A Study of Potential Poly-Lactic Acid from Glycerol as By-Product of Biodiesel Production in Indonesia

Ully IHR, Puspitaningrum EPA, and Rosiyana N

Abstract—Plastic becomes an important issue in the world today. The increasing amount of plastic wastes in Indonesia has exceeded 175,000 ton/day or equal to 64 million ton/year. Many municipalities are unable to recycle many types of plastics, whether due to outdated equipment or because the technology is still emerging. Burning the plastic wastes is still in the top of the list (69.88%) to reduce the plastics, followed by throwing haphazardly (21.64%), burying (18.07%), and many are still throwing to the oceans or rivers (11.51%). Even though, in fact, an imperfect combustion of plastic (below 8000°C) can form dioxin, a compound that can trigger cancer, hepatitis, liver inflammation, and nervous system disorder. Plastics use also releases at least 100 million tons, and maybe as much as 500 million tons, of carbon dioxide into the atmosphere each year. That’s the equivalent of the annual emissions from 10 to 45 percent of U.S. drivers. Based on this urgency, biodegradable plastic is one of the solutions needed now. Poly Lactic Acid (PLA) 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 (by product of biodiesel production). In 2012, the production capacity of biodiesel has attained 4 million kilo liter/year, meaning that approximately 400,000-600,000 ton/year of crude glycerol is produced. This study reveals the potential of glycerol as lactic acid raw material and the sustainability of biofuel industries especially in Indonesia due to the impact for economy and environment.

Index Terms— By-Product, Glycerol, Plastics, Poly Lactic Acids.

I. INTRODUCTION

Nowadays, plastics waste become problem in many countries. Many municipalities are unable to recycle many types of plastics, whether due to outdated equipment or because the technology is still emerging. Burning the plastic wastes is still in the top of the list (69.88%) to reduce the plastics, followed by throwing haphazardly (21.64%), burying (18.07%), and many are still throwing to the oceans or rivers (11.51%). Even though, in fact, an imperfect combustion of plastic (below 8000°C) can form dioxin, a compound that can trigger cancer, hepatitis, liver inflammation, and nervous system disorder. Plastics use also releases at least 100 million tons, and maybe as much as 500 million tons, of carbon dioxide into the atmosphere each year. That’s the equivalent of the annual emissions from 10 to 45 percent of U.S. drivers. Based on this urgency, biodegradable plastic is one of the solutions needed now. Poly Lactic Acid (PLA) 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 (by product of biodiesel production). In 2012, the production capacity of biodiesel has attained 4 million kilo liter/year, meaning that approximately 400,000-600,000 ton/year of crude glycerol is produced. This study reveals the potential of glycerol as lactic acid raw material and the sustainability of biofuel industries especially in Indonesia due to the impact for economy and environment.

III. CURRENT CONDITION

Amount of Plastic waste in Indonesia

Indonesia is listed as the world number two country with total of plastic debris after China[1]. Based on statistical data in 2013 on Waste Statistics Book Indonesia in 2008, there were approximately 38.5 million tons of waste per year, and 14 million of the total garbage are plastics [2]. Ministry of Environment and Forestry declare 100 members of Indonesian Retailers Association (APRINDO) contribute in plastic waste. In just one year, it has reached 10.95 million pieces of plastic garbage bags. The ministry is targeting reduction of plastic waste more than 1.9 million tons by 2019.

High demand of plastic products in Indonesia can be opportunity for producers of plastic. Plastics demand is primarily driven by growth in food and beverage industry and FMCG (Fast Moving Consumer Goods), the growth achieves 60%. Industry Minister, MS Hidayat said the current national plastic industry structure is quite complete from upstream to downstream. However, he admitted there are still challenges facing the industry in the development of production capacity due to mostly raw materials such as polypropylene and
polyethylene are still imported, the lack of capacity of oil refinery that produces naphtha and condensate feedstock for the petrochemical industry upstream raw materials.

Currently, there are about 892 plastic packaging industries which produce rigid packaging, flexible packaging thermoforming, and extrusion. Those industries spread across several areas Indonesia. Total installed capacity is about 2.35 million tons per year with average utilization achieve 70%. This mean average production of plastics is 1.65 million tons.

Meanwhile, Vice Chairman of the Indonesian Olefin, Aromatic and Plastic Association (Inaplas) Budi S Sadiman revealed that plastic consumption in Indonesia is projected to reach 1.9 million tons by the first half of 2013. It showed increasing amount approximately 22.58% over the same period last year of 1.55 million tons. Plastic industry sales in the domestic market reached Rp 47.5 trillion in the first half of 2013, assuming consumption reached 1.9 million tons (1.9 billion kilograms / kg) and the price is Rp 25 thousand per kg. Turnover of the first quarter of 2013 amounting to Rp 22.5 trillion and in this quarter Rp 25 trillion.

