed conditions. Renewable Energy 2003;28:171–81.

[30] Meher LC, Naik SN, Das LM. Methonolysis of Pongamia pinnata (Karanja) oil for production of biodiesel. Journal of Scientific & Industrial Research 2004;63: 913 – 918.

[31] Pratt G. Sunflower oil for fuel. In: North Dakota University seminar on vegetable oil as diesel fuel. Peoria, IL, USA: Northern Agricultural Energy Centre; 1981.

[32] Agarwal D, Agarwal AK. Performance and emissions characteristics of Jatropha oil (preheated and blends) in a direct injection compression ignition engine. Applied Thermal Engineering 2007;27:2314–23.

[33] Vivek, Gupta AK. Biodiesel production from Karanja oil. Journal of Scientific & Industrial Research 2004;63:39–47.

[34] Raheman H, Phadatare AG. Diesel engine emissions and performance from blends of Karanja methyl ester and diesel.Biomass and Bioenergy 2004;27:393–397.

[35]   Pramanik K. Properties and use of Jatropha curcas oil and diesel fuel blends in compression ignition engine. Renewable Energy 2003;28:239 – 248.

[36]   Guibet JC, Stern R, Graille J. Revue de l'Institut Franc-ais du pe´ trole. Janv-Fe´v 1983;38:121.

[37]   Barsic N J. and Humke A L. SAE Paper No. 8 10262, Sot. Auto Engg., PA, USA, 1981

[38]   Forgiel R. and Varde K S. SAE Paper No. 811214, Sot. Auto Engg., PA, USA, 1981

[39]   Seddon R H. Gas Oil Power 1942, 8, 135

[40]   Baranescu RA. and Lusco, J. J. Proc. Int. Conf. Vegetable Oils.ASME, 1982 312-328

[41]   Ziejewski M. and Kaufman K R. SAE Paper 820257, Sot. Auto Engg., PA, USA, 1982

[42]   Quick G R. Developments in use of vegetable oils as fuel for diesel engines. ASAE 1980; paper no 80-1525.

[43]   Tahir AR, Lapp, HM and Buchanan LC. Proc. Int. Conf. Vegetable Oils, ASAE, 1982 : 82-91

[44]   Ryan TW, Callahan T J and Dodge L G. Proc. Int. Conf. Vegetable Oils, ASME, 1982 (August).

[45]   Goering C E, Schwab AW,Daugherty M J, Pryde E H and Heakin A J. ASAE Paper No. 81-7019, 1981

[46]   Kumar MS, Ramesh A, Nagalingam B. Use of Hydrogen to enhance the performance of a vegetable oil fuelled compression ignition engine. International Journal of Hydrogen Energy. 2003; 28:1143-1154.

[47]   Phuan S, Vedaraman N, Ram BVB, Sankarnarayanan G, Jeychandran. K Mahua oil(Madhuca Indica) methyl ester as biodiesel preparation and emission characteristics. Biomass and Bioenergy 2005; 28:87-93.

[48]   Hideki F, Akihiko K, Hideo N. Biodiesel fuel production by transesterification of oils. Journal of bioscience and bioengineering. 2001; 92(5): 405-416.

[49]   Pramanik K, Srivani K, Chandra V. Catalytic studies on transesterification of jatropha oil for use as diesel fuel. Indian chemical engineering congress 2000; Dec:18-21.

[50]   Dalai A.K, Bakhshi NN, Lang X, Reaney MJ, Hertz PB and Munson J. Production of Diesel Fuel Lubricity Additives from Various Vegetable Oils. Annual Interim Report for Canodev Research Inc. April 2000..

[51]   Thomson JC, He BB. Characterization of crude glycerol from biodiesel production from multiple feedstocks. Appl Engg Agric 2006; 22 : 261 – 265.

[52]   Haas MJ. Improving Economics of Biodiesel Production Through the Use of Low Value Lipids as Feedstocks: Vegetable Oil Soapstack. Fuel Processing Technology 2005 ; 86, 1087-1096

[53]   Claude S. Research on New Outlets for Glycerol – Recent Developments in France. 52nd International Congress and Expo of DGF, Magdeburg, Germany, September 1998;13-15 .

[54]   Garcia R, Besson M and Gallezot P. Chemoselective Catalytic Oxidation of Glycerol with Air on Platinum Metals. Applied Catalysis A: General .1995 ; 127:165-176 .

