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POSSIBILITIES OF USING BIODIESEL BY-PRODUCT: GLYCEROL II

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ABSTRACT
A rapid growth in biofuels production leads to a surplus of by-products generated. By-products can be utilized and offer a wide range of opportunities. This paper reports the utilization of glycerol as by-product of biodiesel, soap and fatty acid industry. It includesuse of glycerol as feedstock to synthesis of chemicals, his biochemical and energetic applications.

KEY WORDS: *Glycerol, Biodiesel, by-product, feedstock*

INTRODUCTION

Glycerol (also called glycol or glycerine) is a by-product of biodiesel, soap andfatty acidmanufacturing plants. His properties offer a wide range of opportunities based on its transformation in many applications.
Physically, glycerol is a water-soluble, clear, almost colourless, odourless, viscous, hygroscopic liquid with a high boiling point. At low temperatures, glycerine tends to supercool, rather than crystallize. Water solutions of glycerine resist freezing, a property responsible for glycerine's use as permanent antifreeze in cooling clear liquidand systems.
Chemically, glycerol is a trihydric alcohol (1,2,3-propanetriol, $CH_2OHCHOHCH_2OH$), capable of being reacted as an alcohol yet stable under most conditions. One, two or three of his hydroxyls can be replaced with other chemical groups, thus permitting the synthesis of many different derivatives with properties designed for specific applications.
Biologically, glycerol is nontoxic in the digestive system and non-irritating to the skin and sensitive membranes, except in very high concentrations when a dehydrating effect is noted. It is also odourless and has a warm sweet taste.
Glycerol has a unique combination of physical and chemical properties (Tab. 1), which are utilized in many thousands of commercial products.

Tab.1 Physico-chemical properties of glycerol.[1]

CAS Number	56-81-5	Melting point	17.8 °C
Molar mass	92.02 g mol^{-1}	Boiling point	290.0 °C
Density	1.261 g cm^{-3}	Flash point	160.0 °C
Viscosity	1 412 Pa s	Self-ignition	393.0 °C
Surface tension	63.4 mN m^{-1}	Specific heat	2.43 kJ kg^{-1}K^{-1}
Refractive index	1,4746	Heat of vaporisation	82.12 kJ kmol^{-1}
Freezing point (66.7 % solution)	- 46.5 °C	Heat of formation	667.8 kJ mol^{-1}

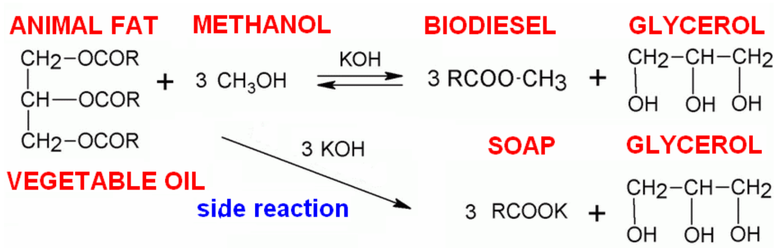

Fig.1: The main reactions of glycerol production

Glycerol is currently produced from the transesterification process during biodiesel production and the saponification and hydrolysis processes in fatty acid and soap manufacturing plants (Fig. 1). Generally, for every 3 mol of methyl esters produced, 1 mol of glycerol is synthesized, which is nearly 10 wt.% of the total product.[2] The crude glycerol generated from biodiesel plants include many impurities and other chemicals, for instance, methanol, organic and inorganic salts, water, vegetable colours, mono and diglyceride traces and soap. The percentage of glycerol present in the crude glycerol can vary from as low as 45 % to upwards of 90 % depending on various reaction conditions, as well as the extent to which the crude glycerol is produced by the biodiesel plant. The chemical composition mainly depends on the type of catalyst used to produce biodiesel, the transesterification efficiency, recovery efficiency of the biodiesel, other impurities in the feedstock, and whether the methanol and catalysts were recovered. All of these considerations contribute to the composition of the crude glycerol fraction. Hence, large-scale biodiesel producers can refine the crude glycerol into a

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refined form with purities up to 95.5 % and 99 % to be used in the pharmaceutical, food or cosmetic industries. The purification of crude glycerol is an expensive process, requiring expensive processing equipment. [3, 4]

1. CHEMICAL PRODUCTS

Glycerol is a feedstock for many chemicals with a wide range of applications. The three-hydroxyl group in glycerol structure allows its transformations into other chemicals. Dehydration, hydrogenolysis, selective oxidation and fermentation are the major routes for glycerol utilisation. Common chemicals derived from glycerol are for example:[4, 5, 6]