Nowadays, there are thirty retail companies that use biodegradable plastic bags with consumption reaching 500,000 units every month. While consumption continues to increase every year about 1% -2% of the production of plastic bags standard. Meanwhile, this usa4e is still behind the real potency, considering that raw material for biodegradable plastics are excess in Indonesia. But, degradable plastic products in circulation today are made from food agricultural raw materials. On the other hand, Indonesia is still facing problems fulfillment of foodstuffs.

Unrefined Glycerol Potential

Based on the data from Ministry of Energy and Mineral Resources, biodiesel still need subsidy from government in order to increase its competitiveness from solar. In 2012, average amount of subsidy is Rp 1,234/ liter and in 2013 amount of subsidy is Rp 380/liter. The decrease amount of subsidy caused by the increase of selling price in fuel[3].

From the production data, renewable energy such as biodiesel, bioethanol and bio oil showed significantly increase trends. In 2005 biodiesel produced as much as 120 thousand kiloliters and in 2010 biodiesel produced as much as 2,674.57 thousand kiloliters[4]. In the other hand, fossil fuel showed decrease trends from 2008 until 2011 the production decreased as much as 12,574 thousand barrels[5]. In 2013, Indonesia became exporter of biodiesel to more than 10 countries. In 2016 Indonesia targeted to become first biodiesel production in the world, currently Indonesia produce 2 million kiloliters per year and will be developed into 5 million kiloliters per year[6].

Increase of biodiesel production will increase glycerol production too, glycerol obtained about 10 percent from total biodiesel production [7].

Crude glycerol obtained from the process are unrefined glycerol. Characterization of crude glycerol, refined glycerol from glycerol residue, and commercial glycerol can be seen in Table 1. From the data, in the end of 2016 crude glycerol from byproduct of biodiesel project reached approximately 500,000 kiloliters per year. 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 [8]. Purification of glycerol is an expensive process and the low process it has fetched recently have rendered it economically unfeasible[9]. In order to gain sustainability of biodiesel industry, crude glycerol must find feasible solution.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Crude</th>
<th>Refined</th>
<th>Commercial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol (%)</td>
<td>60-80</td>
<td>9.1-99.8</td>
<td>99.2-99.98</td>
</tr>
<tr>
<td>Water (%)</td>
<td>1.5-6.5</td>
<td>0.11-0.8</td>
<td>0.14-0.29</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>1.5-2.5</td>
<td>0.054 &lt;0.02</td>
<td></td>
</tr>
<tr>
<td>Acidity</td>
<td>0.7-1.3</td>
<td>0.1-0.16 -</td>
<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>-</td>
<td>1 ppm 0.6-9.5 ppm</td>
<td></td>
</tr>
</tbody>
</table>

Poly lactic acid (PLA)

According to Indonesian Ministry[6], lactic acid demand in Indonesia fulfilled by import. There was increase trend of lactic acid demand about 16.7% from 2007 until 2016. PLA as biopolymer can be transformed into food service ware, fresh food packaging, electronics, flexible films, apparel and home textiles.

There are several industries produce poly lactic acid for many applications such as Ingeo biopolymer from NatureWorks LLC and Corbion Purac from Corbion. Those biopolymer is made from dextrose (sugar) that is derived from field corn [11][12]. From the data from World Corn Production (2004), Ingeo (PLA) biopolymer used only 0.04% annual global corn crop today and didn’t give impact on food prices and supply. Increase trend of PLA demand make industry must innovate and find another feedstock due to limited supply.

Available Technology

Recent studies show some alternatives way. In this study alternative process bio-/chemo catalytic route based on the enzymatic oxidation of glycerol to 1,3-dihydroxyacetone (DHA) followed by isomerization in water or in methanol via an alkyl lactate (AL) intermediate was evaluated. At the catalyst level, the stability upon reaction, the ability to process concentrated feeds and reusability become crucial parameters. The highest performance of catalyst which has been studied is Sn-MFI[13]. Sn-containing MFI zeolites (Sn-MFI) which processed by post-synthetic alkaline-assisted stagnation of silicalite-1 (Dapsens et al. 2014 and Mal et al. 1997 in [13]).

