

Research Article

Glycerolysis of Glycerol Carbonate from Crude Glycerol for Synthesis of Polyurethane

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Abstract: 10% by weight of crude glycerol is produced during biofuel fermentation process, which has impacted the price of biofuel due to impurity content. In addition, the government's regulations have prohibited the usage of crude glycerol as fuel source due to the emission of hazardous gases. This study provides the insight study of the properties and source of crude glycerol that can be converted into glycerol carbonate by glycerolysis process, where the particular glycerol carbonate is used as catalyst for synthesizing of polyurethane polymer that has a number of applications in real life. Glycerolysis process of glycerol carbonate using Pro-II 9.3 simulator is proposed and is feasible for implementation that would effectively utilize crude glycerol that is abundant in biodiesel market.

Keywords: Biodiesel, crude glycerol, glycerol carbonate, glycerolysis process

INTRODUCTION

Worldwide energy consumption is in continuous increasing trend due to rapid industrialization and increase of human population (Hoffmann, 2011; Walker, 2010). The growing public concern towards the environmental issues and exhaustion of fossil fuel reserves are factors that have elevated the urgency to explore for the alternative energy source such as biodiesel, a promising source to ameliorate this predicament.

Biofuel is produced from fermentation of living matters such as plant oil and animal waste. In particular, biodiesel is one of the biofuel which is synthesized from vegetable oil or animal fats (The Sustainability Co-Op, 2013). Biodiesel has more advantages than fossil fuel because it is non-toxic, economical and biodegradable. Incomplete combustion of fossil fuel will emit harmful gases such as carbon monoxide (CO), unburned hydrocarbons (HCs) and nitrogen oxide (NO). These gases are the major contributors of environmental pollution and greenhouse effect. However, complete combustion of biofuel not only emits lesser harmful gases (Anderson *et al.*, 2012) but also improves the efficiency of engine if it is blended properly.

Malaysia is rich with resources especially palm oil. It has great potential and advantages in biofuel production. Biodiesel production in Malaysia increases

from 140,983 tons in year 2012 to 330,032 tons in year 2013 in which 175,032 tons was exported and 155,000 tons was used domestically (Agrochart, 2014). Biodiesel (B5) produced in Malaysia is a blended fuel consists of 5% palm methyl ester and 95% regular diesel. Biodiesel production is expected to expand tremendously throughout year 2015 in Malaysia (Agrochart, 2014). The forecasted biodiesel production from year 2015 to 2022 for Malaysia is shown in Fig. 1 (OECD-FAO, 2013).

In biodiesel production, about 10% by weight of crude glycerol will be produced as the main by-product (Extension-American's Research Based Learning Network, 2014). It is forecasted that the worldwide biodiesel production will achieve 140 billion litres in 2016 that would produce approximately 15 billion litres of crude glycerol (Yang *et al.*, 2012). The forecasted crude glycerol production from year 2015 to year 2022 in Malaysia is shown in Fig. 2. Inevitable abundance of crude glycerol and costly purification process to manufacture refined glycerol for further utilization are considered as the main obstacles hindering biodiesel market from expanding. Therefore, it is indispensable to reconnoitre and research on enhancing the sustainability of crude glycerol to optimize this promising energy resource.

Objectives: The paper is aimed to study the properties and source of crude glycerol that can be converted into

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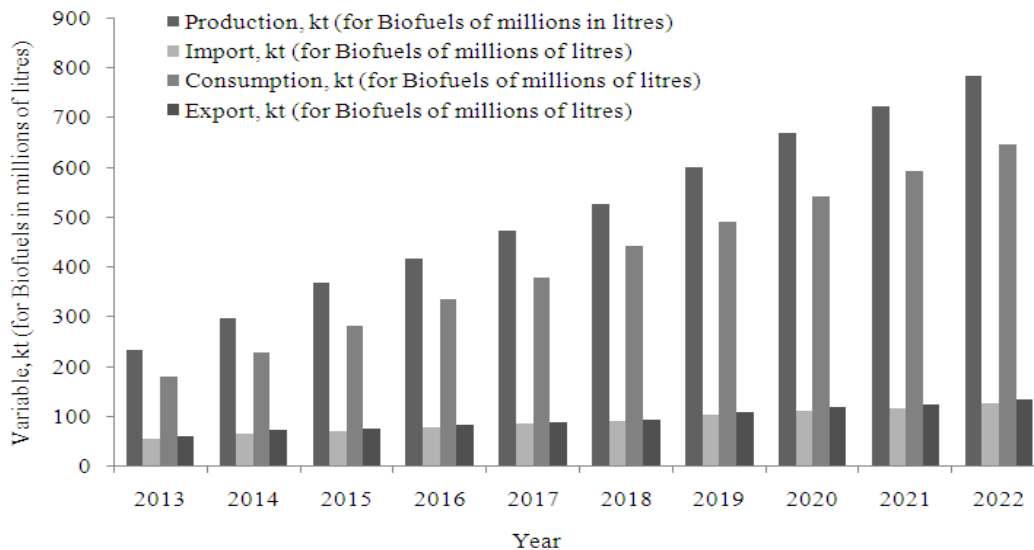