- *1,2-Propanediol* produced by hydrogenolysis is used as plasticizer and stabilizing agent,
- *1,3-Dihydroxyacetone (DHA)* produced by direct and indirect oxidation of glycerol is used as ingredient in cosmetic products and as intermediate in the synthesis of miscellaneous chemicals,
- *1,3-Propanediol* produced by dehydroxylation,hydrogenolysis or fermentation using *Klebsiellapneumoniae*, *Lactobacillus reuteri*, *Citrobacterfreundii* isused in the solvent, adhesives and as raw material for the production of lubricants, polymers and food,
- *Acrolein* produced by vapor/gas phase or liquid phase dehydration is used as intermediate for the generation of acrylic acid and its esters,
- *Butanol* and *1,3-propanediol* produced by fermentation using *Clostridium pasteurianum*is a new generation of biofuel or intermediate for other chemical production,
- *Citric acid* produced by fermentation by*Yarrowia lipolytica* is used as a flavoring and preservative in food and beverages, especially soft drinks,
- *Ethanol* produced by fermentation using *Pachysolentannophilus*CBS4044, *Klebsiellapneumoniae*GEM167, *Kluyveracryocrescens*, *Enterobacteraerogenes* and *Escherichiacoli* is used as fuel, solvent and widely used as an intermediary for the synthesis of bulk chemicals,
- *Formic acid* produced by selective oxidation is usedas antibacterial additive in livestock feed and as energy carrier in direct formic acid fuel cell (DFAFC),
- *Glycerol carbonate* produced by transesterification or carboxylation is used in gas separation membranes, electrolyte in batteries and as feedstock in the synthesis of polymers,
- *Hydrogen* produced by fermentation using *Escherichia coli*, supercritical water reforming,steam and autothermal steam reforming is used for synthesis of other valuable chemicals such as methanol, ammonia, it is fuel for internal combustion engines and energy carrier in fuel cells,
- *Lipids*: as the sole carbon source, crude glycerol could be used for culturing *Schizochytriumlimacinum*SR21 and *Cryptococcus curvatus* to produce lipids, which might be a sustainable biodiesel feedstock. The produced lipid had high concentration of monounsaturated fatty acid and was good biodiesel feedstock.
- *Polyesters* produced by polycondensation is used in textile industry and as component in plastic making industry,
- *Poly(hydroxyalkanoates) (PHA):* represent a complex class of naturally occurring bacterial polyesters and have been recognized as good substitutes for non-biodegradable petrochemically produced polymers. Crude glycerol could be used to produce PHA polymer using *Paracoccus denitrificans*, *Cupriavidus necator* or *Zobellella denitrificans*MW1.
- *Propanol* produced by fermentation using *Escherichia coli* is used as solvent,
- *Propionic acid* produced by fermentation using *Propionibacteriumacidipropionici* is used as preservative in feed and food industry and as precursor for the production of pharmaceuticals,
- *Succinic acid* produced by fermentation with *Actinobacillus succinogenes*is used as intermediate for the production of chemicals in pharmaceutical and food industry.

2. BIOCHEMICAL APPLICATIONS

The biochemical processes of organic substances transformation by selected bacteria is described in above chapter. Glycerol is well known as a carbon source for biological processes. It is used for the cometabolism of biological wastes, e.g. in waste water treatment processess or soil remediation. The main biochemical applications are: [5, 6]

- *Glycerol as fermentation substrate in biological processes*:Glycerol can be fermented into many types of products, such as 1,3-propanediol, acetate, butyrate, butanol, ethanol, lactate, hydrogen and other organic acids. Certain bacterial groups can ferment glycerol effectively, e.g.*Bacillus*, *Enterobacter*, *Clostridium*, *Lactobacillus*, *Klebsiella*species.
- *Glycerol in wastewater processes:*Common source of carbon used in wastewater treatment plants for the removal of nitrates, phosphorus etc., is methanol. However, alternative carbon sources are being sought. Glycerol is non-toxic, in water good soluble carbon rich material.
- *Glycerol in soil remediation processes:*Glycerol addition has potential in biostimulation of indigenous soil microbial populations such as *Rhodococcus, Pseudomonas* and *Desulfosporosinus* to enhanced POPs degradation under aerobic or anoxic conditions. [7]

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- *Animal feedstuff:* The possibilities of using crude glycerol in feeds has been investigated because of the increase in the price of corn and the surplus of crude glycerol. Glycerol has high absorption rates and is good energy source. Once absorbed, it can be converted to glucose for energy production in the liver of animals by the enzyme glycerol kinase. Although crude glycerol can be added to animal feed, excess glycerol in the animal diet may affect normal physiological metabolism. [4]

3. ENERGETIC APPLICATIONS

The production of renewable energy and some industrial productions bring other raw materials, which can be used for energy production.The physico-chemical and biological properties of glycerol,such as non-toxicity, non-flammability and non-volatility(important for the ease production, storage and use) and has high energy density (6.26 kWh l^{-1}) allow its use for power applications. The unrefined glycerol can by utilized by digestion, fermentation, liquefaction and gasification etc.detailed reporting in followed section: [5, 6]

