Sub-Products of Agro-based Industries as Valuable Raw Materials for the Production of PHA : A Review

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ABSTRACT

Due to increase in the use of fuel additives, like methyl esters there is an expected rise in the production of glycerol. As a result of this rise, the importance of glycerol as a common raw material for the production of value-added products would be enhanced. The demand and supply of glycerol and the possible application in the industries have something in common with its future scenario in the global market. Due to intensive research, technologies have been developed which has put in place proper investigation to convert low-value glycerol using different strategies and approaches. Lately, new opportunities for transforming glycerol into high-valued chemicals have emerged. This development could be attributed to the unique properties of glycerol, its structure and high features of renewability. Hence, this review highlights the glycerol global market, future trends and forecasts in recent years, and uses especially as a valuable raw material for the chemical industry.
Keywords: Glycerol, Methanol, Agro-Based, Transterification, Catalyst.

I. INTRODUCTION

Biofuels are liquid fuels produced from biomass for either transport or burning purposes. They can be produced from agricultural and forest products, also from the biodegradable part of industrial and municipal waste. Bioethanol and biodiesel account for more than 90 percent of global biofuel usage (Dufey, 2006).

Bioethanol is a distilled liquid derived from the fermentation of sugars from sugar plants and cereal crops. Such crops include sugarcane, corn, beet, sorghum, wheat and cassava.

Biodiesel is produced from the reaction of vegetable oil with ethanol or bio ethanol in the presence of a catalyst to yield mono alkyl esters and glycerine (Dufey, 2006).

Generally, the world is gradually moving away from fossil fuels and embracing the future and promising source of energy which is friendlier to the environment. Renewed interest in biofuels has been shown in the rapid expansion of global biofuel markets. Commonly cited driving forces behind the current market development of biofuels include: high oil prices, opportunities for greater energy security, and currency savings through a reduced oil bill. Due to their alleged reduced greenhouse gas emissions, it would really help countries to combat the global warming problem (Dufey, 2006). The recent growth of the global biodiesel industry has created a somewhat oversupply of glycerol in the global market. It is mainly obtained as a by-product of biodiesel production from fats and oils. Other methods include production from allyl chloride, from propene oxide, fermentation from sugar, hydrogenation of carbohydrates, and other non-commercial processes.

II. METHODS AND MATERIAL

1. Glycerol and Overview

Glycerol is a material with outstanding utility with many areas of application. One of the keys to its technical versatility is a unique combination of physical and chemical properties, ready compatibility with other substances and easy handling. Also, its no toxicity to human health and the environment is worthy of note. It

finds application among a broad diversity of end uses. In some, glycerine is the material of choice because of its physical properties while other uses rely on its chemical properties (Division, 1990). Glycerine (also known as glycerol and glycerine) is a colourless, viscous, odourless, and water-soluble liquid with slightly sweet taste (César A.G Quispe, 2013). It is a three carbon alcohol which serves as the backbone of the triglyceride molecule. Due to its non-toxicity, it can be used in cosmetics or consumed in food products and pharmaceuticals. Glycerine is made synthetically using petroleum as a feedstock. Naturally, it is derived using two methods:

- Soap and fatty acid production (hydrolysis).
- Biodiesel production (transesterification).

Glycerol produced from oleochemical or biodiesel plant is unrefined or crude and it contains such impurities like oily, alkali, and soap components, a salt or diols depending on the process followed during production and type of materials processed (Ueoka H., 2001), (Amin INHM, 2010). It is made up of glycerol, water, inorganic salts, soap, alcohol, traces of glycerides and colour (Hajek M, 2010)., but crude glycerol from the hydrolysis reaction contains glycerol, water, free fatty acid, unreacted triglycerides, organic and inorganic salts matter organic non-glycerol (Ueoka H., 2001), and for the saponification of fats and oil crude glycerol has been reported to contain glycerol, fatty acids and salts (Ooi TL, 2001). Crude glycerol is a low value product because its low purity limits the application as feedstocks in the industries. Purified glycerol can be sold as a commodity because it is still highly required as an important industrial feedstock especially in some chemical industries. Therefore, as a result it is necessary to establish purification methods for glycerol since it is still needed in the industries as feed stocks (Manosak R, 2001).

As of present, numerous techniques are being adopted for the purification of crude glycerol, such as conventional filtration, micro filtration, and ultra-filtration using organic polymer membranes, simple distillation, and vacuum distillation, chemical and physical treatments, ion exchange technique and adsorption. If two or more of these techniques are combined, higher purity glycerol would be achieved (Isahak WNRW, 2010).