[55]   Buhler W, Dinjus E, Ederer HJ, Kruse A and Mas C. Ionic Reactions and Pyrolysis of Glycerol as Competing Reaction Pathways in near- and Supercritical Water. Journal of Supercritical Fluids. 2002; 22: 37–53 .

[56]   Cortright RD, Davda RRand Dumesic JA. Hydrogen from Catalytic Reforming of Biomass-Derived Hydrocarbons in Liquid Water . Nature. 2002; 418 : 964-967.

[57]   Kimura H, Tsuto K, Wakisaka T, Kazumi Y, Inaya Y. Appl. Catal. A 1993; 96 : 217

[58]   Abbadi A, Bekkum HV. Appl. Catal., A .1996 ;148:113.

[59]   Carrettin S,   McMorn P, Johnston P, Griffin K,   Hutchings GJ. Selective Oxidation of glycerol to glyceric acid using a gold catalyst in aqueous sodium hydroxide, Chem. Commun 2002 ; 696.

[60]   Carrettin S, McMorn P, Johnston P, Griffin K, Kiely CJ, Hutchings GJ. Phys. Chem. Chem. Phys. 2003 ; 5 : 1329.

[61]   Fordham P, Garcia R, Besson M, Gallezot P. Stud. Surf. Sci. Catal. 1996 ; 101:161.

[62]   Fordham P, Garcia R, Besson M, Gallezot P, Appl. Catal. A 1995; 133:L179.

[63]   Bianchi L , Canton P , Dimitratos N , Porta F , Prati L , Selective Oxidation of Glycerol with oxygen using mono and bimetallic catalysts based on Au, Pd and Pt metals, Cat. Today,2005;102 – 103:

[64] McMorn, Roberts, Hutchings, Oxidation of glycerol with hydrogen peroxide using silicalite and aluminophosphate catalysts Cata. Lett. 1999 63:193–197.

[65] Carrettin S, McMorn P, Johnston P, Griffin K, Kiely CJ, Attard CA, Hutchings GJ . Oxidation of Glycerol using supported Gold Catalysts, Top. Catal 2004; 27:131.

[66] Dimitratos N, Lopez – Sanchez JA, Lennon D, Porta F, Prati L, Villa A . Effect of Particle Size on Monometallic and Bimetallic (Au, Pd)/C on the Liquid Phase Oxidation of Glyerol Catal. Lett. 2006;108:147

[67] Under basic conditions: a) P Gallezot, Appl. Catal. A 1995, 133:179 b.) H Kimura, Jpn. Pat. Application. 952253, 1993;under acidic conditions: c.) H Kimura, Jpn. Pat. Application. 253062, 1994; d.) H. Kimura, Jpn. Pat. Application, 315624, 1994.

[68] Criminna R, Pagliaro M. One – Pot Homogenous and Heterogenous Oxidation of Glycerol to ketomalonic Acid Mediated by TEMPO, Adv. Synth. Catal. 2003, 345:383

[69] Criminna R, Pagliaro M, G Palmisano G, Della Pina C, Rossi M, One – pot electrolytic oxidation of glycerol to DHA, Tetrahedron Lett. 2006, 47:6993

[70] Kimura H, Tsuto K, Wakisaka T, Kazumi Y, InayaY, Appl. Catal. A 1993, 96:217

[71] Kimura H, Polym J. Sci. Part A 1998, 36:195

[72] Kimura H. Recent Res Dev. Polym. Sci 1999, 3:327

[73] Gupta VP. US Patent 5476971: 1995

[74] Noureddini H, Dailey WR, Hunt BA Production of Ethers of Glycerol from Crud Glycerol 1998. Paper posted at DigitalCommons at the University of Nebraska-Lincoln: http://digitalcommons.unl.edu/chemeng_biomaterials/18

[75] Spooner-Wyman J, Appleby D. B. Heavy-Duty Diesel Emissions Characteristics of Glycerol Ethers, 25th Symposium on Biotechnology for Fuels and Chemicals, Breckenridge,Colorado,2003:

http://www.nrel.gov/biotechsymp25/session5_pp.html.

[76] Chaudhari ST and Bakhshi N N. Steam Gasification of Chars and Bio-oil , Report to Bioenergy Development Program enewable Energy Branch, Energy,Mines and Resources Canada, Ottawa, Canada2002 ; 396-436.

