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Potential lactic acid production from crude glycerol as the precursor of polylactic acid analog : literature review

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Abstract. Biodiesel has gained a significant amount of attention over the past decade as an environmentally friendly fuel. However, the biodiesel production process generates glycerol-containing waste streams which have become a disposal issue for biodiesel plants and generated an abundant of crude glycerol, a low-value byproduct of biodiesel manufacturing. Conversion crude glycerol to valuable chemical such as lactic acid, a precursor of polylactic acid (PLA), has a great potential to substitute traditional feedstocks of PLA, i.e., carbohydrate or sugar sources. Some of the process perspectives and the potential of glycerol to produce lactic acid by chemical transformation or microbial conversion are discussed in this paper, as well as the possibility of extending lactic acid to polylactic acid (PLA).

1. Introduction

Indonesia produces biodiesel 2 million kiloliters per year in 2016 and will raise to be 5 million kiloliters per year. Furthermore, under a mandatory of biodiesel Indonesia is expected to increase from 20 % (B20) in 2016 to 30 % (B30) by 2020 [1]. The increase of biodiesel production has thus resulted an inevitable abundance of glycerol as a by=products. This high amount of crude glycerol must be used for efficiency of biodiesel industry. Almost all industry use only refined glycerol as raw material, consequently unrefined glycerol has become potential environmental pollutant [2]. Purification of glycerol is an expensive process and the low process it has fetched recently have rendered it economically unfeasible. In order to gain sustainability of biodiesel industry, it is important to find feasible solution and efficient approaches to convert waste glycerol into valuable products. An alternative solution to handle the crude glycerol waste is by converting it into more valuable product, such as lactic acid (2-hydroxypropanoic acid) [3] [4] [5]. Lactic acid can be polymerized to produce Polylactic acid (PLA) [6].

PLA is the most intensively developed bioplastic coming from renewable resources and is used as a raw material for biodegradable plastic. Currently, PLA is established from starch. The problems are the limited resources and its effect to food sovereignty. PLA should be made from non-food raw materials and the alternative is glycerol from by-product of biodiesel production. PLA has already been industrially

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produced in an amount of 180 kton in 2012 and its manufacture is projected to reach 1 Mton per year by 2020. This means, the demand for lactic acid is increasing along with the increasing demand for PLA.

Synthesis PLA from glycerol, known as PLA analog can be divided into three main stages: ***firstly***, the synthesis of glycerol to lactic acid through a chemical reaction [7][8][9] or through microbial fermentation [10] [11]; ***secondly***, transformation of monomer lactic acid to lactide; ***thirdly***, the lactide is polymerized into PLA [6]. Generally, all stages of the process involves a catalyst during the process to increase the yield and accelerate the reaction rate.

The challenge in producing analog PLA is that it must have the same physical and chemical properties, or at least come near to the physical and chemical properties of conventional PLA. Adopted from [12], the successful of lactic acid into PLA transformation is influenced by: 1) the purity of lactic acid, 2) the acid endurance of microorganism used, 3) the quality of PLA produced must fulfill industrial PLA criteria. This paper reveals the challenges in developing poly lactic acid analog from glycerol as biodiesel by product.

2. Methodology

This research consists of exploratory research aimed at identifying the challenge of poly lactic acid synthesis from glycerol as biodiesel by product. This was followed by a review of journals, magazines, textbooks, etc. available on internet to identify the current conditions. A bibliographic review of national and international journals was carried out to identify available method in producing poly lactic acid and lactic acid from glycerol.

3. Discussion

Lactic acid is conventionally produced through carbohydrate fermentation and Lactonitrile chemical synthesis[13]. These two methods have been used in commercial production. The weakness of these method is the availability of feedstocks. Even though lactic acid is produced from renewable source, carbohydrate, the availability of carbohydrate as the feedstock competes with its use as food source. Whereas lactonictrile chemical synthesis uses unrenewable petrochemical ingredient and produces lactic acid in racemic mixture. The downside of this racemic lactic acid is its low purity value which only enables it to be used as co-monomer of other polymers [9].

Naturally, lactic acid is composed of two optical isomer: D(–)-lactic acid and L(+)-lactic acid. D(–)-lactic acid is hazardous to human, which makes L(+)-lactic acid is more preferable in food industry and pharmacy.

Value-added transformation processes of glycerol to lactic acid can be accomplished by chemically [7], [8] [3] [14], microbiologically [10] [11]. The method is quite widely reported to synthesize lactic acid from glycerol is in an alkaline hydrothermal and hydrothermal oxidation of glycerol. The second drawback of this method is to use a strong acid such as H_2SO_4 to convert the sodium lactate into lactic acid which may cause corrosion on the equipment used. Acidity is one factor affecting the success of the conversion of glycerol into lactic acid. In addition, this method produces lactic acid which is not pure, but in the form of racemic mixture comprising: L (+) - lactic acid, D (-) - lactic acid, and meso-lactic acid. Dimerization of racemic lactic acid will produce a racemic lactide comprising a mixture of: L-Lactide, D-lactide, and meso-lactide. Results of racemic lactide polymerization will produce PLA amourf so limited in its use. On the other side, the advantages of using microbial fermentation method compared to chemical method in producing lactic acid are its ability to produce pure lactic acid, uses low energy input (pressure / temperature), and no needs intensive pretreatment requirements [15].