A. Physical, structural and chemical properties of glycerol:

A unique combination of physical and chemical properties of glycerol makes it technically a versatile product. It is the simplest of the alcohols known by propane-1,2,3-triol, according to IUPAC; commercially referred to as glycerine, 1,2,3-propanotriol, trihydroxypropane, glyceritol or glycidic alcohol (Rahmat N, 2010). It is very much compatible with other substances and quite easy to handle. Some of its physical properties include its water-solubility and hygroscopy, which is due to its three hydrophilic hydroxyl groups (Perry RH, 1997) (JE, 1990). Due to its hygroscopic nature, it is volatile and has a low vapour pressure. Low vapour pressure is a characteristic of alcohols, water and other polar compounds due to molecular association (César A.G Quispe, 2013). Glycerol causes less reduction in water's vapour pressure and this can be explained by molecular contraction which could be as a result of hydrate formation (Miner CS, 1953). It is odourless, almost colourless and viscous even with a high boiling point. Chemically, glycerol is a trihydric alcohol and due to this property it is able to react as an alcohol and still stable under most conditions (Muhammad Ayoub, 2012). Glycerine attains a complete miscibility in many substances such as alcohol (isopropyl, methyl, ethyl, n-butyl, isobutyl, secondary butyl, and tertiary amyl); ethylene glycol, propylene glycol, trimethylene glycol mono methyl ether and phenol (Chung YH, 2007) (César A.G Quispe, 2013). In acetone, glycerine is soluble to 5% by weight and 9% in ethyl acetate. In dioxin and ethyl it is slightly soluble, and partially soluble in superior alcohol, fatty acids and hydro carbonates, also in chlorinated solvents like hexane, benzene and chloroform. At 100% concentration, glycerine still remains very viscous without crystallizing; it rather super cools at low temperatures as high viscosity fluid (César A.G Quispe, 2013). Meanwhile, crystallisation which could be achieved at 291 K cannot be directly possible from the liquid state, it requires special procedures (Mario Pagliaro, 2010). Glycerol readily forms a super cooled liquid, which by minimising the temperature undergoes at about 187 K glassy state transition (Mario Pagliaro, 2010). In the glassy state, a single hydrogen-bonded network is observed involving 100% of the molecules present (Mario Pagliaro, 2010). Glycerol in aqueous solutions

are resistant to freezing, instead they are used as antifreeze in cooling systems (César A.G Quispe, 2013). Also in the aqueous phase it is stabilized by a combination of intramolecular hydrogen bonds and intermolecular solvation of the hydroxyl groups, while in the condensed phase it is about its high degree of association due to hydrogen bonding (Mario Pagliaro, 2010). Based on recent single-molecule analysis, there exist a foam-like structure for glycerol at temperatures higher than the glass transition temperature (Tg=190 K), this foam-like structure consists of fluid pockets which are isolated from another by glass-like regions (Mario Pagliaro, 2010). Under very normal conditions, glycerol cannot oxidize in the atmosphere but can rather be oxidized easily by other oxidants (César A.G Quispe, 2013). During exposure to heat and metals, the salt constituents of these metals like copper can easily catalyse oxidation; therefore it is necessary to introduce inhibitors to the solutions (César A.G Quispe, 2013). If exposed to strong oxidizing agents like potassium chlorate, it might turn explosive (HW Tan, 2013).

A multipurpose substance used in many applications. Finally, glycerol can be used as a renewable resource for biodegradable products and could be applied in green refinery process. Due to the gradual depletion of petroleum and fossil fuel feedstock, and the move to favour green energy; glycerol has a high environmental value in our modern society (Muhammad Ayoub, 2012).

Table 1 : Physical properties of glycerol.

Properties	Unit	(LR., 2014)	(Mario Pagliaro, 2010)	(SIDS, 2002)
Molecular formula			$C_3H_5(OH)_3$	$C_3H_8O_3$
Molecular mass	g/mol	92.09	92.09382	92
Relative density	Kg/m^3	1260	1261	1260
Viscosity	Pa s	1.41	1.5	1.41
Melting point	^{o}C	18	18.2	18
Boiling point	^{o}C	290	290	290
Flash point	^{o}C	177	160(closed cup)	160
Specific heat	kJ/kg	2435(25°C)		
Heat of vaporisation	kJ/k-mol	82.12		
Thermal conductivity	W/(m k)	0.28		
Heat of formation	kJ/mol	667.8		
Surface tension	mN/m	63.4	64.0	63.4
pH(solution)		7		
Auto flammability	^{o}C			393

Table 2: Physical properties of glycerol (Perry RH).

Properties	Values
Chemical formula	CH_2OH-$CHOH$-CH_2OH
Formula weight	92.09
Form and colour	Colourless and liquid
Specific gravity	$1.260^{50/4}$
Melting point	17.9^{o}C
Boiling point	290°C
Solubility in 100 parts	
Water	Infinity
alcohol	Infinity
ether	Insoluble
Heat of fusion at 18.07^{o}C	47.49cal/g
Viscosity of liquid glycerol	(DL * 10^5 sq cm/s)
at 100% purity	10cP
at 50% purity	25cP
Diffusivity in	
i-Amyl alcohol	0.12
Ethanol	0.56
Water	0.94

Specific heat in aqueous solution (mol %)	15°C(cal/g^{o}C)	30°C(cal/g^{o}C)
2.12	0.961	0.960
4.66	0.929	0.924
11.5	0.851	0.841
43.9	0.670	0.672
100	0.555	0.576