The process comprises the following main steps: (i) fermentation of crude glycerol (75.8 % w.t.), (ii) concentration of the reaction mixture and crystallization of DHA out of butanol and (iii) recovery of butane from the water-containing mother liquor through heterogeneous azeotrope distillation. Impurities removed by additional treatment of crude glycerol. DHA obtained from the process followed by chemo catalytic LA production using catalyst Sn-MFI in methanol. DHA is fully transformed into Methyl Lactate (ML), as intermediate product, followed by hydrolyzed via a low-pressure reactive distillation producing pure LA and a mixture of methanol and water, which is further separated by conventional distillation to recover the organic fraction [13]. Table 2 shows Life Cycle

http://dx.doi.org/10.15242/IAE.IAE0416422
unrefined glycerol and biodiesel has competitiveness advantage promising. Lactic acid production can give added value to assessment. Increase trends of biodiesel become opportunity to develop lactic acid. Although there are several alternatives to are advantageous. Either economical or environmental producer. Against fossil fuel. Indonesia is potential to become first USD per kg 15 times higher than conventional process (0.61 profit of LA production methanol based isomerization resulting 1.20 USD per kg glycerol (110 USD per ton). The production of LA through the methanol for LA from glucose while chemo catalytic estimated at 96 MJ kgLA-1. Lower CED showed that the route need lower waste, material and energy. Based on operating costs as an economic metrics, conventional LA production was found have the highest operating cost with 1.88 USD per kg DHA isomerization in methanol is.

### Inventory (LCI) for the chemo catalytic production of LA from DHA in methanol.

<table>
<thead>
<tr>
<th>LCI data</th>
<th>Sn-MFI 7a</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHA</td>
<td>1.09</td>
<td>kg kgLA-1</td>
</tr>
<tr>
<td>Process</td>
<td>0.41</td>
<td>kg kgLA-1</td>
</tr>
<tr>
<td>Water</td>
<td>0.03</td>
<td>kg kgLA-1</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.10</td>
<td>kg kgLA-1</td>
</tr>
<tr>
<td>Catalyst</td>
<td>12.7</td>
<td>MJ kgLA-1</td>
</tr>
<tr>
<td>Steam (6 bar)</td>
<td>649</td>
<td>kg kgLA-1</td>
</tr>
<tr>
<td>Cooling water</td>
<td>0.59</td>
<td>kg kgLA-1</td>
</tr>
</tbody>
</table>

*7 corresponds to the number of cycles in which the catalyst was reused without loss performance*

This method has more advantages compared to the conventional way. Based on non-renewable cumulative energy demands (CED) as one of LCA metrics, the conventional enzymatic process requires 109 MJ kg-1 to produce 1 kg of LA from glucose while chemo catalytic estimated at 96 MJ kgLA-1. Lower CED showed that the route need lower waste, material and energy. Based on operating costs as an economic metrics, conventional LA production was found have the highest operating cost with 1.88 USD per kg DHA. This originates from the higher price of glucose (400 USD per ton) compared to crude glycerol (110 USD per ton). The production of LA through the methanol based isomerization resulting 1.20 USD per kgLA. Considering an LA price of 1800 USD per ton, the marginal profit of LA production via DHA isomerization in methanol is 15 times higher than conventional process (0.61 versus 0.04 USD per kgLA) [13].

### IV. RESULT AND DISCUSSION

In Indonesia, development of poly lactic acid from glycerol are advantageous. Either economical or environmental assessment. Increase trends of biodiesel become opportunity to develop lactic acid. Although there are several alternatives to process unrefined glycerol, development of poly lactic acid still promising. Lactic acid production can give added value to unrefined glycerol and biodiesel has competitiveness advantage against fossil fuel. Indonesia is potential to become first producer.

1. **Potential Market**

   With the total citizens of 250 million people in the country, Indonesia has potencies to dominate the market share of plastic consumer. Plastic consumption is still high demand and there are at least 892 plastic packaging industry that can used PLA as their raw material.

2. **Raw Material Availability**

   In 2016 Indonesia targeted to become first biodiesel production in the world, currently Indonesia produce 2 million kiloliters per year and will be developed into 5 million kiloliters per year [6]. Increase of biodiesel production will increase glycerol production. There will excess glycerol. This excess can cause negative impact to the environment unless it process into products. Lactic acid production using glycerol as raw material are highly feasible and potential both for economic and environmental solution because of high demand of lactic acid in the market and biodegradable plastic as an end product.

