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Potential of Glycerol and Derivatives Based on Palm Oil as a Green Solvent

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Abstract

The need for more environmentally friendly and sustainable chemicals has led to a large amount of research into the processing of renewable raw materials. Palm oil is a potential source of energy. As an agraria country, Indonesia has a great potential to play a role in the palm oil industry. Moreover, in 2007 Indonesia was recorded as the largest producer and exporter of palm oil in the world. Until 2010, the total area of oil palm plantations in Indonesia reached 7.8 million hectares. In the past 15 years the production of palm oil increased almost five times, from 4.8 million tons of crude palm oil (CPO). The increase in the production capacity of the biodiesel industry causes high production of raw glycerol because glycerol is a by-product of biodiesel, so it must be accompanied by market expansion and increase in added value so that the price of glycerol is not low. Glycerol can be used as a green solvent. Glycerol is capable of dissolving many organic and inorganic compounds, including complex metal-transitions. The use of glycerol as a solvent also has several notable disadvantages, such as high viscosity (1200 cP at 20ºC) and low solubility of compounds and gases that are very hydrophobic, which limits the possibility of their use. Weakness of viscosity is usually overcome by heating above 60 ºC or by using co-solvent. Glycerol with a higher level of purity (80-99%) is needed as raw material for the cosmetics industry, pharmaceutical industry, paper industry, paint and varnish industry, textile industry, food industry, tobacco processing, oleochemicals, and lubricants. Glycerol is used as a precursor for the production of various chemical commodities such as 1,2-propanediol, 1,3-propanediol, ethylene glycol, propanol, hydrocarbons, acrolein, dihydroxyacetone, glyceric acid, syngas, hydrogen, glyceril ether, glyceril ester, glycerol carbonate, 1,3-dichloro propanol, polyglycerol and glycerol acetal and ketal through several methods such as fermentation, hydrogenolysis, pyrolysis, oxidation, etherification, dehydrasesterification, carboxylation, halogenation, polymerization and glycerol acetalization.

Keywords: Green Solvent, Glycerol, Palm Oil, Glycerol Derivatives, By-product Biodiesel.

1. Introduction

The problem of decreasing air quality, environment, health and safety is becoming a serious problem in the processing of fossil-based raw materials. The need for more environmentally friendly and sustainable chemicals has led to a large amount of research into the processing of renewable raw materials.

It can be seen that domestic bioenergy consumption continues to increase because it is supported by the mandatory biodiesel policy through ESDM Regulation No. 20 of 2014. The regulation stipulates the obligation to use minimum biodiesel as a fuel mixture gradually until 2025 by 30% so that it triggers an increase in biodiesel production activities which is certainly also in line with the increase in glycerol production. The amount of glycerol produced globally has reached 1.2 million tons and will continue to increase in the future due to increasing demand for biodiesel (Zhou et al, 2008). The realization of national biodiesel industry production has reached 3.2 million kL for 2014, which means that roughly 400 thousand kL of crude glycerol is also produced (Wahyuni et al, 2016) because the biodiesel industry produces large amounts of glycerol as a by-product 10-20% of the total product volume (Darnoko et al, 2000).

Increasing the production capacity of the biodiesel industry causes an increase in crude glycerol production, so it must be accompanied by market expansion and an increase in added value so that the price of glycerol does not fall (Wahyuni et al, 2016). Can be seen in Fig. 1, glycerol has more than 2000 applications, and its derivatives are valuable starting materials for the preparation of drugs, food, drinks, chemicals and synthetic materials (Gu et al, 2010).

However, the price of glycerol is quite low, causing an unbalanced supply. At present, a proportion of these renewable chemicals are wasted. This phenomenon has produced negative feedback on the economic viability of the biodiesel industry in the future and has a negative impact on the environment due to improper disposal (Pagliaro et al, 2008). Glycerol shows high boiling point, polarity and non-flammability and is a suitable substitute for organic solvents, such as water, dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Green solvent is a bio-based product that is highly sought after (Gu et al, 2013). Because to reduce the use of hazardous substances (especially volatile solvents (VOC)), it is flammable, toxic and produces waste in chemical processes. Thus, glycerol is considered a green solvent and as an important subject regarding research in green chemistry.

2. **Palm oil**

Palm oil is a potential source of energy. As a country with fertile soil, Indonesia has enormous potential to play a role in the palm oil industry. Moreover, in 2007 Indonesia was recorded as the largest producer and exporter of palm oil in the world. Until 2010, the total area of oil palm plantations in Indonesia reached 7.8 million hectares. In the past 15 years the production of palm oil increased almost five times, from 4.8 million tons of crude palm oil (CPO) in 1996 to 19.8 million tons in 2010 (Julianti et al, 2014).