[77] Stein YS and Antal Jr M.J. A Study of the Gas-Phase Pyrolysis of Glycerol . Journal of Analytical and Applied Pyrolysis 1983 ; 4: 283-296 .

[78] Xu X., Matsumura Y, Stenberg J and Antal M.J. Carbon-Catalyzed Gasification of Organic Feedstocks in Supercritical Water. Ind. Eng. Chem. Res. 1996;35: 2522-2530.

[79] Huber GW, Shabaker JW and Dumesic J.A. Raney Ni-Sn Catalyst for H_2 Production from Biomass-Derived Hydrocarbons. Science 2003;30: 2075.

[80] Czernik S, French R, Feik C and Chornet E. Production of Hydrogen from Biomassderived Liquids. Proceedings of the DOE Hydrogen Program Review; 2000.

[81] Vieville C, Yoo JW, Pelet S. and Mouloungui Z, Synthesis of glycerol carbonate by direct carbonatation of glycerol in supercritical CO2 in the presence of zeolites and ion exchange resins. Catalysis Letters 1998 ; 56: 245–247.

[82]   Pelet S, Yoo J W, Mouloungui Z. Analysis of Cyclic Organic Carbonates with Chromatographic Techniques. J. High Resol. Chromatogr1999; 22: 276-278,.

[83]   Michele A, Angela D, Francesco N, Carlo P. A study on the carboxylation of glycerol to glycerol carbonate with carbon dioxide: The role of the catalyst, solvent and reaction conditions, Journal of Molecular Catalysis A. Chemical 2006;257: 149–153.

[84]   Rokicki G, Rakoczy P, Parzuchowski P, Sobiecki M. Hyperbranched aliphatic polyethers obtained from environmentally benign monomer: glycerol carbonate Green Chem. 2005; 7:529.

[85]   Long Haung,1,2 Yu-Lei Zhu,1,3 Hong-Yan Zheng,3 Yong-Wang Li1,3 and Zhi-Yong Zeng1,2. Continuous production of 1,2-propanediol by the selective hydrogenolysis of solvent – free glycerol under mild conditions. Journal of Chemical Technology and Biotechnology J Chem Technol Biotechnol 2008.

[86]   Perosa A. and Tundo P. Selective hydrogenolysis of glycerol with raney nickel. Industrial andEngineering Chemistry Research 2005; 44 : 8535-8537

[87]   Dasari M.A, Kiatsimkul PP, Sutterlin WR and Suppes GJ. Low-pressure hydrogenolysis of glycerol to propylene glycol. Applied Catalysis A: General 2005; 281: 225-231.

[88]   Long Huang, Yu-Lei Zhu, Hong-Yan Zheng, Yong-Wang Li1, and Zhi-Yong Zeng, Continuous production of 1,2-propanediol by the selective hydrogenolysis of solvent-free glycerol under mild conditions, Journal of Chemical Technology and Biotechnology, DOI: 10.1002/jctb

[89]   Mohanprasad A. D, Kiatsimkul PP, Sutterlin WR, Suppes GJ, Low-pressure hydrogenolysis of glycerol to propylene glycol, Applied Catalysis A: General 2005; 281 : 225–231

[90]   Haas T, Jaeger B, Weber R, Mitchell SF. Appl. Catal. A 2005;280: 83.

[91]   Dasari MA, Kiatsimkul PP, Sutterlin WR, Suppes GJ, Appl. Catal. A2005; 281: 225.

[92]   Sohounloue DK, Montassier C, Barbier J. React. Kinet. Catal. Lett.1983; 22 : 391.

[93]   Casale B, Gomez AM, US Patent 5,276,181 (1994).

[94]   Casale B, Gomez AM, US Patent 5,214,219 (1993).

[95]   Montassier C, Giraud D, Barbier J, Boitiaux JP. Bull. Soc. Chim. Fr. 2 (1989) 148.

[96]   Montassier C, Giraud D, Barbier J. Stud. Surf. Sci. Catal. 1988; 41: 165.

[97]   Montassier C, Dumas JM, Granger P, Barbier J. Appl. Catal. A 1995;121: 231.

[98]   Montassier C, Ménézo JC, Moukolo J, Naja J, Hoang LC, Barbier J, J. Mol. Catal. 1991;70: 65.