3. **Environmental Issues**

   Comparison between eco-profile data PLA and PET (the commercial plastic) and PS data from US producers concluded PLA (Ingeo polymer) carbon footprint is 75% lower than traditional materials. PLA are compatible to process with existing recycling systems, can be clearly incinerated, and are completely stable in landfill. Even in the landfill, PLA results 75% less greenhouse gases than the oil-based PET or PS plastic [11]. Those are beneficial because material in anaerobic system in landfill may produce methane, a greenhouse gas (GHG) ten times greater global warming potential than CO2 [14].

   In the study about comparative assessment of PLA and PET found that PLA is more sustainable alternative to PET on a vehicle miles traveled basis. PLA use less energy to produce and less GHG emissions of the plastics assuming that each plastic does end up at the assigned end-of-life option. From the study, PLA emitting only 0.26 tons of carbon while PET plastic production process emitting 1200 tons of carbon. PLA producing less carbon because of less distance travelled, cleaner energy, and biodegradable properties [15].

5. **Related Research and Development**

   Biodegradable polymers has developed more than 10 years ago, but the research and development of biodegradable plastic packaging technology is still very limited. This happens because in addition to human resource capacity in the mastery of science and technology of materials, as well as research funding is limited. It is understood that in the field of basic science research takes a long time and funds. Actually, the development prospects of biopolymers for biodegradable plastic packaging in Indonesia is very potential. This premise is supported by the lack of natural resources, especially agricultural products that is abundant and can be obtained throughout the year. Various agricultural products with the potential to be developed into biopolymers are maize, corn, soybeans, potatoes, tapioca, cassava (vegetable) and chitin from shrimp shells (animal) and others. Wealth will be the source of basic materials such as mentioned above, on the contrary become a serious potential problem for countries that have developed and mastered the science and technology of packaging biodegradable, particularly in Germany. The country with the mastery of science and technology high technology field of packaging, worrying shortage of basic material resources (raw materials) and will be highly dependent on countries rich in natural resources.

   In 2005, the production process engineering poly lactic acid (PLA) from sago starch as raw material for biodegradable plastic, using a variety of bacterial types and operating conditions fermentation process to produce lactic acid, and with direct condensation polymerization process can produce PLA [16]. In 2006, conduct research on the synthesis of PLA from waste Manufacture Indigenous Starch for Plastic Manufacturing Environmental Friendly, which in this study, the variation used is the type of bacteria for...
fermentation, which later acquired the bacteria best to produce lactic acid, which is the process of polycondensation azeotropic can produce PLA[17]. Ery Susiany Retnoningtyas, et al. conduct research on biodegradable plastics manufacture of a banana skin. Still using a variety of operating conditions of fermentation to produce PLA [18].

Most studies conducted in Indonesia is the variation of raw materials, to obtain natural materials are most appropriate to make PLA, and also the process of fermentation and not by variation of the catalyst. The study ever done of synthesis of PLA with raw materials derived from sago starch, starch indigenous waste, banana peels, cassava starch, corn starch, peel shrimp, taro, and so forth.

If the terms of the industry, in Indonesia until now hard to find products made from bioplastics other than edible, even though the government since Pelita VI has prioritized program to produce biopolymer feedstock through plantation and agriculture. However, the program launched more than two decades still not be realized until now. For that we need the government's seriousness in the use of bioplastics program for the sake of protecting the environment in addition to conserve petroleum thinner stocks. Indonesian society should also be aware of the importance of the use of bioplastics as an alternative that can solve most environmental problems.

6. Most Possible Production Process

Process visible by industry is important. Industry need a process with high efficiency, stable product and process. Fermentative process has disadvantages such as expensive media and higher cummulative energi demand (CED). Catalyst used in production of lactic acid should has stability upon reaction, the ability to process concentrated feeds, and reusability become crucial parameters. All of this properties can be found in bio-chemo catalyst using SnMFI. The other factor is the character of glycerol. Based on the data, the glycerol still have high moisture content. Some catalyst such as CaO can’t work well with the absence of moisture content.

V. CONCLUSION

Growth of biodiesel production to fulfil the energy demand will increase glycerol production as by-product. Glycerol as by-product must be treated in order not to harm environment. In other side, the plastic waste become urgent issue and biodegradable plastic can be massive solution. Lactic acid from alternative route comprising the bio catalytic oxidation of glycerol to dihydroxyacetone followed by chemo catalytic isomerization have been evaluated. These route were more beneficial in economic, environmental, and social. Indonesia have great potential as the biggest producer of palm oil. Development of PLA from glycerol can empower people and better environment in Indonesia.

REFERENCES