Table 1: Components and Compositions Available in Palm Oil

Components	Compositions (%)
Trigliserida	95,62
Asam lemak bebas	4,00
Air	0,20
Phosphatida	0,07
Karoten	0,03
Aldehid	0,07

(Gunstone, 1997)

Tabel 2. Composition and Types of Fatty Acids in Palm Oil

Types of Fatty Acids ini Palm Oil	Compositions (%)
Laurat (C12:0)	<1,2
Miristat (C14:0)	0,5-5,9
Palmitat (C16:0)	32-59
Palmitoleat (C16:0)	<0,6
Stearat (C18:0)	1,5-8
Oleat (C18:1) Linoleat (C18:2) Linolenat (C18:3)	27-52 5,0-14 <1,5

(Salunkhe et al, 1992)

3. **Transesterification reaction**

The predominant triglyceride content in palm oil can be converted to glycerol through transesterification. The triglyceride content reacts with alcohol (accelerated by the catalyst) and produces biodiesel, and will produce a by-product in the form of glycerol (Haryanto et al, 2015).

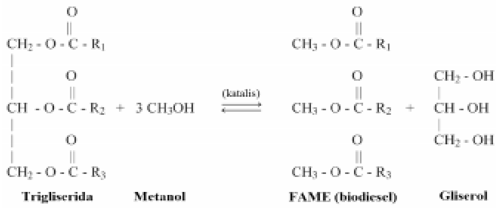

Fig. 1: Transesterification reaction

(Haryanto et al, 2015)

4. Glycerol

Glycerol (also known as glycerin) is polyol (1,2,3-propanetriol), which is naturally present in the structure of triglycerides, which are fatty acid esters from alcohol (Garcia et al, 2013). Glycerol, as a polyol, is capable of dissolving many organic and inorganic compounds, including complex metal-transitions. The incompatible nature of some common organic solvents, such as hydrocarbons, ethers and esters, allows easy separation of reaction products, and in the best case, the possibility of reusing the glycerol phase in subsequent reactions. This is very useful in the case of reactions catalyzed by transition metal complexes. The use of glycerol as a solvent also has several notable disadvantages, such as high viscosity (1200 cP at 20ºC) and low solubility of compounds and gases that are very hydrophobic, which limits the possibility of their use. Weakness of viscosity is usually overcome by heating above 60 ºC or by using co-solvent.

There are classifications of solvents derived from glycerol such as esters (such as acetone), carbonate (glycerol carbonate), acetal (formal glycerol) and ketal (solketal).

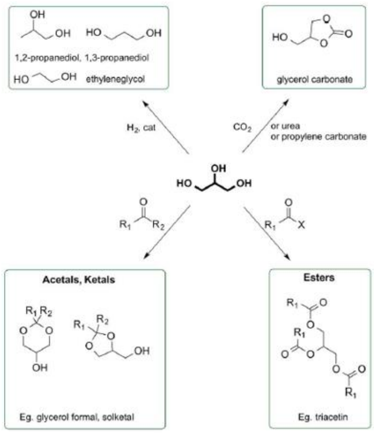

Fig. 2: Types of Green Solvent produced from Glycerol

(Moity et al, 2015)

5. Purification glycerol

Crude glycerol byproduct of the biodiesel industry generally has a low purity level with 40-50% glycerol content because it still contains a lot of impurities in the form of methanol residues, catalyst residues, and water. In order to be used in various industries and increase the selling value, the glycerol needs to be purified first. Glycerol with a higher level of purity (80-99%) is needed as raw material for the cosmetics industry, pharmaceutical industry, paper industry, paint and varnish industry, textile industry, food industry, tobacco processing, oleochemicals, and lubricants. One way is to use a vacuum distillation method in the hope that the purity of glycerol reaches 90% (Mulia, 2015). The choice of vacuum distillation as an advanced purification method is based on the type of impurities that are still present in 80% glycerol in the form of methanol and water that can be removed by evaporation but does not require temperatures too high as in simple distillation so as to minimize the energy used.

6. Glycerol derivative products methods

Glycerol is used as a precursor for the production of various chemical commodities such as 1,2-propanediol, 1,3-propanediol, ethylene glycol, propanol, hydrocarbons, acrolein, dihydroxyacetone, glyceric acid, syngas, hydrogen, glyceril ether, glyceril ester, glycerol carbonate, 1,3-dichloro propanol, polyglycerol and glycerol acetal and ketal through several methods such as fermentation, hydrogenolysis, pyrolysis, oxidation, etherification, dehydrasesterification, carboxylation, halogenation, polymerization and glycerol acetalization. Furthermore, glycerol is of great concern as a 'green solvent' in synthetic organic chemistry because of its good physical and chemical properties. Compatibility with most organic / inorganic compounds, high boiling point, negligible vapor pressure, easy dissolution and harmless properties, simple handling and storage provides an innovative way to utilize glycerol used as a green solvent.