Fig. 1: Forecast of biodiesel production in Malaysia from year 2015 to 2022 (OECD.Stats, 2014)

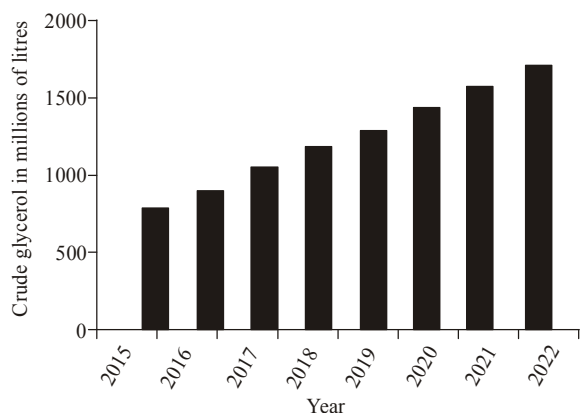


Fig. 2: Forecasted crude glycerol production from year 2015 to year 2022

glycerol carbonate by glycerolysis process to synthesize polyurethane polymer for a number of applications. It is also aimed to simulate a feasible process for synthesis of glycerol carbonate from crude glycerol using Pro-II 9.3 simulator.

LITERATURE REVIEW

Glycerol is known as glycerine or propane-1, 2, 3-triol. It is the main by-product of the biodiesel transesterification process. Vegetable oil such as palm oil instead of animal fats is mostly used in synthesis of biodiesel due to abundant supplies in Malaysia. During the transesterification process, vegetable oil reacts with methanol and potassium hydroxide as the catalyst to form biodiesel and crude glycerol. The chemical reaction for the transesterification process is shown in Fig. 3 (Biodiesel, 2013).

Crude glycerol contains impurities such as methanol, ash, soaps, glyceride, water and largest composition of glycerol. Glycerol has the molecular formula of $C_3H_8O_3$ and its molecular weight is 92.09 g/mol. The chemical structure of glycerol is shown in Fig. 4 (Modric, 2014). It is a viscous, odourless and sweet tasting liquid, which is soluble in water due to presence of three hydroxyl groups. Thus, it has hygroscopic property (Segur and Oberstar, 1951). Owing to this property, it is used widely to produce cosmetic and pharmaceutical products. Apart from these usages, it can also be used to make soaps or catalyst such as glycerol carbonate.

The industrial application of glycerol is shown in Fig. 5 (Tan *et al.*, 2013).

Currently, crude glycerol is mostly used as combustive fuel, landfill and animal feeding (Extension-American's research Based Learning Network, 2014). There are few process methods capable to convert it into useful material instead of going into waste stream. Current methods such as chemical conversion, biological conversion, composting, anaerobic digestion and water based treatment at a Publicly Owned Treatment Works (POTW) (Great lakes Information Network, 2014) are the most common methods. Anaerobic digestion is considered as the most environmental friendly way to dispose crude glycerol because it is able to generate biofuel like bio-ethanol. Purification process of crude glycerol is too expensive which hinders its usage in pharmaceutical, cosmetic and food industries. Inevitable excess of crude glycerol available in biodiesel market must be utilized in the profitable ways.