B. Characterisation of Crude Glycerol

It is very important to utilize crude glycerol, the main product of biodiesel production, in order to manufacture high value added chemicals. Owing to the wide variety of triglycerides, alcohols, catalysts and separation processes used in biodiesel production, crude glycerol composition varies extensively, leading to different crude glycerol purifications (Yang Xiao, 2013). "Glycerin" normally applies to purified commercial products with contents usually more than 95% glycerol. They slightly differ in glycerol content and other characteristics like colour, smell and traces of impurities (DB, 2005). They are obtained after the removal of salts, methanol, and free fatty acids. Methanol is recovered through heating and later reused in biodiesel production process. In some commercial applications, the quality of glycerine in use passed through complex improvement processes until an acceptable level of purity completely different from those achieved in biodiesel facilities has been attained (WJ, 2008) (D, 1996). Many actions and processes are adopted in biodiesel purification, recovering useful agents for recycling and by-product (glycerol) processing (César A.G Quispe, 2013). Some post-process of glycerol include: acidification and neutralisation to adjust pH and evaporation/distillation to

separate water and excess methanol for reuse (César A.G Quispe, 2013). Table 3 below shows that glycerol from biodiesel can be classified into three main categories: crude, purified, and commercially synthesized; thereby showing the insignificant difference between purified and commercial glycerol while there are considerable differences between crude and purified glycerol (Zahra Gholami, 2014). During preparation, purified glycerol shares almost same qualities with commercially synthesized type due to its sensitive application areas like food, medicine and cosmetics. Moisture, soap and ash contents appear in higher quantity in crude glycerol. Its acidic value is slightly higher than the rest. The dark colour equally suggests the presence of impurities. A purified glycerol from crude glycerol a product of biodiesel industry is generally sold as 99.5-99.7% pure in the market (Muhammad Ayoub, 2012).

Table 3: Differences between types of glycerol (Zahra Gholami).

Parameter	Crude glycerol	Purified glycerol	Refined/ commercial glycerol.
Glycerol content (%)	60-80	99.1-99.8	99.20-99.98
Moisture content (%)	1.5-6.5	0.11-0.8	0.14-0.29
Ash (%)	1.5-2.5	0.054	<0.002
Soap (%)	3.0-5.0	0.1-0.16	0.04-0.07
Acidity (pH)	0.7-1.3	0.10-0.16	0.04-0.07
Chloride (ppm)	ND	1.0	0.6-9.5
Colour (APHA)	Dark	34-45	1.8-10.3

In order to handle this superfluity of glycerol and build the "green" qualities and characteristics of this compound, need is that innovative and greener catalytic process be initiated. This would assist in converting glycerol into more value-added product (Zahra Gholami, 2014). This value-added molecular synthesis from glycerol is quite attractive since it serves as a good replacement to improper disposal of glycerol perhaps by incineration (Liu X, 2011).

Table 4: Elemental analysis results of crude glycerol from biodiesel industries (da Silver GP).

Element	Weight %
Carbon (C)	52.8
Hydrogen (H)	11.1
Nitrogen (N)	<0.0001
Sulphur (S)	-
Balance Oxygen (O)	36.2

The table 4 above shows a typical elemental analysis result of crude glycerol, indicating that C, H and O are the major constituents. Glycerol is a good renewable energy source for a lot of applications, basically due to its high carbon content (52.8 %). Also, the high oxygen content is another indication of how valuable the compound is (Zahra Gholami, 2014).

Methylated glycerol is made up of about 50 to 70 % glycerol, 10 to 20 % methanol, 5 to 10 % salts, <3 to 10 % water, <1 to 5 % fatty acids, and 5% non-glycerol organic material by weight. Demethylated glycerol has up to 70 to 88 % glycerol. According to (Bohon MD, 2011), glycerol could equally be classified into three different groups: USP, Methylated and Demethylated, where USP refers to glycerol in the market that are manufactured to meet up with the standard of United States Pharmacopeia (Muhammad Ayoub, 2012). The table 5 below explains.

Table 5: Analysis of three glycerol fuels (Bohon MD).

	USP Glycerol	Methylated	Demethylated
C (%)	39.1	42.05	67.27
H (%)	8.7	10.14	11.43
N (%)	0	<0.05	<0.05
O (%)	52.2	43.32	17.06
S (%)	0	0.078	<0.05
H_2O (%)	0	1.03	1.47
Ash (%)	0	3.06	2.23
Ca (ppm)		<23	119
Na (ppm)		11600	17500
K (ppm)		628	541
Cl (ppm)		124	154
Mg (ppm)		<8	29
P (ppm)		2220	1750
HHV (MJ/kg)	16.0	21.8	20.6

On the other hand, the quality of purified glycerol can be identified by its grade, in this case it is divided into three

main grades based on purity and potential end uses. Crude glycerol with its origin from biodiesel is quite costly for purification in order to attain a purified level to 99%. The refined or purified glycerol market appears strong when compared to crude glycerine market and may be as a result of its new feed and chemical applications (Muhammad Ayoub, 2012). Currently, there are different types of glycerol available in the open market; this may depend on the purity that would affect the end uses, such as food, pharmaceuticals, cosmetics and preparation of chemical components. And presently, majority of purified glycerol available in the market comes from biodiesel (Muhammad Ayoub, 2012).

Therefore, still in the market the quality of purified glycerol can be identified by its grade which is not certified as USP or another. This type can be divided into three basic grades as the table 6 below explains (Muhammad Ayoub, 2012).

Table 6 : Commercially available basic grade for purified glycerol (Muhammad Ayoub).

Grade	Type of glycerol	Preparation and usage
Grade I	Technical grade ~99.5%	Prepared by synthetic process and used as a building block for various chemicals but not applicable to food or drug formulation.
Grade II	USP grade 96-99.5%	Prepared from animal fat or plant oil sources, suitable for food products, pharmaceuticals and cosmetics.
Grade III	Kosher or USP/FCC grade 99.5-99.7%	Prepared from plant oil sources, suitable for use in kosher foods and drinks.

