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Improved Utilization of Crude Glycerol By-Product from Biodiesel Production

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1. Introduction

During the last ten years a significant increase in biodiesel production and its commercial applications was observed (Rahmat et al., 2010). Nowadays, biodiesel is only one alternative fuel which may replace crude oil because it can be used in vehicles with a diesel engine without modifications of major engine or fuel elements (Johnson & Taconi, 2007). Presently, the most often used biodiesel fuels are vegetable oil fatty acid methyl or ethyl esters produced by transesterification (Andre et al., 2010; Sendzikiene et al., 2007). For every three mol of ethyl esters one mol of crude glycerol is produced, which is equivalent to approximately 10 wt% of the total biodiesel production (Karinen & Krause, 2006; Pagliaro et al., 2009; Rahmat et al., 2010). It is estimated that by 2016 the world biodiesel market will achieve the quantity of 37 billion gallons, which means that significantly more than 4 billion gallons of crude glycerol will be produced every year. The potential sale of this fraction might have an influence on the total price of biodiesel and make it cheaper (Fan et al., 2010; L. Wang et al., 2006). Pure glycerol may be used in many branches of industry, for example in food products (to sucrose liqueurs), cosmetics (as a moisturizing factor), textile industry, in pharmaceuticals, cellulosic industries; moreover, one can use it in nitrocellulose production as well as a supplement in fodder for pigs, swine, and hogs (Pagliaro et al., 2007; Z.X. Wang et al., 2001). In contrast, use of raw glycerol is strictly limited because of its composition and a presence of pollutant substances. The main pollutants of this raw material include spent catalysts, residual methanol, mineral salts, heavy metals, mono- and diacylglycerols, free fatty acids and soaps (Dasari, 2007). The main biodiesel producers, thanks to the adequate installations inside their production plants, are able to purify raw glycerol. This is done via filtration, chemical steps, and filtration vacuum distillation. Then the technical grade glycerol (>97% pure, used for industrial type applications) or even refined USP grade glycerol (>99.7% pure, used in cosmetics, pharmaceuticals or food) is obtained. Unfortunately, such installations are too expensive for small or medium production plants. One solution to this problem is to sell raw glycerol to refineries in order to increase its value. Nevertheless, glycerol producers must pay for transportation of this glycerol fraction. Because transportation cost often equals or exceeds the price of raw glycerol, it does not make sense. Accordingly, this solution cannot be accepted (Johnson & Taconi, 2007). Therefore, new uses for crude glycerol must be sought and, luckily, many innovative methods of utilizations of this waste are under investigation. This chapter

summarizes currently available studies and discusses possible ways of crude glycerol utilization, undertaken with the aim to improve economic viability of the biodiesel industry.

2. Crude glycerol as an animal feedstuff

An increase of price of maize (which results from an increase of biodiesel production) and accumulation of huge amount of crude glycerol, as a by-product during biodiesel production, resulted in new ideas: some scientists checked the possibility of application of this cheap crude glycerol as an animal feed ingredient instead of maize (Cerrate et al., 2006; Donkin, 2008; Dozier et al., 2008; Lammers et al., 2008a; Lammers et al. 2008b; Mourot et al., 1994). Biodiesel can be produced by a variety feedstock's such as mustard, rapeseed, canola, crambe, soybean oil, palm oil, sunflower oil, and waste cooking oils (Gerpen, 2005; F. Ma & Hanna, 1999; Moser, 2009; Thompson & He, 2006). The feedstock source and manufacturing process of biodiesel production are the key factors determining the composition of crude glycerol and therefore its nutritional value (Hansen et al., 2009; Thompson & He, 2006). Thereupon, it is indispensable to analyze physical, chemical and nutrient properties of crude glycerol with the prospect to include it into the animal diet. Hansen et al. (2009) conducted analytical tests of 11 crude glycerol samples collected from seven Australian biodiesel manufacturers. On the basis of conducted analyses they found that chemical composition of tested samples of crude glycerol varied considerably. The content of glycerol oscillated between 38 and 96%. In one sample the content of ash was more than 29%. This data confirms prior Tyson's et al. (2004) report which informed that content of mineral salts from transesterification can be 10 up to 30% of the crude glycerol by weight depending on the feedstock and process. It is known that high levels of potassium or sodium salts in the diet may result in electrolyte imbalance in animals (Dasari, 2007). Another potential hazardous compound in crude glycerol is methanol. Hansen et al. (2009) detected more than 4% of methanol in one of their research sample of crude glycerol and more than 11% of methanol in two other samples. The result of the methanol metabolic pathway is the accumulation of formate which excess cause toxic effect of methanol. Methanol poisoning may cause central nervous system injury, weakness, headache, vomits, blindness or Parkinsonian-like motor diseases (Dorman et al., 1993). FDA's Center for Veterinary Medicine decided that acceptable level of methanol in crude glycerol, which is used as a supplement in forage, cannot exceed 150 ppm, unless biodiesel producers prove that it has no negative influence on animal health (Dasari, 2007). Crude glycerol can be an attractive energy source for animal feed because of the similar energy value in comparison with corn and soybean meal, but the users of crude glycerol should bear in mind that it can pose a potential danger to the animals when the qualities of this biodiesel byproduct are not monitored properly (Dasari, 2007; Kerr & Dozier, 2008).