Glycerol carbonate or glycerine carbonate is one of the products that can be produced from the crude glycerol. It is a clear colourless liquid at room

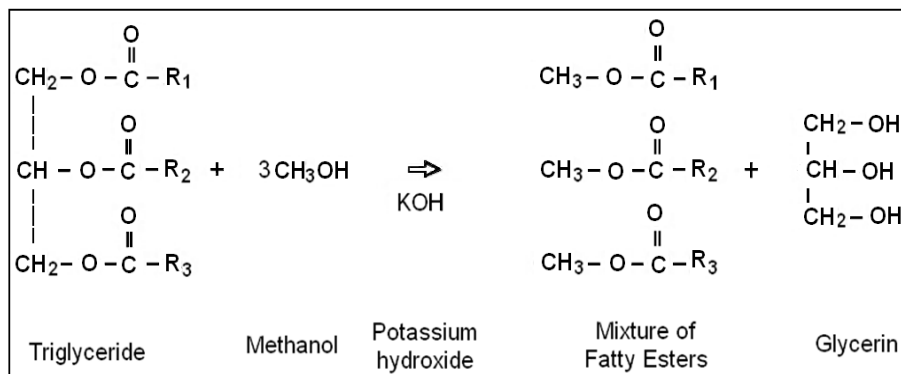


Fig. 3: Transesterification of biodiesel production (Biodiesel, 2013)

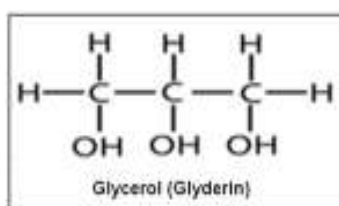


Fig. 4: Chemical structure of glycerine (Modric, 2014)

temperature with slight odour. It has boiling point of 239°C and its melting point is between -70°C to -60°C. It is a stable compound and is considered as a non-hazardous chemical by OSHA Hazard Communication Standard (29 CFR 1910.1200) (Huntsman, 2007). There are many methods used to synthesize glycerol carbonate. Using crude glycerol as the feeding raw material is the most environmental friendly method because it consumes the abundant crude glycerol available in market. However, the crude glycerol must be purified before synthesizing into glycerol carbonate in which the process is quite costly.

According to the market source, the cost for glycerol carbonate in 2014 ranges from US\$2.4 to US\$3 per kilogram which means US\$2,400 to US\$3,000 per metric tonnes (Nguyen and Demirel, 2013). This would increase the production cost of biodiesel by US\$0.021/L for US\$0.22/kg reduction in glycerol (Nguyen and Demirel, 2013).

Glycerol carbonate is a higher added-value product which can be used in many applications. This is due to the presence of hydroxyl group and carbonate group with four reactive electrophilic centres and possesses versatile activity (Mathers and Meier, 2011). It is a biodegradable, economical, non-toxic and inflammable chemical. Owing to its hydroxyl content and low evaporation property, it acts as the wetting agent in cosmetic product and as a carrier solvent in active pharmaceutical product.

Glycerol carbonate is used as crucial catalyst in manufacturing of polyurethane coating. It can also be

used as novel component of gas separation membranes, a surfactant component, a component of detergents, non-volatile solvent in paint industry and as the key monomer in synthesize various types of polymers such as polycarbonate, polyurethane and polyether (Mathers and Meier, 2011). Glycerol carbonate is gaining attention nowadays due to the public demand for safer chemical utility and effective way to reduce the amount of crude glycerol

Polyurethane is a polymer in which its monomers are linked by the urethane (carbamate) links. Polyurethane is classified into two categories, which are thermosetting (elastomeric) polymers and thermoplastic polymers. Traditionally, polyurethane is produced by the exothermic chemical reaction between isocyanate (polyisocyanates) and polyol with the aid of glycerol carbonate as catalyst. Alternatively, polyurethane can also be manufactured by inserting the carbon dioxide (CO₂) into the epoxy materials. However, the epoxy material is expensive to be used in generating polyurethane commercially. The elastic property of polyurethane is due to the low molecular weight of two or more hydroxyl-containing molecules per chain which is approximately 400 to 6000 per chain. This polyol has low melting point, which is less than 70°C and low glass transition temperature (T_g) ranges from -50°C to -86°C. Consequently, the polyurethane polymers produced possesses some degree of flexibility and rubber-like softness (Rlhudson, n.d.). Elastomeric polyurethane is mostly used due to its versatility.