2. Biodiesel Production Process.

It is well known that glycerol can be obtained from the following processes: soap manufacture, fatty acid production, and microbial fermentation, but it can also be got from the synthesis of propylene oxide (Othmer, 2001) (Wang ZX, 2001). Glycerol can be generated from the transesterification reaction of fats and oils in a typical biodiesel plant. Transesterification is a chemical reaction process involving fats and oils (triglycerides) and alcohol such as ethanol or methanol, and this takes

place in the presence of a catalyst which in turn yields fatty acid methyl esters and glycerol as a by-product (Gonzales-Pajuelo M, 2004) (Canacki M, 2008). This catalysed reaction is also a balanced one in which one mol of triglycerides reacts with three mols of methanol. This is so as excess of alcohol is needed in the reaction medium in order to achieve a forceful reaction thereby obtaining results in a high yield (Bournay L C. D., 2005). Most of the reactions in real industrial process use a mol ratio of about 6:1 in favour of alcohol with an excess of 100% so that the reaction can be completed (César A.G Quispe, 2013).

A. Transesterification Reaction

The transesterification reaction is carried out in a batch or continuous equipment. As the reaction progresses, the reaction stream is separated into two phases: biodiesel-rich phase (top layer) and glycerol-rich phase (bottom layer). This is as a result of the differences in their densities and polarities (Hasheminejad M, 2011) (N, 2010).

Triacylglycerols in vegetable oil or animal fats are transesterified with alcohol in the presence of acid or alkali catalyst (Salamatinia B, 2010). The most commonly used alcohol for this process is methanol because of its very low cost. This process entails removing the glycerin from vegetable oil or fat. During this, methyl esters are separated as the useful or desired product whereas the glycerol is left behind as the by-product (Muhammad Ayoub, 2012). On approximate basis, its quantity is about 10% by weight during the entire biodiesel production (Melero JA & Morales G, 2012). The figures 1 below show the illustration of the transesterification reaction.
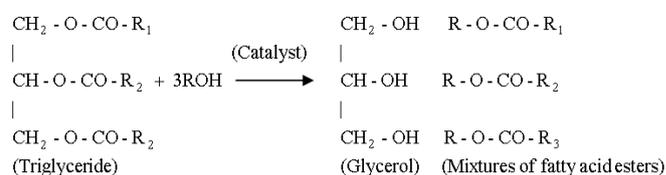
$$
\begin{array}{ccc}
CH_2\text{-}O\text{-}CO\text{-}R_1 & & CH_2\text{-}OH \quad R\text{-}O\text{-}CO\text{-}R_1 \\
| & (Catalyst) & | \\
CH\text{-}O\text{-}CO\text{-}R_2 + 3ROH \longrightarrow & CH\text{-}OH \quad R\text{-}O\text{-}CO\text{-}R_2 \\
| & & | \\
CH_2\text{-}O\text{-}CO\text{-}R_2 & & CH_2\text{-}OH \quad R\text{-}O\text{-}CO\text{-}R_3 \\
(Triglyceride) & & (Glycerol) \quad (Mixtures\ of\ fatty\ acid\ esters)
\end{array}
$$

Figure 1 : Transesterification reaction to produce crude glycerol in a bioprocess (Muhammad Ayoub)

Where R_1, R_2, and R_3 are long chain hydrocarbons, sometimes called fatty acid chains.

Glycerol production from transesterification in the biodiesel industry has dominated the market, but as the biodiesel industry has rapidly grown lately the market is now flooded with excess glycerol. This has caused a decrease in the prices of glycerol and also environmental concerns associated with the disposal of contaminated glycerol (Lopez JAS, 2009).

According to (HW Tan, 2013), feedstock costs account for about 75% of the total cost of biodiesel production, the selection of proper feedstock is important in order to ensure that biodiesel production cost remains low. Generally, biodiesel feedstocks can be classified into three groups: first generation, second generation and three generation biodiesel feedstocks (HW Tan, 2013). This is shown in the table 7 below.

Table 7 : Current feedstock for biodiesel production (HW Tan).

Feedstock	Types	Remarks
First generation	Palm oil Rapeseed Soyabean oil Sunflower oil Peanut oil	Known as food feedstock. They are limited and caused the competition with the edible oil market. High impact on food markets and security. Negative environmental impact as large portions of land were needed for planting the biodiesel crops.
Second generation	Jatropha oil Sea mango Tobacco seed oil Salmon oil Waste cooking oils Tallow	Reduced competition for food and feedstock. Environmentally friendly as less farmland are required. Poor performance in cold temperature. The use of animal fats brings a biosafety issue as they may obtain from contaminated animals.
Third generation	Microalgae	Fast production as they are easier to cultivate. Economic, renewable and carbon neutral source of biofuel. Enhanced cost efficiencies. Environmentally friendly as microalgae do not compete for farmland with crops and capable of fixing CO_2 in the atmosphere. Produce valuable by-products such as biopolymers and proteins.