2.1 Glycerol in swine diets

Kijora et al. (1995) conducted two experiments with 48 fattening pigs to test the influence of glycerol as a component in diets. The pigs were fed up to 30% glycerol in barley-soya bean oil meal diets. In both these experiments, glycerol was used instead of barley. In the first experiment a fattening pig, which weights ca. 32 kg, eats fodder consisting of 5 and 10% of glycerol. In the second experiment, a fattening pig, which weight ca. 31.2 kg, is given fodder consisting of 5, 10, 20, and 30% of glycerol. In both of these experiments the control groups of pigs eat fodder without glycerol. The first experiment showed that pigs which eat fodder

containing 5 and 10% of glycerol, had higher daily body weight gain. Probably it resulted from sweeter taste and better structure in fodder with glycerol. In the second experiment, no significant improvement in performance was detected in diets with 0, 5, 10, 20, 30% inclusion levels of glycerol. However, a diet containing 30% glycerol resulted in the significantly different feed conversion ratio in comparison with all other groups. These experiments did not demonstrate any pathological changes in kidney and liver in animals fed with fodder consisted glycerol. Moreover, diets have no influence on meat quality or carcass yield. Kijora et al. (1995) recommended supplementation of fodder with 10% of glycerol. In subsequent experiments, Kijora & Kupsch (1996) checked the possibility of application as a fodder supplement two technological distinct glycerols obtained in the process of biodiesel production. The dry weights of these glycerols were 77.6% and 99.7% and the ash content was 18.7 % and 4.8 %. Glycerol was added to fodder in quantity of 5 and 10%. The results from this experiment were collated with the results from the earlier experiments. The scientist found out that pigs in growing period ate 7.5% more fodder with glycerol (regardless of the type and its percentage content) then pigs which ate fodder without glycerol. Moreover, it was demonstrated that an increase of daily body weight strictly depended on the real consumption of glycerol. This effect was not observed in the finishing period. In 1997, Kijora et al. collated influence of application of glycerol, free fatty acids, and vegetable oil, as fodder supplements, on swine carcass backfat thickness and backfat composition in fattening pigs. In this experiment five different fodders were composed. To test each diet six pigs were used. The animals were fed with adequate amount of fodder during 14 weeks. After this time, the group of pigs which eat fodder with 10% of glycerol demonstrated the highest daily body weight gain. However, in collated to the feed conversion ratio there were any significant variations between these animal groups. These researches stated that supplemented animal's diet of glycerol caused decrease of content of polyenic acid in backfat in collated to other diets. The highest contents of palmitic and stearic acid were also observed in backfat pigs which eat fodder without additional fat. Doppenberg and Van Der Aar (2007) during experiments observed that sweet taste of fodder caused that pigs eat more and it resulted in higher daily body weight gain. They also stated that the maximum level of glycerol content in fodder was 5%. Lammers et al. (2007c) used 96 nursery pigs during 33 days of experiments in order to evaluate the influence of diet on weight gain. All pigs were 21 day-old and had the same weight. Animals had free access *ad libitum* to corn soybean isocaloric or isolysin diets containing 0, 5, or 10% glycerol. No difference in pig performance according to diet was observed. The conclusion was that glycerol can be used as a fodder supplement for young pigs. Zijlstra et al. (2009) in their research used 72 weaned pigs in which three pelleted wheat-based diets containing 0, 4 or 8% glycerol were applied. It occurred that glycerol used instead of wheat (up to 8%) can enhance growth performance of weaned pigs. Schieck et al. (2010) tested results of application of corn-soybean based diets containing 0, 3, 6 or 9% glycerol in lactating sows. No difference was observed in sows' performance according to diet. In conclusion they stated that glycerol (up to 9%) can be used as a supplement in diet of lactating sows as an alternative energy sources instead of maize.

2.2 Glycerol in poultry diets

Simon et al. (1996) in their research tested an influence of supplementation of glycerol on body weight gain, feed conversion ratio and N-balance in broiler chickens. The animals had *ad libitum* access to fodders with 0, 5, 10, 15, 20 and 25% of glycerol. It was stated that in result

of a 31-day diet with forage supplemented of 5 and 10% of glycerol advantageous effects occurred with respect to the above parameters. The highest glycerol doses, the body weight gain, feed conversion ratio and N-balance in broiler chickens decreased. Pathological changes in kidney and liver were observed when the highest dose of glycerol was added. What is noteworthy, when 10% of glycerol was added to forage, chickens needed more water (Simon, 1996). In further experiments, Simon et al. (1997) observed an advantageous correlation between addition of glycerol to low-carbohydrate diet and an increase of nitrogen retention in the body. This effect was not observed in high-carbohydrate diets. Cerrate et. al. (2006) evaluated the usefulness of crude glycerol from biodiesel production as an energy source in broiler diets. Experiments were divided into two steps, each diet lasted 42 days. In the first step, 0, 5, and 10% of crude glycerol were added to forage. In the second step, 2.5 and 5% of glycerol were used. With an increase of crude glycerol in forage, the quantity of maize was decreased and quantity of soybean meal and poultry oil, to maintain these diets isocaloric and isonitrogenous, increased. The conclusion after the first step of this research was that the diet supplemented with 5% of glycerol had no influence in broilers performance in collate with diet without glycerol. It was also observed that the forage with 10% of glycerol was not gladly consumed by animals what resulted in decrease in body weight gain. The second step of these experiments demonstrated that supplementation of forage with 2.5 and 5% of glycerol had no influence on body weight gain. However, significantly greater breast yield accounted as a percent of the dressed carcass for broilers fed with glycerol was observed. Abd-Elsamee et al. (2010) in their experiments use forage with 0, 2, 4, 6, and 8% of crude glycerol in broilers diets. The highest body weight and the body weight gain were observed when the forage with 6% of glycerol was used. What is important, the diet with 8% of glycerol did not cause any negative results on broiler chick performance, nutrient utilization or carcass characteristics. An influence of glycerol on egg performance and nutrient utilization in laying hens was tested by Świątkiewicz & Koreleski (2008). They tested forages in which corn starch was relieved by 2, 4, and 6% of glycerol. This forage was used in the diet of chicken between 28 and 53 weeks old. Effects showed that up to 6% of glycerol in the diet of laying hens had no negative influence on the performance or quality of eggs, nutrient retention, and metabolizability of energy. Other experiments demonstrated that supplementation of forage with 15% of glycerol had no negative influence on egg production, egg weight or egg mass of laying hens (Lammers et al., 2008b).