Polyurethane is non-soluble in water and stable under normal storage condition. Polyurethane is always the prior material choice by engineer due to its excellent physical and chemical properties. It has excellent tensile strength, compression strength, chemical resistance, noise abatement ability, impact resistance, abrasion resistance and tear-strength. Besides, it has a strong bonding property which enables it to bind with other materials such as metals, wood and plastics (Precision urethane and Machine Inc., n.d.). All

Table 1: Typical physical properties of compounds of polyurethane (American Urethane Inc, n.d.)

Polyurethane type	L42	L100	L167	L315
Hardness, durometer value (ASTM d676-59T)	80A	90A	95A	75D*
specific gravity	1.07	1.10	1.13	1.21
Tensile strength, MPa (psi) (ASTM D412-61T)	20.7 (3,000)	31.0 (4,500)	34.5 (5,000)	62.0 (9,000)
Elongation at break, % (ASTM D412-61T)	800	450	400	270
100% Modulus, MPa (psi) (ASTM D412-61T)	2.8 (400)	7.6 (1,100)	12.4 (1,800)	32.0 (4,650)
Compression Set, %	45	27	40	-
Method B (ASTM D395) Method A (ASTM D395)**	-	9	10	10
Resilience, %	-	45	40	45
Rebound (Bashore)				
Impact resistance, Izod notched J/m (ft.lb./In) (ASTM D256)	Flexed	Flexed	Flexed	800.7 (15) 58.7 (1.1)
24°C (75° F)	-	-	-	
-40°C (-40° F)				
Solenoid brittle temp., Degrees C (Degrees F) (ASTM D746-57)	Below-80 (Below-120)	Below-70 (Below-94)	Below-70 (Below-94)	- 64 (-83)
Abrasion Index, NBS, % (ASTM D1630, Nat'l Bureau of Standards Abrader)	110	175	400	435
Tear Strength Split, kN/m (pli) (ASTM D470)	12.2 (70)	13.1 (75)	26.2 (150)	192.2 (110)

*: The D Scale is used to measure durometer hardness above 95A by Shore, Rex, or Wallace durometers; **: Measured at 9.3 MPa (1,350 psi)

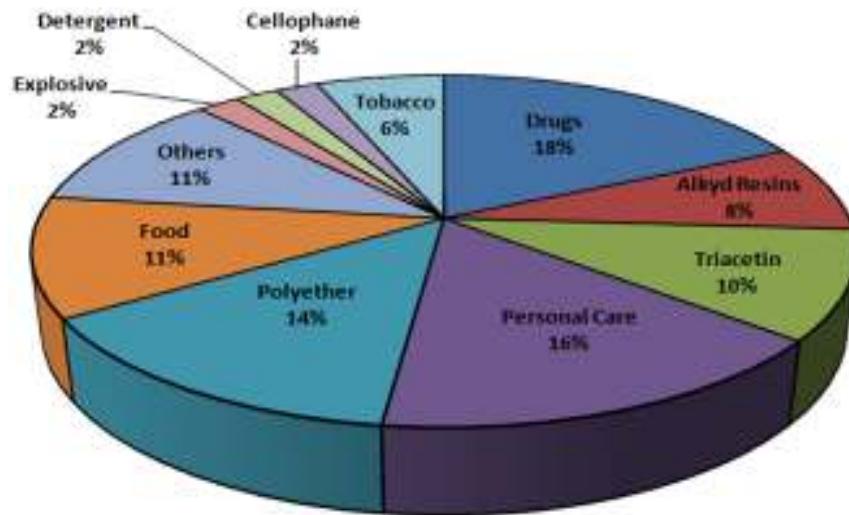


Fig. 5: Industrial application of glycerol (Tan *et al.*, 2013)