Quite a lot of laboratory and industrial experiments have been carried out to demonstrate this method of production, especially in the laboratory. For instance, the production carried out by (Md Enamul Hoque, 2011) was done with used cooking oil and animal fat. At optimum conditions, the following parameters were maintained: methanol to oil ratio 6:1, catalyst concentration of 1.25 % by weight of oil, reaction temperature of 65°C, stirring speed of 150rpm. These reactions were repeated using beef fat and chicken fat, and the maximum yields of biodiesel achieved in each were 88.3% for used cooking oil, 89% for chicken fat, and 87.4% for beef fat. The authors were able to draw an inference stating that economically viable biodiesel could be produced from low cost feedstock by ensuring adequate working conditions and process parameters. (Miao X, 2006) produced biodiesel from microalgae lipids using sulphuric acid as a catalyst. At optimum conditions, temperature of 30°C and mol ratio of 56:1 of methanol was maintained. The reaction time was about 4 hours during which the best biodiesel yield was obtained. According to (Moazami N, 2012), roughly about 60000L of biodiesel could be produced from microalgae strain PTCC 6016 (Nanochloropsis sp.). However, irrespective of the type of feedstock employed, glycerol will be generated in the homogenous or heterogeneous catalysed process. In the reaction performed by (Asad-ur-Rehman, 2008), methanol was mixed with sunflower oil in the molar ratio of 10:1, thereby maintaining an rpm of 400 at 60°C with 0.55% by weight of sodium hydroxide. They obtained glycerol with the following composition: 30% glycerol, 50% methanol, 13% soap, 2% moisture, 2-3% salts approximately (non-glycerol organic matter). There was also a report from

(Thompson JC, 2006) stating that the the process was conducted keeping the temperature at 50°C, and at 240rpm for 1hour using sodium methylate as a catalyst. According to their report, crude glycerol produced from different types of feedstocks ranges between 60% weght and 70% weight, and the crude glycerol yield for first-used oils ranged from 8.8-12.3g per 100g of input oil which is about 62% by weight.

Meanwhile, crude glycerol from waste vegetable oil contains more soaps and impurities, on average 22g per 100g of input oil (HW Tan, 2013). Another experiment was carried out on biodiesel production from algae (Oedogonium and Spirogyra) in order to investigate produced amount of biodiesel and its physical properties (yield of biodiesel, glycerol and sediments). From their results, biodiesel can be produced from both algae species where about 90% or more of biodiesel is formed. After the transesterification reaction, the generated sediments (glycerol, water and pigments) were higher in biodiesel produced from Spirogyra and Oedogonium. They concluded that Oedogonium sp is a better feedstock than Spirogyra for biodiesel production through transesterification process.

In transesterification process, the use of a catalyst is very necessary as it splits the oil molecules and an alcohol to combine with the separated esters and also boost the rate of the reaction (Hasheminejad M, 2011). The catalysts are in the nature of acids, alkalis or enzymes which are in homogenous or heterogeneous form. This actually depends on the amount of free fatty acids present in the oil (Helwani Z, 2009).

If there are more water and free fatty acids in the triglycerides, acid catalysts can be used, but when the triglycerides contain low free fatty acids, then alkali catalysts can be used (A, 2009). A catalyst can be either homogenous or heterogeneous. A homogeneous catalyst is one that remains in the same phase (liquid) as the reactants, while a heterogeneous catalyst remains in a different phase (solid, immiscible liquid or gaseous) to the reactants during the process of reaction (Mosali R, 2011). Separation of heterogeneous catalysts from the product as well as regeneration and reutilisation are carried out easily due to its insolubility in the product, whereas homogenous catalysts cause contamination and generation of waste which makes product separation and purification more expensive (Lam MK, 2010).

Table 8 : Advantages and disadvantages of types of catalysts used in transesterification reaction (Lam MK) (HW Tan):

Types of catalyst	Advantages	Disadvantages
Homogenous base catalyst NaOH KOH	Very fast reaction rate. The reaction can occur at mild reaction condition and less energy intensive. High conversion can also be achieved. They are widely available and economical	The usage limits for oil with less than 0.5% by weight FFA. Soap will be formed if the FFA content in the oil is more than 2% by weight. Excessive soap formation will reduce the biodiesel yield
Heterogeneous base catalyst CaO MgO	Relatively faster reaction rate than caid catalysed transesterification reaction. The reaction can occur at mild reaction condition and less energy intensive. Easy separation of catalyst from product. High possibility to reuse and regenerate the catalyst.	Sensitive to FFA content in the oil due to its basicity property. Soap will be formed if the FFA content in the oil is more than 2% by weight. Excessive soap formation would decrease the biodiesel yield and cause the problem during product purification. Leaching of catalyst active sites may result to product contamination.
Homogeneous acid catalyst H_2SO_4 HCl	Insensitive to FFA content and water content in the oil. Preferred method if low-grade oil is used. Esterification and transesterification can occur simultaneously. The reaction can occur at mild reaction condition and less energy intensive. More economical than base catalysed process.	Very slow reaction rate. Required high reaction temperature and high molar ratio of alcohol to oil. Corrosive catalysts used such as H_2SO_4 can cause corrosion on reactors and pipelines. Separation of catalyst from product is problematic.
Heterogeneous acid catalyst ZrO_2 TiO_2 TnO_2	Insensitive to FFA content and water content in the oil. Preferred method if low-grade oil is	Complicated catalyst synthesis procedures lead to higher cost. Required high

Zeolite	used. Esterification and transesterification occur simultaneously. Eliminate the washing step of biodiesel. Easy separation of catalyst from product. High possibility to reuse and regenerate the catalyst. Reduce corrosion problem.	reaction temperature, high alcohol to oil molar ratio. Ratio and long reaction time are required. Energy intensive. Leaching of catalyst active sites may result to product contamination.
Enzyme Mucor miehei(lipozym IM 60) C. antartica(novozym 435) Basillus subtilis	Insensitive to FFA and water content in the oil. Preferred method, if low-grade oil is used. Transesterification can be carried out at low reaction temperature, even lower than homogenous base catalyst. Only simple purification step is required.	Very slow reaction rate, even slower than acid based transesterification. High cost. Sensitivity to alcohol, typically methanol that can deactivate the enzyme.