[99]   Ludwig S, Manfred E, US Patent 5,616,817 (1997).

[100]   Tessie C, US Patent 4,642,394 (1987).

[101]   Braca G, Raspolli Galletti AM, Sbrana G, Organomet J. Chem. 1991;417 : 41.

[102]   M. Schlaf, Ghosh P, Fagan P.J, Hauptman E, Bullock R.M., Angew. Chem. Int. Ed. 2001;40: 3887.

[103]   Chaminand J, Djakovitch L, Gallezot P, Marion P, Pinel C, Rosier C, Green Chem.2004; 6 : 359.

[104]   Montassier C, Ménézo JC, Hoang LC, Renaud C, Barbier J, J. Mol. Catal.1991; 70 : 99.

[105]   Lahr DG, Shanks BH, Ind. Eng. Chem. Res. 2003;42 : 5467.

[106]   Lahr DG, Shanks BH, J. Catal. 2005; 232 : 386.

[107]   Furikado I, Miyazawa T, Koso S, Shimao A, Kunimori K, Tomishige K, Catalytic performance of Rh/SiO2 in glycerol reaction under hydrogen, Green chemistry , 2007; 9: 582-588

[108]   Keyi Wang, Martin C. Hawley, and Scott J. DeAthos, Conversion of Glycerol to 1,3-Propanediol via Selective Dehydroxylation, Ind. Eng. Chem. Res. 2003; 42: 2913-2923.

[109]   Solomon B.O., Zeng A. P., Biebl H., Schlieker H., Posten C., Deckwer W. D., Comparison of the energetic efficiencies of hydrogen and oxychemicals formation in Klebsiella pneumoniae and Clostridium butyricum during anaerobic growth on glycerol, Journal of Biotechnology 1995;39: 107-117.

[110]   Deckwer W. D., Microbial conversion of Glycerol to 1,3-Propanediol, FEMS Microbiology Reviews 1995;16: 143-149.

[111]   Menzel K., Zeng A. P., and Deckwer W. D., High concentration and productivity of 1,3-propanediol from continuous fermentation of glycerol by Klebsiella pneumoniae. Enzyme Microb. Technol., 1997; 20: 82-86.

[112]   Barbirato F., Himmi E. H., Conte T., Bories A., 1,3-Propanediol production by fermentation: An interesting way to valorize glycerin from the ester and ethanol industries, Industrial Crops and Products 1998: 7; 281–289.

[113] Xiu ZL, Song BH, Sun LH and Zeng P., Theoretical analysis of effects of metabolic overflow and time delay on the performance and dynamic behavior of a two-stage fermentation process, Biochemical Engineering Journal 2002; 11 : 101–109.

[114] Xiu ZL, Song BH., Wang ZT, Sun LH, Feng EM, Zeng AP, Optimization of dissimilation of glycerol to 1,3-propanediol by Klebsiella pneumoniae in one- and two-stage anaerobic cultures, Biochemical Engineering Journal 2004;19: 189–197.

[115] Chen X, Xiu Z, Wang J, Zhang D, Xu P, Stoichiometric Analysis and Experimental Investigation of Glycerol Bioconversion to 1,3-Propanediol by Klebsiella Pneumoniae Under Microaerobic Conditions. Enzyme Microbial Technology 2003; 33: 386–394.

[116] Barbirato F, Astruc S, Soucaille P, Camarasa C, Salmon J M and Bories A. Anaerobic pathways of glycerol dissimilation by Enterobacter agglomerans CNCM 1210: limitations and regulations. Microbiology 1997; 143: 2423–2432.

[117] Barbirato F, Himmi E H, Conte T, Bories A. 1,3-Propanediol production by fermentation: An interesting way to valorize glycerin from the ester and ethanol industries, Industrial Crops and Products 1998 ;7: 281–289.

[118] Himmi E, Bories A, Barbirato F, Nutrient requirements for glycerol conversion to 1,3propanediol by Clostridium butyricum. Bioresource Technology 1999;67:123-128

[119] Papanikolaou S, Ruiz-Sanchez P, Pariset B, Blanchard F, Fick M. High production of 1,3-propanediol from industrial glycerol by a newly isolated Clostridium butyricum strain, Journal of Biotechnology 2000;77: 191–208.