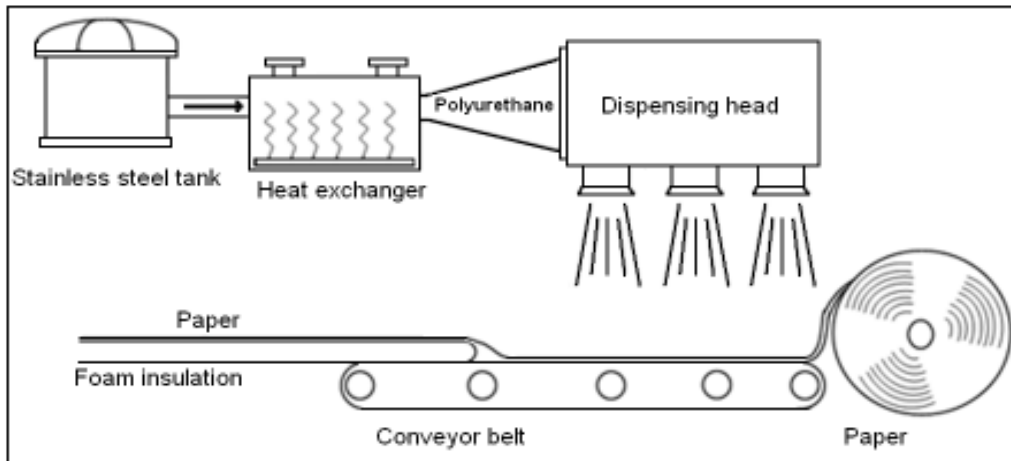


Fig. 6: Manufacturing process of polyurethane foam insulation (Madehow, n.d.)

Table 2: Comparison of the physical properties of polyurethane with rubber, metal and plastic (Precision urethane and Machine Inc., n.d.)

Polyurethane vs rubber	Polyurethane vs metal	Polyurethane vs plastic
High abrasion resistance	Lightweight	High temperature resistance
High cut and tear resistance	Noise abatement	Elastic memory
Superior load bearing	Abrasion resistance	Abrasion resistance
Thick section molding	Less expensive fabrication	Noise reduction
Colourability	Corrosion resistance	Variable coefficient of friction
Oil resistance	Resilience	Resilience
Ozone resistance	Impact resistance	Thick section molding
Radiation resistance	Flexibility	Lowest cost tooling
Broader hardness range	Easy mouldable	Low temperature resistance
Castable nature	Non-conductive	Cold flow temperature
Low pressure tooling	Non-sparking	Radiation resistance

these properties enable polyurethane to be utilized in different extreme environment. Its durability makes it widely used in various industries. In brief, polyurethane is a flexible, durable and tough material. Table 1 shows the typical physical properties of a few compound types of polyurethane while Table 2 shows the comparison of the physical properties of polyurethane with rubber, metal and plastic.

Elastomeric polyurethane is normally used to produce cushion foam in upholstery or insulator foam. Figure 6 depicts the manufacturing processes to produce rigid polyurethane foam insulation (Madehow, n.d.). It is the most common application of polyurethane since it is flexible and can maintain its rigidity. It can also be used appropriately as the wheels of dolly because it absorbs the shock without over compression. In coating industry, it plays the role to protect finishing that not only resistance to abrasion and solvents but also easy to be cleaned and maintained (American Chemistry Council, n.d.).

Thermoplastic polyurethane is mostly used in packaging crates on a truck or sitting seats due to its rigid, smooth, durable and impermeable to water properties. It can also be used in electrical appliances, automotive, building and construction, composite wood, electronics, furnishings, marine, medical, packaging industries etc. (American Chemistry Council, n.d.).

METHODOLOGY

Synthesis of glycerol carbonates: Synthesis of glycerol carbonate can be direct synthesis routes or indirect synthesis routes. Two direct methods to synthesize glycerol carbonate are carboxylation and oxidative carboxylation. As for the indirect methods, there are many methods such as phosgenation, transesterification and glycerolysis etc. Glycerolysis of glycerol is preferable because lanthanum oxide as the catalyst is cheaper than the process using dimethyl carbonate catalyst in carboxylation. Secondly, direct carboxylation of crude glycerol to glycerol carbonate is thermodynamically limited and has lower yield. Besides, this process requires more energy for separation of product and recovery of reactants which eventually end with high production cost. Thus, ideally glycerolysis of crude glycerol is an economical process to produce glycerol carbonate.