3. Catalytic conversion of glycerol

Recently, an increasing interest in the production of value-added chemicals from glycerol is observed. This tendency may lead to a decrease in biodiesel prices. Moreover, it can improve the glycerol market. Glycerol can be completely converted, among other compounds, into esters, ethers, propanediols, epichlorohydrin, acrolein and dihydroxyacetone.

3.1 Glycerol esters

Monoglycerides, polyglycerol esters and their derivatives can be obtained by the direct esterification of glycerol with carboxylic acids or by the transesterification of glycerol with carboxylic methyl esters or with triglycerides (Behr et al., 2007; Guerrero-Pérez et al., 2009). These compounds have wide applications as emulsifiers in food, cosmetic and pharmaceutical industries. Diaz et al. (2000, 2001) and Pérez-Pariente et al. (2003) reported

the synthesis of monoglycerides by esterification of glycerol with lauric and oleic acids with functionalized ordered mesoporous materials containing R-SO₃H groups as catalysts. Diaz et al. (2005) investigated the influence of the alkyl chain length of HSO₃-R-MCM-41 on the esterification with the fatty acid mentioned above. On the basis of conducted research, the optimum balance between the nature of the organic groups supporting the sulfonic acid, the distance between sulfonic groups, and the porosity of material was determined. R. Nakamura et al. (2008) conducted the esterification of glycerol with lauric acid catalyzed by multi-valent metal salts to form mono- and dilaurins. They found that ZrOCl₂·8H₂O and AlCl₃·6H₂O are chloride's catalysts which are active in the formation of monolaurin, and Fe₂(SO₄)₃·nH₂O and Zr(SO₄)₃·nH₂O are sulfate's catalysts which have beneficial effects for dilaurin production. These compounds have numerous applications in pharmaceutical industry, e.g. monolaurin is biologically active against HIV virus.

Another interesting compound is glycerol carbonate which is the cyclic ester of glycerol with carbonic acid (Behr et al. 2008). Glycerol carbonate has a tremendous potential in the chemical industry as a novel component of gas separation membranes, as a solvent, e.g. in colours, glues, cosmetics and pharmaceuticals, and as a source of new polymeric materials such as glycidol used in the production of polyurethanes and polycarbonates (Guerrero-Perez et al., 2009; Johnson & Taconi, 2007; Pagliaro et al., 2007; Rokicki et al., 2005). Vieville et al. (1998) described production of glycerol carbonate by direct carboxylation of glycerol with carbon dioxide in the presence of zeolites or ion exchange resins. Aresta et al. (2006) reported the first evidence of direct carboxylation of glycerol with carbon dioxide under Sn-complexes catalysis. However, those catalytic conversions need high pressures or supercritical conditions. Kim et al. (2007) reported the first enzymatic example of glycerol carbonate synthesis. They demonstrated the procedure of transesterification of renewable glycerol and dimethyl carbonate in the presence of immobilized lipase isolated from *Candida antarctica*. Enzymatic synthesis of glycerol carbonate has a huge potential because of the mild reaction conditions and high selectivity (Carrea & Riva, 2000).

3.2 Glycerol ethers

It is well known that glycerol cannot be directly added to fuel because of its polymerization in high temperatures and partial oxidation to toxic acrolein (Pagliaro et al., 2007). However, glycerol can be transformed into fuel additives, thanks to selective etherification. The glycerol tert-butyl ethers (GTBEs) can be synthesized by the reaction of glycerol with tert-butanol as well as with isobutene (Behr et al., 2008). GTBEs have been studied as analogs of environmentally unfriendly methyl tert-butyl ethers (MTBEs) or ethyl tert-butyl ethers (ETBEs) which are currently added to fuels (Karinen & Krause, 2006; Monbaliu et al., 2010). The application of GTBEs leads to reduction of particulate matter, carbon monoxide, hydrocarbons and unregulated aldehydes in emissions (Pagliaro et al., 2007). The addition of these ethers into biodiesel also decreases the cloud point to a value similar to conventional diesel (Rahmat et al., 2010). Klepáčová et al. (2003) demonstrated the etherification of glycerol with tert-butanol at the presence of catex Amberlyst 15 as catalyst. On the basis of conducted experiments, almost 96% conversion of glycerol was detected at 90°C, reaction time 180 min and at the molar ratio tert-butanol/glycerol = 4:1. Klepáčová et al. (2005) also presented a comparative study of etherification of glycerol with tert-butanol and isobutene without solvent in a liquid phase. It was found that conversions of glycerol in the same temperature and with the same catalyst were always higher when isobutene was used. The 100% conversion of glycerol with selectivity of glycerol di- and tri- ethers higher than 92% in the etherification of

glycerol with isobutene and over strong acid macroreticular ion-exchange resins as catalyst was achieved. Similar results were obtained by Melero et al. (2008) who reported the results of etherification of glycerol with isobutene and sulfonic mesostructured silicas used as catalysts. They also obtained 100% conversion of glycerol and selectivity of glycerol di- and tri-ethers up to ca. 90% without undesirable isobutylene formation. Another method of crude glycerol utilization is telomerization with 1,3-butadiene to form C₈ chain ethers, which have a wide range of applications such as useful building blocks for commercially valuable products such as detergents and surfactants (Behr et al. 2009). Most recently, direct telomerization of pure as well as crude glycerol with 1,3-butadiene carried out over palladium complexes as catalysts was reported (Palkovits et al., 2008a, 2008b).