- *Glycerol as fuel additive*:Glycerol-derived fuel additives can improve the fuel properties, such as increased octane rating, reduced cloud point, enhanced viscosity and cold properties of liquid fuels, and, more importantly, less harmful substances or particulates emitted into the atmosphere.[8]Glycerol can be transformed into branched oxygen-containingmolecules, especially alcohol and ethers like methyl tert-butyl ether (MTBE), di-tert-butyl glycerol ether (DTBG) and tritert-butyl glycerol ether (TTBG). Catalytic glycerol transformation to oxygenated fuel additives includes etherification, esterification, acetylationand transesterification.
- *Combustion*:Direct combustion of glycerol in furnaces for heat generation is disapproved of because of its harmful emissions into the atmosphere, particularly acrolein gas, a toxic gas formed at low temperature by thermal degradation of glycerol. Glycerol also has low heating value, high self-ignition temperature, high viscosity and crude glycerol salt content thereby hindering its use in oven.
- *Glycerol pyrolisis and gasification*:Pyrolysis and gasification of glycerol (the decomposition at high temperatures in the absence of oxygen) are promising methods for its transforming.Glycerol decomposes to methanol, carbon monoxide, carbon dioxide, hydrogen, formaldehyde, alcohol, acetaldehyde and many more compounds. Pyrolysis and gasification of glycerol produce three forms of products - gases, liquid products (bio-oil) and char.
- *Liquefactionof glycerol (crude glycerol mixed with waste biomass)*: Liquefaction is a thermochemical process in which biomass isconverted to a bio-oil with an improved heating value under moderatelyhigh temperatures but relatively high pressures.Hydrothermal liquefaction is a complex process involving many possible reactions such as hydrolysis, dehydration, dehydrogenation, esterification, re-polymerization, etc.
- *Glycerol digestion:*Anaerobic co-digestion involves the decomposition of crude glycerol along with biomass (usually sewage sludge or manure) by a microbial community at mild temperatures to produce mixture of methane and hydrogen – biogas. Application of a two-stage digestion using acidogenic digester and methanogenic digester in sequence could better control bacteria population and reduce the impact of acids on methane generation. The digested sludge can be suitable as a fertilizer.
- *Glycerol for hydrogen gas production*:Hydrogen production from glycerol is favourable, as hydrogen is clean, has a very high energy density, and the only by-product is water. There are many methods available to convert glycerol into hydrogen: aqueous phase reforming, supercritical water reforming, autothermal and steam reforming. Steam reforming is the most widely applied method in the chemical industry. Glycerol reacts with water steam with the aid of a catalyst and forms hydrogen, carbon monoxide and carbon dioxide. Theoretically, 1mol of glycerol can be converted to 7 mol of hydrogen via steam reforming of glycerol. [9]The fermentation of crude glycerol to hydrogen can be done through twodifferent forms of fermentation known as dark fermentation andphotofermentation. Dark fermentation uses a variety of microbes,usually isolated from soil samples, such as *Klebsiella sp.*, *Clostridiumpasteurianum*, *Clostridium butyricum*, *Thermotoganeapolitana*, or acollection of various microbes. Photofermentation, as the name implies, requires a light source. The most popular microbes are used *Klebsiella sp.* TR17 and *Rhodopseudomonaspalustris*TN1.
- *Methanol production from glycerol*:Methanol is an energy carrier in direct methanol fuel cell (DMFC) applications, and there is the potential for using methanol as a fuel for internalcombustion engines, directly or blended with gasoline. In addition, methanol is an important component in the transesterification process in biodiesel manufacturing, where it aids the transformation of triglyceride oils into biodiesel.
- *Ethanol production from glycerol*:Microorganisms like *Saccharomyces cerevisiae* is able to use glycerol as a sole source of carbon. Glycerol fermentation in these organisms is mediated by a two-branch pathway, which results in the synthesis of glycolytic intermediate dihydroxyacetone phosphate (DHAP) and fermentation product ethanol.[10]Anhydrous ethanol can be combined with gasoline in any concentration up to pure ethanol (E100). It is increasingly used as an oxygenate additive for standard gasoline, as a replacement for methyl t-butyl ether (MTBE). Ethanol can also be used to power fuel cells.
- *Glycerol for fuel cell applications*:The beneficial features of direct oxidation of glycerol in direct alcohol fuel cell (DAFC) applications are the generation of power and the production of oxygenated products, such asglycerate,

hydroxypyruvate, mesoxalate and tartronate ions, whichare very expensive and difficult to synthesize via catalytic or biologicalprocesses.[11]

CONCLUSIONS

Glycerol generated as by-product from biodieselsoap and fatty acid industry should be a promising feedstock for the variety of application. There are a number of excellent review papers in the literature addressing the utilization of crude glycerol. Our contribution provides a brief summary of various opportunities for its chemical, biochemical and energetic use.

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