✓ **Acid Catalysed Transesterification Reaction:**

Acid catalysed transesterification reaction: This is more suitable for waste oil. Due to its slower reaction rate and high alcohol to oil molar ratio requirement, it has not gained much attention like the base catalysed reaction (HW Tan, 2013). This can be carried out in both homogenous and heterogeneous systems. In homogeneous acid catalysed systems, transesterification reaction is carried out by Brønsted acid like hydrochloric acid and sulphuric acid (Koh MY, 2011). During this process, a glycerol layer is formed which results in the loss of the catalyst. By using acid catalysts, high yield of alkyd esters could be obtained, meanwhile the reaction is slow whereby reaction temperature above $100^{o}C$ and above 3 hours are needed to achieve a complete conversion (Graille J, 1986). Lee et al reported that the most common type of acid catalysed transesterification reaction using sulphuric acid requires a reaction temperature of $65^{o}C$ and more than 50 hours to achieve complete conversion of soya bean oil a methanol/oil ratio of 3:1 (Lee DW, 2009).

Generally, solid acid catalysts have the strong ability to replace liquid acid catalysts due to their insensitivity to free fatty acid content, easy separation of catalysts from the reactant medium as well as minimise the corrosion problem even with the presence of acid species (Bournay L C. D., 2005). Heterogeneous acid catalysed transesterification reaction can be carried out using a solid acid catalyst like Fe-Zn double metal cyanide, zirconium oxide and titanium oxide (Bournay L C. D., 2005).

✓ **Base catalysed transesterification reaction:**

This proceeds on a faster rate than acid catalysed transesterification reaction. Such base catalysts as alkaline metal alkoxides and hydroxides, sodium or potassium carbonates are used. Alkaline metal alkoxides give the highest yield >98%at low molecular concentration of 0.5%, and this is achieved within a short reaction time of 30 minutes. There has been some reported works on this base catalysis, for example Schuchardt et al and Demirbas reported a process that starts with the reaction of the base with the alcohol producing an alkoxide and a protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate. It is from here that the alkyl ester and the diglyceride anion are formed. Diglycerides and monoglycerides are then converted by the same mechanism to a mixture of alkyl esters and glycerol. According to the experiments conducted by Vicente et al, the reactions were carried out at $65^{o}C$ with 6:1 M ratio of methanol to oil and 1% of basic catalyst by weight of vegetable oil. The experiment compared the biodiesel yield and the glycerol content using sunflower oil made of different basic catalysts like sodium methoxide, potassium methoxide, sodium hydroxide and potassium hydroxide.

✓ **Enzymatic catalysed transesterification reaction:**

This process is developed to abate the problems constituted by acid and base catalysed transesterification processes. Some of these inherent problems include: high energy need during reaction, environmental pollution, and some difficulties involved in recovering the catalyst and glycerol. The enzyme catalysis yields high purity by-product (glycerol), easy product recovery, reuse of catalyst and mild reaction condition (HW Tan, 2013). At industrial scale, some of the possible

drawbacks of the enzyme catalysed reaction include slow reaction rate, high cost of enzymes, and deactivation of enzymes (Bajaj A, 2010). Biocatalysts such as lipases are used in catalysing hydrolysis, alcoholysis, esterification and transesterification of triglycerides (Basri M, 1995).

B. Saponification

This is simply the hydrolysis of fats and oils (triglycerides) with alkali yielding two products: salts of fatty acids (soap) and glycerol. In the saponification process, the alkali breaks the ester bond thereby releasing the glycerol and soap of alkali metal. During this process, three molecules of soap are formed and the interaction between one triglyceride molecule and three alkali molecules eventually liberates one molecule of glycerol. There is spontaneous reaction between caustic alkali and free fatty acid and soap is immediately formed under proper mixing and agitation (HW Tan, 2013). Saponification as demonstrated in figure 2 below is the basic process used in the soap making industry. The process of soap manufacture of fats and oils usually yields glycerol to about 10% of the value of the soap formed, yet better reaction routes and condition with efficient purification of glycerol are essential in maximizing the economics of soap production in large scale (HW Tan, 2013).
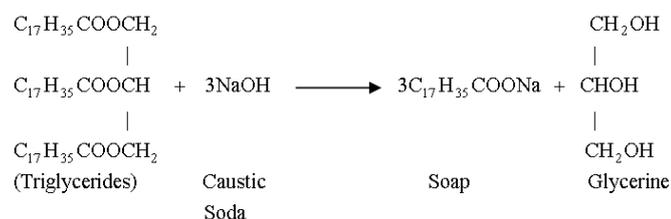
$$C_{17}H_{35}COOCH_2$$
$$|$$
$$C_{17}H_{35}COOCH \quad + \quad 3NaOH \longrightarrow 3C_{17}H_{35}COONa \ + \ CHOH$$
$$|$$
$$C_{17}H_{35}COOCH_2$$

| $C_{17}H_{35}COOCH_2$ | | | CH_2OH |
| (Triglycerides) | Caustic Soda | Soap | Glycerine |

Figure 2 : Saponification reaction (HW Tan).