3.3 Propanediols

Glycerol can be used in chemical production of a value-added compound called 1,2-propanediol known also as propylene glycol. It is widely used as a humectant food additive (E1520), to maintain moisture in medicines, cosmetics and tobacco products, and as a solvent for food colors and flavorings. 1,2-propanediol can be also used as a substitute for ethylene glycol in anti-freeze, especially since ethylene glycol unlike 1,2-propanediol is toxic and is banned in Europe (Johnson & Taconi, 2007). Dasari et al. (2005) evaluated the production of 1,2-propanediol by glycerol hydrogenation in presence of nickel, palladium, platinum, copper, and copper-chromite catalysts at 200°C and less than 14 bar hydrogen pressure. They obtained 1,2-propanediol yields > 73% when copper-chromite was used as a catalyst. Perosa & Tundo (2005) converted glycerol to 1,2-propanediol in presence of Raney-nickel as hydrogenation catalyst, at 150°C and low hydrogen pressure 10 bar. In these conditions, they detected 93% selectivity toward 1,2-propanediol and small amounts of ethanol and CO₂. When temperature of reactions increased to 190°C, it proceeded faster, but the selectivity of 1,2-propanediol dropped to 70-80% and ethanol and CO₂ as the sole by-products. They also observed that addition of a phosphonium salts improved the selectivity and rate toward 1,2-propanediol. S. Wang & Liu (2007) converted glycerol to 1,2-propanediol on Cu-ZnO catalysts in temperatures between 180-240°C and high hydrogen pressure 42 bar. They found that glycerol conversion and 1,2-propanediol selectivity depends on Cu and ZnO particle sizes. The 83.6% 1,2-propanediol selectivity at 22.5% glycerol conversion was achieved at 200°C in presence Cu-ZnO catalyst with relatively small Cu particles. Marinoiu et al. (2009) conducted the hydrogenolysis process with nickel catalyst which resulted in up to 98% 1,2-propanediol selectivity and 30% glycerol conversion in moderate temperature and pressures (200°C and 20-25 bar, respectively). Recently, Wu et al. (2011) reported hydrogenolysis of glycerol to 1,2-propanediol *via* hydrogen spillover by using Cu-Ru nanoparticle catalyst supported on nanotubes. Another propanediol with numerous applications is 1,3-propanediol. It is used as a monomer in the synthesis of a new type of polyesters such as polytrimethylene and terephthalate. It also found an application as a chemical intermediate used in the manufacture of polymers, cosmetics, medicines and heterocyclic compounds (Saxena et al., 2009). The catalytic conversion of glycerol to 1,3-propanediol was examined by Kurosaka et al. (2008) where glycerol hydrogenolysis was catalyzed by Pt/WO₃ supported on ZrO₂ with yields up to 24% toward 1,3-propanediol. Nakagawa et al. (2010) reported direct hydrogenolysis of glycerol over rhenium-modified iridium nanoparticle catalyst with 1,3-propanediol yield of 38% at 81% of glycerol conversion. These results are promising, nevertheless, special attention is paid to microbiological conversion of glycerol to 1,3-propanediol.

3.4 From glycerol to epichlorohydrin

The availability of large amount of crude glycerol has encouraged the development technologies that can use glycerol as a raw material in the production of epoxides. One such product is epichlorohydrin (Lewandowski et al., 2008). Epichlorohydrin is largely used in the production of epoxy resins (Herliati et al., 2011). It also found application in the production of pharmaceuticals, textile conditioners, dyes and paper sizing agents (Gerrero-Pérez et al., 2009). Dow Chemical Company has made epichlorohydrin from crude glycerol by using a GTE process which proceeds in two main steps (Bell et al., 2008). The process is comprising hydrochlorination of glycerol with hydrogen chloride gas at elevated temperature and pressure over carbocyclic acid as catalyst resulting in a 30-50:1 mixture of 1,3-dichloropropan-2-ol and 2,3-dichloropropan-1-ol, followed by reaction with base to give epichlorohydrin (Bell et al., 2008). The Solvay Company has produced the epichlorohydrin at the reserved name Epicerol. First glycerol is chlorinated with anhydrous hydrogen chloride at moderate temperature to give 1,3-dichloropropan-2-ol and then by the addition of sodium hydroxide Epicerol is formed (Behr et al, 2008; Pagliaro et al., 2007).

3.5 Dehydration of glycerol to acrolein

Acrolein is a valuable versatile intermediate used in the production of acrylic acid, acrylic acid esters, detergents or super absorber polymers which can be used as retention agents in the production of paper (Corma et al., 2008; Fan et al., 2010; Ott et al., 2006). Ott et al. (2006) reported the usage of sub- or supercritical water as the reaction media. The maximum 75 mol% selectivity of acrolein with 50% of glycerol conversion was obtained at 360°C, 25 MPa and with the addition of zinc sulfate. Watanabe et al. (2007) dehydrated glycerol to acrolein in hot-compressed water. About 80 mol% selectivity of acrolein at 90% glycerol conversion at 400°C, 34.5 MPa over H₂SO₄ as a catalyst was achieved. Tsukuda et al. (2007) studied acrolein production over several solid catalysts. The acrolein selectivity >80 mol% with almost 100% glycerol conversion was achieved over silicotungstic acid supported on silica with mesopores of 10 nm, at 275°C and ambient pressure. Atia et al. (2008) investigated conversion of glycerol to acrolein using various heteropolyacid catalysts as active compounds. In this study, alumina was found to be superior to silica as support material. The 75% selectivity of acrolein at 100% glycerol conversion over silicotungstic acid supported over alumina and aluminosilicate was achieved. Corma et al. (2008) converted glycerol to acrolein by reacting gas-phase glycerol/water mixtures with a zeolite catalyst. The highest yield to acrolein was found at 350°C with a ZSM5 zeolite-based catalyst. They also detected that by increasing the temperature from 350°C to 500°C the conversion of glycerol from acrolein toward acetaldehyde was favored. Yan & Suppes (2009) investigated low-pressure packed-bed gas-phase dehydration of glycerol to acrolein. At the 0.85 MPa pressure, 260°C and over H₃PO₄/activated carbon catalyst, the 85% selectivity and almost 67% yield of acrolein was achieved. Ulgen & Hoelderich (2011) reported the dehydration of glycerol to acrolein with 85% selectivity in the presence of novel WO₃/TiO₂ catalysts in a continuous flow fixed bed reactor.