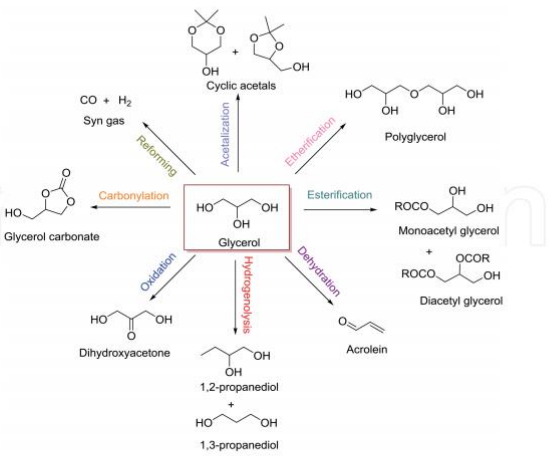

Fig. 3: Various Types of Green Solvent and Methods produced from Glycerol

6.1 Glycerol Hydrogenolysis

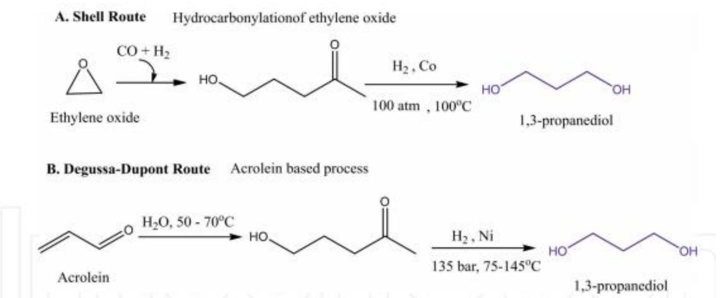

Fig. 3: Conventional Methods for Producing 1,3-Propanediol

One of the derivatives of the hydrogenolysis method is 1,3-propanediol. There are two well-known chemical methods for the synthesis of 1,3-propanediol (1,3-PDO). The first method uses ethylene oxide as a raw material and is known as the 'Shell' route is a two-step process that uses hydroformylation of ethylene oxide to 3-hydroxypropionaldehyde (3-HPA) and subsequent hydrogenation from 3-HPA to 1,3-PDO. The second 1,3-PDO synthesis method is the 'Degussa-DuPont' route and uses acrolein as a raw material. Hydration produces 3-HPA which is then hydrogenated to 1,3-PDO. However, the chemical synthesis method 1,3-PDO is a petroleum-based method and has many advantages such as high pressure, high temperature and catalyst. Support, the 1.3-PDO production cost is very high. The application of 1,3-propanediol is in the manufacture of polymethylene terephthalate (PTT) or polypropylene terephthalate (PPT), biodegradable polyester used in the manufacture of textiles and carpets, cosmetics, chemicals, chemicals, and cooling chemicals, food and beverages , cleaning fluid, water-based ink, heat transfer liquid and unsaturated polyester resin.

6.2 Glycerol Acetalization

Glycerol acetylation is one of the most common ways to produce monoacetin, diacetin and triacetin. Acetylation is a reaction that initiates acetyl functional groups into chemical compounds. Acetylation includes substitution of a hydrogen atom of a hydroxyl group with an acetyl group to produce an acoxy group. The chemical used is glycerol which has a hydroxyl group and acetic acid that belongs to the acetyl functional group.

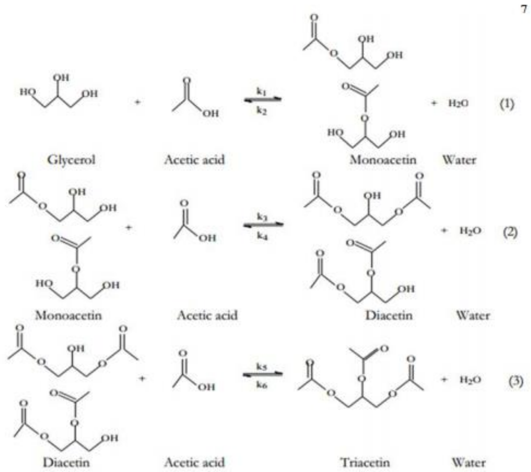

Fig. 4: Acetalization Reaction Produced from Glycerol

6.3 Glycerol Carbonylation

Glycerol carbonate (GC) is already an industrial common product, commercially available, with applications in many industrial processes. There are several general procedures to prepare glycerol carbonate from glycerol, either directly or through reactive intermediates, such as chlorohydrins or glycidol.