[120] González-Pajuelo M, Andrade J C, Vasconcelos I Production of 1,3-propanediol by Clostridium butyricum VPI 3266 using a synthetic medium and raw glycerol, J. Ind. Microbiol. Biotechnol. 2004 :31: 442–446.

[121] Bouvet O, lenormand P, Ageron E and Grimont P. Taxonomic Diversity of Anaerobic Glycerol Dissimilation in the Enterobacteriaceae, Res. Microbiol. 1995: 146: 279-290.

[122] Zeng AP, Biebl H, and Deckwer WD. Microbial Conversion of glycerol to 1,3-propanediol:Recent Progress. ACS Symposium Series 666: 1997;264-279.

[123] Zeng AP. Pathway and kinetic analysis of 1,3-propanediol production from glycerol fermentation by Clostridium Butyricum. Bioprocess and Biosystems Engineering 1996;14(4): 169-175.

[124] Xiu ZL, Song BH, Wang ZT, Sun LH, Feng EM., and Zeng AP. Optimization of dissimilation of glycerol to 1,3-propanediol by Klebsiella Pneumoniae in one- and two-stage anaerobic cultures. Biochemical Engineering Journal 2004;19(3): 189-197.

[125] Cheng KK., Liu HJ, and Liu DH. Kinetic analysis of aerobic batch fermentation of 1,3-propanediol by Klebsiella Pneumoniae. Modern Chemical Industry 2005;25: 185-188.

[126] Chen HW, Wang W, Fang BS, and Hu ZD. Studies on fermentation conditions for key enzymes in 1,3-propanediol production with Klebsiella Pneumoniae. Journal of Chemical Engineering of Chinese Universities 2004;18(5): 621-627.

[127] Chen X., Xiu Z, Wang J, Zhang D, and Xu P . Stoichiometric analysis and experimental investigation of glycerol bioconversion to 1,3-propanediol by Klebsiella Pneumoniae under microaerobic conditions. Enzyme and Microbial Technology 2003; 33(4): 386-394.

[128] Menzel K., Zeng AP, and Deckwer WD. High concentration and productivity of 1,3-propanediol from continuous fermentation of glycerol by Klebsiella Pneumoniae. Enzyme and Microbial Technology 1997; 20(2): 82-86.

[129] Wang JF, Xiu ZL, Liu HJ, and Fan SD. Study on microaerobic conversion of glycerin to 1,3-propanediol by Klebsielle pneumoniae. Modern Chemical Industry 2001; 21(5): 28-31.

[130] Zeng AP, Biebl H, Schlieker H, Deckwer WD. Pathway analysis of glycerol fermentation by Klebsiella Pneumoniae: Regulation of reducing equivalent balance and product formation.Enzyme and Microbial Technology 1993; 15(9): 770-779.

[131] Lin R, Liu H, Hao J, Cheng K, Liu D. Enhancement of 1,3-propanediol production by Klebsiella Pneumoniae with fumarate addition. Biotechnology Letters 2005; 27(22): 1755-1759.

[132] Gottschalk G.. Bacterial metabolism. New York: Springer-Verlag ; 1986 .R. Landucci, B. Goodman, and C.Wyman. Methodology for evaluating the

economics of biologically producing chemicals and materials from alternative feedstocks. Appl Biochem Biotechnology 1994; 45–46: 678–696.

[133] Zeikus JG. Chemical and fuel production by anaerobic bacteria. Annu. Rev. Microbiol 1980; 34: 423–464.

[134] Lee PC, Lee WG, Lee SY, ChangHN. Succinic acid production with reduced by-product formation in the fermentation of naerobiospirillum succiniciproducens using glycerol as a carbon. Biotechnology and Bioengineering 2001;72(1): 41-48.

[135] Eaton ER., Boon , Smith A Chemical Base for Engine Coolant / Antifreeze with improved Thermal Stability Properties. SAE Tech Papers Series, 2001 ; 01 – 1182.

[136] http://www.shellchemicals.com/corterra /1,1098,280,00.html

[137] Forschner TC , Gwyn DE, Xiao HX, Suthar B, Sun LQ, Frisch KC. Polyurethane Hot Melt Adhesives Based on 1,3-Propanediol, Shell Chemicals Data Literature on 1,3 – PDO.

[138] Plasman V, Caulier T, Boulos N. Polyglycerol esters demonstrate superior antifogging properties for films, Plastics Additives & Compounding March/April 2005 .