3.6 Oxidation of glycerol to dihydroxyacetone

Dihydroxyacetone is a value-added chemical currently used in cosmetics as the main active ingredient in all sunless tanning skincare preparations (Nguyen & Kochevar, 2003). It also serves as a building block in the synthesis of various fine chemicals (Enders et al., 2005;

Zheng et al., 2008). Dihydroxyacetone can be produced from glycerol *via* selective oxidation of its secondary hydroxyl groups (Pagliaro et al., 2007). Garcia et al. (1995) studied chemoselective oxidation of glycerol with air on platinum metals. On the basis of conducted experiments it was found that the main product of glycerol oxidation in presence of Pd/C or Pt/C catalyst is glyceric acid (70 and 55% selectivity, respectively). However, deposition of bismuth on platinum particles orientates selectivity toward secondary hydroxyl groups. In this case 50% selectivity of dihydroxyacetone at 70% conversion of glycerol was achieved. Recently, W. Hu et al. (2010) investigated the selective oxidation of glycerol to dihydroxyacetone in semibatch reactor over Pt-Bi catalyst. The optimization study revealed that the maximum dihydroxyacetone yield of 48% at 80% glycerol conversion at 80°C, 0.2 MPa and initial pH=2 was achieved. Still better results were obtained by Kimura et al. (1993) who found that incorporation of bismuth in platinum and usage of fixed-bed reactor causes 80% dihydroxyacetone selectivity at 40% glycerol utilization. Nowadays, microbial route of dihydroxyacetone production by using *Gluconobacter oxydans* is found to be more favorable as compared to chemical methods (Mishra et al., 2008).

4. Crude glycerol utilization in biotechnology

Bioconversion of glycerol, used as a carbon source for microorganisms' growth, makes it possible to eliminate problems of applying this raw material in chemical catalysis processes (such as high temperature and pressure, use of high specific cofactors). Because of higher level of glycerol reduction in comparison to conventional raw materials in microbial media, higher productivity of glycerol conversion is expected (Gonzalez et al., 2008; Himmi et al., 2000). The conversion of glycerol in glycolytic pathway into phosphoenolopyruvate or pyruvate induces production of double amount of reduction equivalents in comparison to glucose or xylose metabolism. Thus, glycerol delivers more energy indispensable to subsequent reactions of conversion (Barbirato et al., 1997; Yazdani & Gonzalez, 2007). From an economical point of view, it is more profitable to use glycerol in oxygen-free processes because of lower costs of equipment and lower consumption of energy (Yazdani & Gonzalez, 2007). Glycerol can be converted among other compounds, into 1,3-propanediol, propionic acid, succinic acid, citric acid, dihydroxyacetone, hydrogen, ethanol, pigments, polyhydroxyalcanoates and biosurfactants.

4.1 1,3-propanediol

1,3-propanediol is a typical and the oldest product of glycerol fermentation (Katrík et al., 2007). A number of microorganisms which can grow anaerobically on glycerol are known among others *Clostridium diolis*, *Clostridium acetobutylicum*, *Clostridium butylicum*, *Clostridium perfringens*, *Clostridium butyricum*, *Clostridium pasteurianum*, *Enterobacter aerogenes*, *Enterobacter agglomerans*, *Klebsiella oxytoca*, *Klebsiella pneumoniae*, *Citrobacter freundii*, *Lactobacillus collinoides*, *Lactobacillus reuterii*, *Lactobacillus buchnerii*, *Pelobacter carbinolicus*, *Rautella planticola*, and *Bacillus welchii* (da Silva et al., 2009; Drożdżyńska et al., 2011). Papanikolau et al. (2004) investigated 1,3-propanediol biosynthesis by *Clostridium butyricum*. In batch fermentation 47.1 g/L of 1,3-propanediol was obtained. In a continuous process at the 0.04/h dilution rate, up to 44 g/L of 1,3-propanediol was formed. Yang et al. (2007) converted glycerol to 1,3-propanediol by using lactate-deficient mutant of *Klebsiella oxytoca*. On the basis of these experiments 83.56 g/L of 1,3-propanediol with yield of 0.62 mol/mol of glycerol and productivity of 1.61 g/L/h. In 2007, Cheng et al. reported the first pilot-scale

1,3-propanediol production using *Klebsiella pneumoniae*. 1,3-propanediol concentration in 5000 L fermentation reached almost 59 g/L with yield of 0.53 mol/mol of glycerol and productivity of 0.92 g/L/h. Guo et al. (2009) reported that *Klebsiella pneumoniae* CPS-deficient mutant (unable to produce capsular polysaccharides) in fed-batch fermentation was able to synthesize 78.13 g/L of 1,3-propanediol with yield and productivity of 0.53 mol/mol of glycerol and 1.95 g/L/h, respectively. Tang et al. (2009) studied bioconversion of glycerol to 1,3-propanediol using engineered strain of *Escherichia coli*. In this study, vector comprising *yqhD* gene of *Escherichia coli*, together with *dhaB1* and *dhaB2* genes of *Clostridium butyricum*, was created. The fermentation process was divided into two stages. First, *Escherichia coli* mutant was cultivated on culture medium with glucose, at 30°C and in the aerobic conditions to obtain high density of culture next followed by anaerobic glycerol fermentation at 42°C in order to enhance 1,3-propanediol production. This strategy allowed to obtain 104.4 g/L of 1,3-propanediol with yield of 1.09 mol/mol of glycerol and productivity of 2.61 g/L/h. Nowadays, Du Pont and Genencor International, Inc. can produce up to 135 g/L of 1,3-propanediol from glucose by genetically engineered strains of *Escherichia coli* (Drożdżyńska et al., 2011; C.E. Nakamura & Whited, 2003; Saxena et al., 2009). However, 1,3-propanediol biosynthesis from crude glycerol, because of its low price, seems to be economically favorable (Maervoet et al., 2011).