Crude glycerol generated during the biodiesel process cannot be used directly because it has to undergo distillation process to obtain pure glycerol. In this process, urea, a biomass feedstock and crude glycerol are the reactants which will react to generate glycerol carbonate and ammonia as the by-product. In addition, this process will generate approximately 89% of glycerol carbonate under specific conditions. For instance, if the reaction is carried out at 140°C at 3.0 kPa with 1.0% lanthanum (III) oxide (La_2O_3) as catalyst, it will yield maximum 90% of glycerol carbonate (Nguyen and Demirel, 2013). Furthermore, the generated ammonia gas can react with carbon dioxide under high pressure and temperature to produce urea as a raw material (Nguyen and Demirel, 2013). Thus, the whole glycerolysis process is optimized. The glycerolysis process is shown in Fig. 7. The figure also shows the chemical equation in which the glycerol carbonate reacts with urea to produce polyurethane coating. Glycerol carbonate acts as catalyst in some of the chemical reactions. For instance, coating composition consisting of blocked isocyanate is commonly used in coating industry to generate one component coating. Therefore, it requires the blocking agent which is glycerol carbonate to prevent the isocyanate from reacting within the molecules themselves and stabilize it during one component packaging.

Simulated Glycerolysis process for synthesis of glycerol carbonate: The process flow of glycerol carbonate and simulated production are derived from Pro-II Ver. 9.3 software which is shown in Fig. 8. The numbers shown in the figure are the simulated production volume and the volume of by-products produced on per year basis.

The initial input stream compositions of crude glycerol are shown in Table 3.

Based on simulation, 4,073.69 tonnes/yr of initial input stream is the amount of crude glycerol processed to produce glycerol carbonate. Firstly, the crude glycerol is heated up from 30.0°C to 80.0°C by using a heat exchanger (E3). The heated crude glycerol is transferred into a flash drum (F1) to separate glycerol and soap. The soap and other constituents are float at the top of the flash drum whereas the glycerol is at bottom of the flash drum (F1). The soap is passed by a heat exchanger (E1) to cool down the temperature of

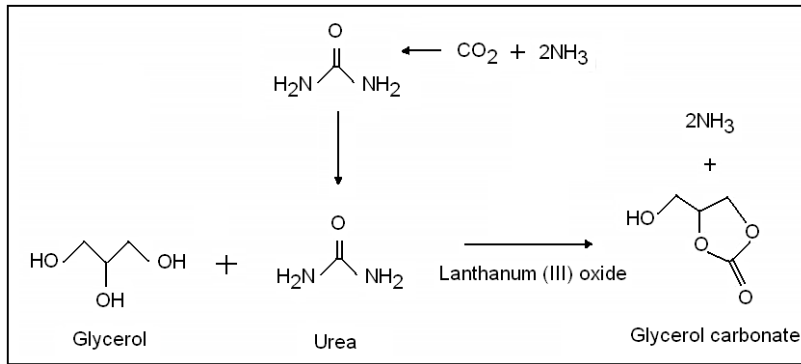


Fig. 7: Glycerolysis process of cruel glycerol into glycerol carbonate (Nguyen and Demirel, 2013)