3.1. The Purity of Lactic Acid

The purity of lactic acid will affect the quality of PLA products, especially on the physical properties. To get a high degree cristallinity and high melting point, the PLA must be made from the pure isomer L (+) - lactic acid or D (-) - lactic acid instead of the racemic of both isomers [16]. PLA with high crystallinity value and high melting point can be used to produce fiber, oriented films, and liquid crystals [17].

In the production of lactic acid from glycerol, the purity of isomer, i.e., L-lactic acid or D-lactic acid, depends on the strain of microbes used. The appropriate microorganism can produce desirable isomer. [18] Reported that lactic acid could be produced with glycerol fermentation by using some *E. coli* strains as an alternative to NAD+ regeneration in the absence of external electron acceptors. Moreover, high chiral purity of D-lactate can be produced by fermenting glycerol using a recombinant strain that overexpresses enzymes that respond to glycolytic intermediates and inactivates fumarate reductase, phosphate acetyltransferase, alcohol/acetaldehyde dehydrogenase, and D-lactate dehydrogenase [10], and reported that 32 g/L of D-lactate (99.9% chiral purity) could be produced from 40 g/L of glycerol by using E. coli D-specific LDH. Furthermore, [19] reported that L-specific LDH from *Streptococcus bovis* could replace the native *E. coli* D-specific LDH from the previous study, e.g., 50 g/L of L-lactic acid (99.9% chiral purity) was produced from 56 g/L of waste glycerol.

Other researchers found that using *Rhizopus* strain as alternative lactic acid producer microbe has many advantages because it produces only L(+)-lactic acid isomer, does not require special nutrition, and also more easier in separating biomass from fermentation media. These could reduce the cost of downstream process [20]. The use of *R. oryzae* NRRL 395 on 75 g/l concentration of crude glycerol produce 3.72 g/g L(+)-lactic acid and the concentration of lactic acid is assumed to be 48 g/l. Interestingly, in this research the increase of lactate productivity is done by adding Lucerne green juice into fermentation media without addition of inorganic nutrient on crude glycerol [21].

3.2. Acid Endurance of Microorganism

Generally, the desirable characteristics of microbe strain in glycerol fermentation is the ability to rapidly converse substrate and to produce high yield. For lactic acid production, specific microbes that can stand at low pH and high temperature are needed. Conventional lactic acid production is conducted via glucose fermentation using homofermentative LAB (Lactic Acid Bacteria) which requires weak acidic to neutral pH. Low pH can give inhibitory effect on cell metabolism which will result in lactic acid production [22]. Generally, LAB cannot grow in under pH 4 even though lactic acid pK value is 3.78. To keep neutral pH to maintain cell growth, lime is frequently added into fermentor which will produce over 90% of lactic acid, however it will result in insoluble calcium sulfate (gypsum) [22]. The use of high concentration sulfuric acid causes corrosion problem. The amount of gypsum is usually higher than the amount of lactic acid produced. Roughly more than 1 ton of gypsum were produced. This will result in waste management which will impose high cost to other commercial product. The cost of purifying lactic acid is relatively high cost component from production cost total.

The advantage of using fungi is that it can grow in low pH medium while able to significantly reduce the use of neutralizing agent ($Ca(OH)_2$) during fermentation stage and can avoid gypsum formation ($CaSO_4$). But there is still a need to emphasize metabolic engineering research in yeast and fungi which can naturally produce pure lactic acid with high productivity.

3.3. Meeting PLA Industrial Criteria

The purity of lactic acid is influenced by fermentation medium composition which depends on the nutrition requirement of microbe strain used. Traditionally, actic acid can be produced by using bacteria and fungi. Lactic Acid Bacteria (LAB) has been widely used for having high growth rate and good product yield. However, LAB has complex nutrition requirement since it has limited ability in synthesizing vitamin B and amino acid. Thus, there is a need for adequate nutrition supplement on the media used such as yeast extract or additional supplementary complex, for example dried blood needed to catalyze active cell mass, in order to produce lactic acid [23]. This relatively high cost downstream process increases the whole cost of lactic acid production if lactic acid bacteria were to be used.

The use of relatively cheap main ingredients in lactic acid industry will reduce production cost and maintaining economic viability of microbial process. Using starch and glucose as main ingredients increases of lactic acid cost, because lactic acid fermentation process takes up 40-70% of production cost total [24].

Several parameters must be considered in choosing main ingredients in lactic acid industry. There are low main ingredient price, minimum contaminant, high fermentation rate, high lactic acid production, few or no by-product formation, and always readily available. Ever since the increase of glucose price for its usage in food industry, production of lactic acid begins to favour other alternative renewable resources and have low price substrate, for example the use of glycerol and lignocellulosic [25] [26] [27].

4. Conclusion

With the increase of biodiesel industry from palm oil, there has been important development by using different bioengineering and chemical techniques to convert glycerol as by-product of biodiesel into lactic acid. There were several excellent reviews published in the past several years with a focus on microbial species or chemical catalytic processes. However, there is still a challenge to find the best method in producing lactic acid with the high purity and high yield (productivity). Nowadays, the price of lactic acid is still high and it has small market capacities. This is likely due to its cost production. The ability to make this compound at a lower cost could help to bring it into a larger market.

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