C. Hydrolysis

This is a reversible reaction whereby steam molecule breaks a fatty acid off the backbone of glycerine of a triglyceride, which eventually ends up in a free fatty acid and glycerol (Gregg F, 2008). The equation in figure 3 represents the reaction process. This is quite similar to saponification reaction, but in this case fat and oil reacts with water to yield a fatty acid and glycerol. This reaction consists of a light phase of fatty acid and a heavy phase which is made up of glycerol known as sweet water and impurities (Gregg F, 2008). During this

process, each molecule of fat and oil will yield one mole of glycerol and three moles of fatty acid (HW Tan, 2013).
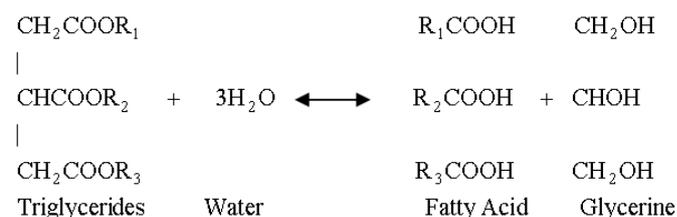
$$CH_2COOR_1 \qquad\qquad R_1COOH \qquad CH_2OH$$
$$|$$
$$CHCOOR_2 \quad + \quad 3H_2O \longleftrightarrow \quad R_2COOH \quad + \quad CHOH$$
$$|$$
$$CH_2COOR_3 \qquad\qquad R_3COOH \qquad CH_2OH$$

| Triglycerides | Water | Fatty Acid | Glycerine |

Figure 3 : Hydrolysis reaction.

Table 1: Composition of the crude glycerol derived from transesterification, saponification and hydrolysis reaction.

Component	Transesterification (%)	Saponification (%)	Hydrolysis (%)
Glycerol	75	83-84	88-90
Ash	10	8.5-9.5	0.7-1.0
Water	10	6-7	8-9
Mong (matter organic non-glycerol)	5	3-4	0.7-1.0
Tmg (trimethylene glycol)	1	0.1	0.2

III. RESULTS AND DISCUSSION

3. Glycerol Supply and its drivers:

It is highly anticipated that glycerol production would be at the increase due to the increasing use of fuel additives like methyl esters. This productivity increase would enhance its importance as a more available and cheaper raw material for new products which are in use in surfactants, lubricants, cosmetics, pharmaceuticals and food additives etc. Therefore, it is very important to develop the green credentials of this compound by adopting innovative greener catalytic processes which aim at converting glycerol into higher value products (Zahra Gholami, 2014).
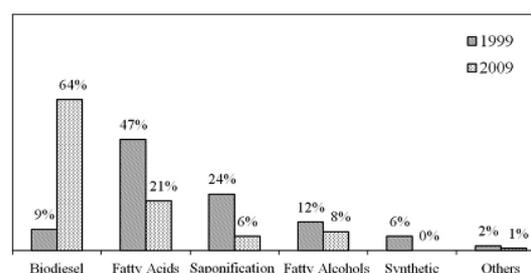
Figure 1: Changes in glycerol supply drivers from 1999-2009 (V).

From historical perspective, a lot of changes have been observed among the various sources of glycerol within 1999 and 2009. There were notable changes in the glycerol drivers since after 2003. It could be concluded from the table that fatty acid use to be the major source of supply of the crude glycerol until around 2008 when biodiesel overtook it (Zahra Gholami, 2014). It means that the utilization of glycerol should increase and new uses identified to open new markets as well.

3.1 Glycerol oversupply problem

The market supply of raw glycerol remained relatively stable until 2003, the increase in biodiesel production in the US not withstanding and thereafter its availability almost doubled but the demand remained almost unchanged (Zahra Gholami, 2014). The concurrent effect of excess supply and almost very limited demand has led to low prices.

The figure 5 below shows the global production of biodiesel and crude glycerol in recent times. Since 2006, the oversupply of glycerol has forced biodiesel producers to settle for raw product sale prices of 2 cents per pound, or even lower. As the glycerol market is limited to a few applications, investigations have shown that continual increase in biodiesel production would eventually lead to a decrease in price by almost 60% (Muhammad Ayoub, 2012).
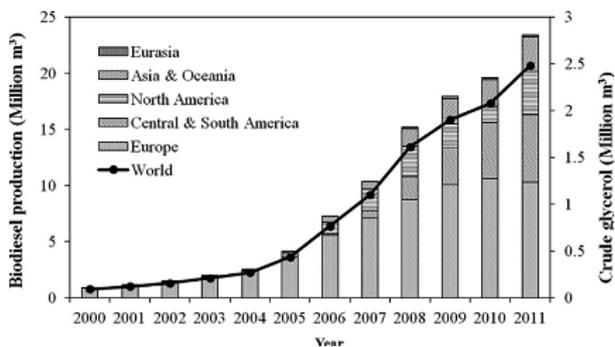

Figure 2 : World bio-diesel and crude glycerol production between 2000 and 2011 (Zahra Gholami).

In the above data, biodiesel production increased considerably along with the residues generated during

production. It shows that Europe remains the highest producer of biodiesel.