4.2 Propionic acid

Microorganisms which are not able to produce 1,3-propanediol, can offer other industry useful metabolite products (da Silva et al., 2009; Yazdani and Gonzalez, 2007). One possible use of crude glycerol is its utilization to propionic acid in fermentation processes. The microorganisms in this process are *Propionibacterium* (Himmi et al., 2000; A. Zhang & Yang, 2009; Zhu et al., 2010). Propionic acid is widely used in chemical, pharmaceutical and food industries. An important application of this acid is use as a fodder preservative and as a fixing agent for cheeses and baker's products (Kumar et al., 2006). Himmi et al. (2000) in their experiment checked an influence of two different bacterial media on the effectiveness of fermentation. The first medium was with glucose as a carbon source and the other with glycerol. The researchers used two bacterial strains, *Propionibacterium acidipropionici* and *Propionibacterium freudenreichii* ssp. *shermanii*. The highest production of propionic acid (in case of both strains) was observed in fed-batch cultivation. The cultivation was fed by glycerol. The productivity was about 49% higher (0.79 mol of propionic acid per 1 mol of glycerol) when *Propionibacterium acidipropionici* strain was used and about 45% (0.58 mol of propionic acid per 1 mol of glycerol) when *Propionibacterium freudenreichii* ssp. *shermanii* strain was used in comparison to cultivation feeding by glucose. Zhu et al. (2010) converted glycerol to propionic acid using propionic acid-tolerant strain of *Propionibacterium acidipropionici* in a large scale of 10m³ bioreactor. The highest propionic acid production reached ca. 47g/L at 240h of process duration. A. Zhang & Yang (2009) studied the production of propionic acid with metabolically engineered *Propionibacterium acidipropionici* (ACK-Tet). It was found that adapted ACK-Tet mutant produced propionic acid with much higher yield than that from glucose (0.54-0.71g/g vs. 0.35 g/g, respectively). The maximum propionic acid concentration of about 106 g/L from glycerol fermentation was obtained.

4.3 Succinic acid

Succinic acid is used in production of synthetic gum and biodegradable polymers, such as polybutyrate succinate and polyamides (Zeikus et al., 1999; Song & Lee, 2006). Lee et al.

(2001) investigated bioconversion of glycerol to succinic acid by *Anaerobispirillum succiniproducens*. During this experiment the efficiency of succinic acid production was about 133% when glycerol was used as a raw material in comparison to use of glucose. The weight ratio of succinic acid to acetic acid (by-product) was 25.8:1 and it was 6.5 times higher than in case of using glucose as a carbon source. The consumption of glycerol by *Anaerobispirillum succiniproducens* cells depended on the quantity of yeast extract in bacterial medium. The highest succinic acid production was observed in cultivation feeding with glycerol and yeast extracts. In this experiment the efficiency of succinic acid production was about 160% and the weight ratio of succinic acid to acetic acid (by-product) was 37.1:1. Scholten & Dägele (2008) reported succinic acid production from crude glycerol by facultative anaerobic rod-shaped bacteria belonging to the family *Pasteurellaceae* with similarity of the genus *Mannheimia*. In experiments as a carbon source three different variants of crude glycerol were used: C1 with 90% of pure glycerol, C2 with 42% of pure glycerol, and 76% of pure glycerol. The results were compared with the results obtained from experiment in which medium contained pure glycerol (99%). After 9 hours of fermentation, the quantity of succinic acid was equal to 7.6 g/L (when glycerol C1 was used), 8.4 g/L (when glycerol C2 was used), and 7.4 g/L (when glycerol C3 was used). When pure glycerol was used the production was on a lower level – 6.2 g/L. Scholten et al. (2009) conducted the continuous fermentation of crude glycerol to succinic acid using *Basfia succiniproducens* DD1 isolated from the rumen of a cow. The highest concentration of 5.21 g/L of succinic acid at the 0.018/h dilution rate was achieved. Recently, several studies have been reported regarding the succinate production from glycerol by metabolically engineered strains of *Escherichia coli* (Blankschien et al.; 2010; X. Zhang et al., 2009, 2010).

4.4 Citric acid

Citric acid is used as a natural food preservative and also as appropriate flavoring feature of food and drinks. Other applications of this acid include a soft detergent, stabilizer and antioxidant (Soccol et al., 2006). In general, citric acid is formed *via* submerged microbial fermentation on molasses using *Aspergillus niger* (Ali et al., 2002; Papagianni, 2007). In recent years, several investigations concerned the use of *Yarrowia lipolytica* in crude glycerol conversion to citric acid (Lewinson et al.; 2007; Rymowicz et al., 2010; Rywińska et al., 2011; Rywińska & Rymowicz, 2011). Lewinson (2007) reported 21.6 g/L of citric acid production in batch fermentation of glycerol with 54% yield using *Yarrowia lipolytica* NRRL YB-423. Imandi et al. (2007) achieved 77.4 g/L of citric acid from crude glycerol using statistically optimized culture medium for *Yarrowia lipolytica* NCIM 3589. Rywińska et al. (2010) studied the efficiency of crude glycerol fermentation toward citric acid in fed-batch system using two acetate negative-mutants of *Yarrowia lipolytica*. In these experiments 155.2 and 157.5 g/L of citric acid was formed from 300g/L of glycerol using *Yarrowia lipolytica* Wratislavia 1.31 and Wratislavia AWD7 mutants, respectively. Rymowicz et al. (2010) converted crude glycerol to citric acid by *Yarrowia lipolytica* A-101-1.22 in different types of cultures. The citric acid production was 112 g/L, 124.2 g/L and 96-107 g/L in batch, repeated batch and cell recycled systems, respectively.