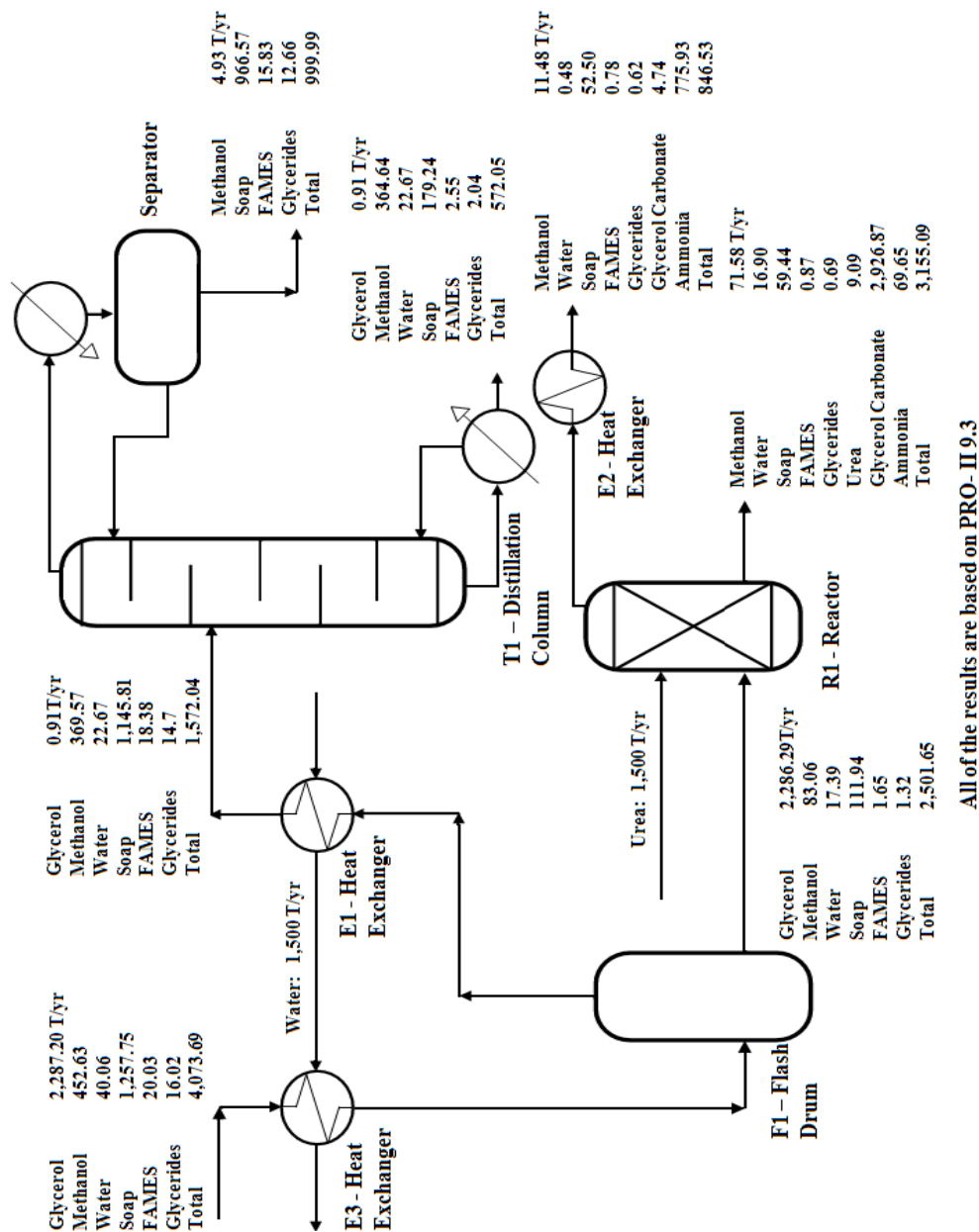


Fig. 8: The glycerolysis process flow of glycerol carbonate and the simulated production

Table 3: Composition of initial input stream of crude glycerol

Initial input stream composition (%)	
glycerol	53.1
Methanol	10.3
Water	1.0
Soap	30.3
FAMES	0.4
Glycerides	0.3
Ash	4.6
Total	100

the soap from 105°C to 39°C. The cooled soap and other constituents such as methanol, FAMES and glycerides are fed into a distillation column (T1) to fractionate the soap and other components. The soap is distilled at the top of column while the methanol is the bottom of the column. Based on the simulation, the amount soap and methanol produced are approximate 966.57 tonnes/yr and 364.64 tonnes/yr respectively. The methanol shall then be recycled for the biodiesel production.

Glycerol is pumped to a reactor (R1) to undergo glycerolysis reaction with urea and 1.0% lanthanum (III) oxide as catalyst. Approximately 15 tonnes/yr of lanthanum (III) oxide is used for the glycerolysis reaction. After the glycerolysis reaction, glycerol carbonate and by-products are produced. Based on the simulation, approximately 2,926.87 tonnes/yr of glycerol carbonate is produced. Besides, the by-products are ammonia, methanol and soap. Ammonia can be used as fertilizer. Methanol from glycerol can be recycled for the production of biodiesel. Soap can be processed into plant pests and detergents.

CONCLUSION

It is a feasible process that the proposed simulation for synthesis of glycerol carbonate from crude glycerol can be implemented for effective utilizing excess of crude glycerol produced as the results of biofuel fermentation process. Glycerol carbonate can then be used as catalyst in synthesis more valuable polymers like polyurethane.

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OECD-FAO (2013)