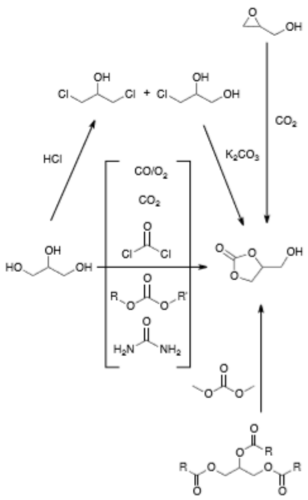

Fig. 5: General procedures for the synthesis of glycerol carbonate from glycerol

One of the advantages of glycerol carbonate in this context is that its ionizing and dissociating abilities are very close to those of water, preventing protein denaturation. These products are popular in the food industry as benign low hydrophilic-lipophilic balance (co)emulsifiers, rheological modifiers and dietary fat and oils.

6.4 Glycerol Esterification

One of the derivative products is glycerol trihepthanoate which is carried out by esterification reaction between glycerol and heptanoic acid (Dakka et al., 2010). The reactions that occur as described are as follows:

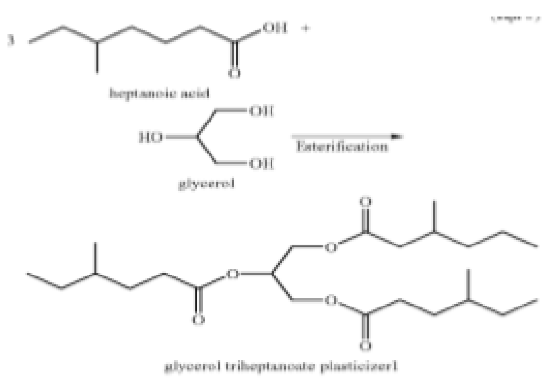

Fig. 6: Reaction of tri heptanoate ester formation

In making this glycerol derivative hexanoic acid is first made from the reaction of hexane with H2 and CO gas. The reaction will produce hexanal, which will then be oxidized to hexanoic acid. The product use of glycerol trihepthanoate is an environmentally friendly plasticizer with advantages: it is pthalat free and easy to melt, low evaporation and is a glass transition (Sears & Darbey, 1982).

7. Conclusion

Palm oil has a lot of trygliceride content when reacted with methanol through a transesterefication reacted that produces biodiesel and will produce a by-product in the form of glycerol. Glycerol has a low price value so that it has the potential to be used as a green solvent. Methods that can be used to obtain glycerol derivatives are fermentation, hydrogenolysis, pyrolysis, oxidation, etherification, dehydrasesterification, carboxylation, halogenation, polymerization and glycerol acetilzation.

8. References

Darnoko, D dan Cheryan, M, 2000. Kinetic of Palm Oil Transesterification in a Batch Reactor. J. Am. Oil Chem. Soc.,77, 1263-1267

Dakka, J.M., Mozeleski., E.J., Baugh,L.S., 2010. Process for Making Triglyceride Plasticizer from Crude Glycerol. US Patent Application Publication.

Gu, Y.; Jérôme, F. 2013. Bio-based solvents: An emerging generation of fluids for the design of eco-efficient processes in catalysis and organic chemistry. Chem. Soc. Rev. 2013, 42, 9550–9570.

Julianti, Wardani, Gunardi, Rosyadi. 2014. Pembuatan Biodiesel dari Minyak Kelapa Sawit RBD dengan Menggunakan Katalis Berpromotor Ganda Berpenyangga γ-Alumina (CaO/MgO/ γ-Al2O3) dalam Reaktor Fluidized Bed. *Jurnal Teknik POMITS*. Vol. 3, No. 2.

Haryanto, Silviana, Triono, Prabawa. 2015. Produksi Biodiesel Daro Transesterifikasi Minyak Jelantah dengan Bantuan Gelombang Mikro: Pengaruh Intensitas Daya dan Waktu Reaksi Terhdap Rendemen dan Karakteristik Biodiesel. Jurnal AGRITECH. Vol. 35, No. 2. Hal 234-240.

Moity, Laurianne, Adrien Benazzouz, Valérie Molinier, Véronique Nardello-Rataj, Mohammed Kamal Elmkaddem, Pascale de Caro, Sophie Thiébaud-Roux,Vincent Gerbaud, Philippe Marion, Jean-Marie Aubrya. 2015. *Glycerol Acetals and Ketals as Bio-based Solvents: Positioning in Hansen and COSMO-RS spaces, Volatility and Stability towards Hydrolysis and Autoxidation.*

N. García, P. García-García, M. A. Fernández-Rodríguez, D. García, M. R. Pedrosa, F. J. Arnáiz, and R. Sanz, Green Chem., 2013, 15, 999–1005.