4.5 Dihydroxyacetone

Bacteria *Gluconobacter oxydans* are able to microbiological bioconversion of glycerol to dihydroxyacetone (Bauer et al., 2005; Claret et al., 2004; Z.C. Hu et al., 2010; Li et al., 2010; L.

Ma et al., 2010). Bories et al. (1991) stated that biosynthesis of dihydroxyacetone by *Gluconobacter oxydans* makes cells of this microorganisms grow slower. The concentration of dihydroxyacetone on the level of 61 g/L completely inhibits growth of the cells. Z.C. Hu et al. (2010) worked on optimization of cultivating media with an aim to increase dihydroxyacetone production by *Gluconobacter oxydans* ZJB09112. The cultivations were carried out in shake flask and bubble column bioreactors. After feed bath cultivation (five-time glycerol feeding) on the optimized medium 161.9±5.9 g/L of dihydroxyacetone at 88.7±3.2% glycerol conversion rate was obtained. Gätgens et al. (2007) reported that over expression of glycerol dehydrogenase in *Gluconobacter oxydans* DSM2343 enhanced dihydroxyacetone production. They achieved up to about 30 g/L of dihydroxyacetone from 50 g/L of glycerol which was 20-40% more in comparison with control strains. Li et al. (2010) also investigated the over expression of glycerol dehydrogenase (GDH) in an alcohol dehydrogenase (ADH)-deficient mutant of *Gluconobacter oxydans* M5AM/GDH in order to improve dihydroxyacetone productivity. It was found that absence of ADH together with over expression of GDH gene substantially improved dihydroxyacetone formation. In four repeated biotransformations biosynthesis of dihydroxyacetone reached 385 g/L.

4.6 Hydrogen and ethanol co-production

Since hydrogen is expected in the future to be a clean energy source and ethanol probably be used as gasoline's additive, there are several important issues regarding co-production of these metabolites. Glycerol fermentation to hydrogen and ethanol using *Enterobacter aerogenes* HU-101 was studied by Ito et al. (2005). In continuous culture with packed-bed reactor with self-immobilized cells and using culture medium with pure glycerol, the maximum hydrogen production rate reached 80 mmol/L/h with ethanol yield of 0.8 mol/mol of glycerol. It was much higher a quantity than obtained from crude glycerol (30 mmol/L/h). Nevertheless, the application of porous ceramics as support material to fix cells in the reactor improved the results in case of crude glycerol fermentation process. In this case, hydrogen production rate was 63 mmol/L/h with ethanol yield of 0.85 mol/mol. In turn, Sakai & Yagishita (2007) reported crude glycerol bioconversion to hydrogen and ethanol by bioelectrochemical cells of wild type of *Enterobacter aerogenes* NBCR 12010 using thionine as an exogenous electron transfer mediator. On the basis of conducted experiments, one can say that the yield of hydrogen as well as ethanol reached more than 80%. Yazdani & Gonzalez (2008) studied co-production of ethanol and hydrogen from crude glycerol using engineered strain of *Escherichia coli* SY03. They inactivated fumarate reductase and phosphate acetyltransferase in order to minimize succinate and acetate co-production and overexpressed glycerol dehydrogenase and dihydroxyacetone kinase which are responsible for glycerol utilization to dihydroxyacetone phosphate (glycolytic pathway intermediate). On the basis of conducted experiments they reported that the ethanol-hydrogen co-production exceeded 95% yield of theoretical and specific rates.

4.7 Pigments

There are several studies regarding glycerol utilization to pigments, such as prodigiosin or carotenoids (da Silva et al., 2009). The red pigment prodigiosin is well known as an antifungal, immunosuppressive and anti-proliferative agent (Casullo de Araújo et al., 2010; Khanafari et al., 2006). Tao et al. (2005) described prodigiosin biosynthesis from glycerol by *Serratia marcescens* mutant obtained *via* ultra violet light mutation and rational screening methods.

They achieved best results in a two-step feeding strategy. In the first step, *Serratia marcescens* mutant was cultivated on culture medium with glucose in order to obtain high density of culture. In the second step, glycerol was used to induce prodigiosin production. This strategy allowed to obtain 583 mg/L of prodigiosin, which was 7.8 times higher a quantity than originally obtained from the parental strain. Among carotenoids, astaxanthin is widely used in aquaculture, pharmaceuticals, supplements and natural coloring (da Fonseca et al., 2011). Having antioxidant activity, astaxanthin helps to prevent, for instance, photo-oxidation from ultra violet light, inflammations, infectious ulcers from *Helicobacter pylori* or diseases related with aging (da Fonseca et al., 2011; O'Connor & O'Brien, 1998). In 1998, Kusdiyantini et al. reported utilization of glycerol to astaxanthin using *Phaffia rhodozyma*. After 168 h of batch fermentation astaxanthin concentration reached 33.7 mg/L. Razavi & Marc (2006) investigated optimal culture conditions for the total carotenoid production from technical glycerol using *Sporobolomyces ruberrimus* H110. In this study, the best results were obtained at 19°C and pH=6.0. In these conditions, the maximum total carotenoid concentration (torularhodin + β -carotene) of 3.84 mg/g of yeast was achieved. Recently, Yimyoo et al. (2011) demonstrated the potential of glycerol bioconversion by *Rhodospiridium paludigenum* as a new carotenoid producer. The maximum total carotenoid concentration (torularhodin + torulene + β -carotene) reached 3.43 mg/L (0.45 mg/ g of yeast) after 132 h of process duration, at 32°C and pH=6 in a medium containing 40 g/L of glycerol.

4.8 Polyhydroxyalcanoates

Polyhydroxyalcanoates (PHAs) belongs to microbial polyesters which are synthesized intracellularly by numerous bacteria under nutrient-limiting conditions, such as carbon and energy storage material (Solaiman et al., 2006; Tian et al., 2009). Since PHAs possesses biodegradable and biocompatible thermoplastic properties, increased attention is paid as to how replace petroleum-derived polymers by PHAs (Albuquerque et al., 2007; Zinn & Hany, 2005). Several bacteria have been explored in order to facilitate PHAs production from glycerol. In 2009, Ibrahim & Steinbüchel investigated several fed-batch cultivation strategies to improve production of polyhydroxybutyrate (PHB) by *Zobellella denitrificans* MV1. The PHB concentration reached up to 54.3±7.9 g/L at cell dry weight of 81.2±2.5 g/L after 50 h of fermentation in presence of 2% NaCl and with optimized feeding of glycerol and ammonia. In this study, PHB content of 66.9±7.6% of dry cell weight was observed. Cavalheiro et al. (2009) reported PHB production from crude glycerol by using *Cupriavidus necator* DSM 545. In this study, the maximum cell dry weight of 82.5 g/L with PHB accumulation of 38% was obtained. In turn, Kawata & Aiwa (2010) obtained 39% PHB yield from 3% crude glycerol culture after 47 h of *Halomonas* sp. KM-1 cultivation. Promising results were obtained by Shrivastav et al. (2010) who used *Halomonas hydrothermalis* in the production of PHB from crude glycerol. In this study, isolated SM-P-3M was found to be the most effective with PHA content of 75% of dry cell weight.

4.9 Biosurfactants

Surfactants have numerous household and industrial applications. Most of them, however, are based on petroleum and are chemically produced (Makkar et al., 2011). Since biosurfactants are less-toxic, biodegradable and have some unique surface-active properties, they might be an excellent substitutes for surfactants derived from petroleum (Banat et al., 2010). A lot of research in recent years was made in a field of biosurfactants production from

glycerol (da Silva et al., 2009). Accordingly, in 2002, Rahman et al. obtained 1.77 g/L of rhamnolipid surfactant from glycerol, using *Pseudomonas aeruginosa* DS10-129. In turn, G.L. Zhang et al (2005) achieved rhamnolipids' concentration of 15.4 g/L, using *Pseudomonas aeruginosa* when cultured on basal mineral medium containing glycerol as a sole carbon source. Da Rosa et al. (2010) investigated the influence of culture medium components on rhamnolipid production by *Pseudomonas aeruginosa* LBM10, using experimental designs and response surface methodology. On the basis of conducted analyses, the maximum rhamnolipid concentration of 4.15 g/L at glycerol concentration of 13.2 g/L, C/N ratio of 12.8 and C/P ratio of 40 was obtained. Morita et al. (2007) investigated microbial conversion of crude glycerol to mannosylerythritol lipids (MELs) as glycolipid biosurfactants, using basidiomycete yeast, *Pseudozyma antarctica*. In this case the concentration of MEL reached 16.3 g/L by intermittent feeding of glycerol. Recently, Liu et al. (2011) optimized culture medium composition and environmental factors in order to improve glycolipids production from crude glycerol in *Ustilago maydis*. As a result of these actions, 32.1 g/L of total glycolipids after 8.2-day fed-batch bioprocess was obtained.

5. Conclusions

Energy from the renewable sources is one of the solutions connected with depletion of the world's nonrenewable energy sources such as carbon, petroleum gas or crude oil. This kind of energy is also beneficial for the natural environment (it can decrease an emission of CO₂). However, the cost of energy production from renewable sources is very high and it exceeds prices of traditional fuels (Fernando et al., 2007; Karinen & Krause, 2006; Wilke & Vorlop, 2004). Thus, alternative solutions are still sought in many places. Nowadays, biodiesel costs more than fuels produced from crude oil. For instance, prices of raw materials (which differ depending on the kind of raw material used), technology of production, taxes, and tax allowances - all have a major influence on the final cost of biodiesel (Hass et al., 2006). Obviously, the production of biofuels could become profitable but only on condition that producers would sell both the biofuels and by-products obtained in the process of manufacture, thus allowing for the development of processes which today are regarded as inexpensive. We may conclude that crude glycerol utilization into higher value products is critical when we want to make biodiesel production more sustainable and profitable.

6. References

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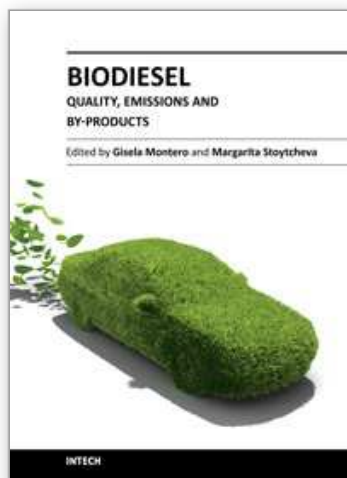
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Biodiesel- Quality, Emissions and By-Products

Edited by Dr. Gisela Montero

ISBN 978-953-307-784-0

Hard cover, 380 pages

Publisher InTech

Published online 16, November, 2011

Published in print edition November, 2011

This book entitled "Biodiesel: Quality, Emissions and By-products" covers topics related to biodiesel quality, performance of combustion engines that use biodiesel and the emissions they generate. New routes to determinate biodiesel properties are proposed and the process how the raw material source, impurities and production practices can affect the quality of the biodiesel is analyzed. In relation to the utilization of biofuel, the performance of combustion engines fuelled by biodiesel and biodiesels blends are evaluated. The applications of glycerol, a byproduct of the biodiesel production process as a feedstock for biotechnological processes, and a key compound of the biorefinery of the future is also emphasized.

How to reference

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Alicja Kośmider, Katarzyna Leja and Katarzyna Czaczyk (2011). Improved Utilization of Crude Glycerol By-Product from Biodiesel Production, Biodiesel- Quality, Emissions and By-Products, Dr. Gisela Montero (Ed.), ISBN: 978-953-307-784-0, InTech, Available from: <http://www.intechopen.com/books/biodiesel-quality-emissions-and-by-products/improved-utilization-of-crude-glycerol-by-product-from-biodiesel-production>

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