Moreover, there are limited market information available for glycerol due to its relative small scale against the global basis and also the constantly changing and small market make it difficult to predict glycerol prices in the future resulting in lack of reliable economic analysis of its application (Zahra Gholami, 2014) (Muhammad Ayoub, 2012).
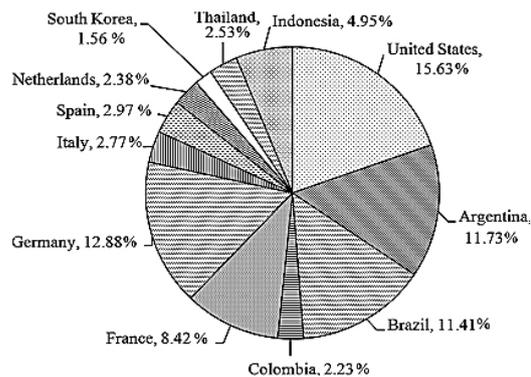

Figure 3: Top biodiesel producing countries in 2011.

There is estimation that the production of glycerol would reach 5.8 billion pounds in 2020 (Muhammad Ayoub, 2012). This is as a result of biodiesel demand which is projected at 8 billion gallons in 2020. From the figure 7 below, after the production dominance by Europe by 2006 the production rapidly increased and many other countries like USA, Malaysia, China and Indonesia went into production of glycerol. The data projected below suggests that its production will reach 4 billion pounds in 2015 if the same pace of production continues, and would likely touch 6 billion pounds by 2020 (Muhammad Ayoub, 2012).
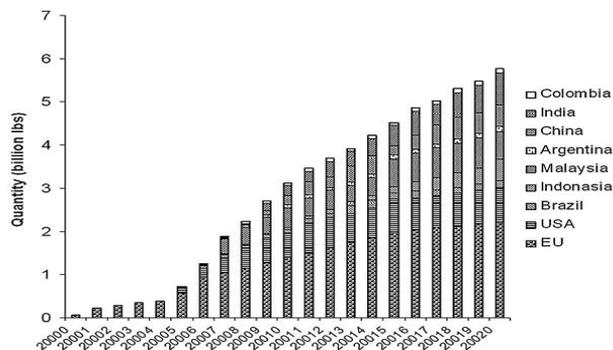

Figure 4: Estimated production of crude glycerol from different countries (Muhammad Ayoub).

In affluent economies, there was a substantial rise in the overall consumption of glycerol. In 2010 in the EU, there was an increase by 21% , to 319698 tones. Similarly, this double digit growth was recorded in the United States and SE Asia (Asia Pacific). In 2009, the SE Asia surpassed Europe as the largest supplier in 2009 (Rosaria Ciriminna, 2014).

The figure 8 below represents the change of the market price of the kosher grade of glycerol which is about 99.6% pure in the US and Europe by 2010 (Rosaria Ciriminna, 2014).
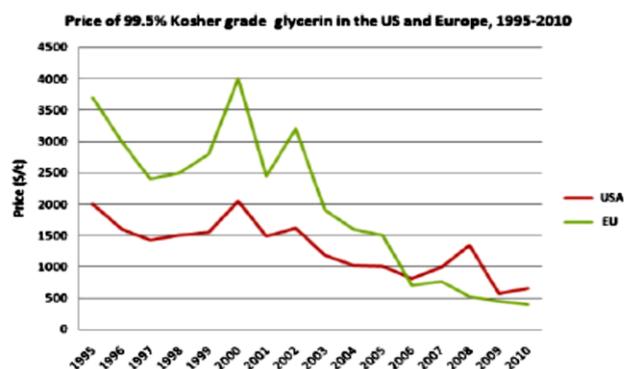

Figure 5 : Market price variation of kosher grade by 2010 in US and Europe.

The price of refined glycerol (99.5% kosher grade) decreased from about 4000€/ton in 2000 to less than 450€/ton during the early of 2010, as of then, the price of the crude or unrefined glycerol drastically fell to almost 0€/ton. In other words, it was such a waste that it could not have any economic value, which found utility in animal feed and low energy content fuel for burning. Due to this drastic fall in price, there arose a high demand for it in countries like Russia, China, India and Latin America. In these regions, it became needed in areas like pharmaceuticals, food, oral and personal care and beverages where glycerol was not used originally due to its high prices (Rosaria Ciriminna, 2014).

4. Higher Oligomers of glycerol

4.1 Polyglycerols

These are highly branched polyols, clear, highly soluble in water and quite viscous. They are also soluble in other organic solvents like methanol, they are also non-volatile at room temperature (Oudshoorn MHM, 2006). At room temperature, polyglycerol is highly viscous and

which increases with molecular weight (Zahra Gholami, 2014).

Polyglycerols are equally derived from controlled etherification of glycerol. This can be done through the anionic polymerisation of glycidol in rapid cation exchange equilibrium. Linking individual glycerol monomers is one the physical ways through which the properties of glycerol can be upgraded. Branched isomers are created from secondary hydroxyls while cyclic isomers result from the intramolecular condensation of the previous ones (Barrault J P. Y., 2002).

The table 10 below represents the properties of glycerol compared to its higher oligomers.

In the market, polyglycerol includes different oligomer mixtures which include diglycerol, triglycerol and tetraglycerol etc.

Table 2: The properties of glycerol, diglycerol and higher oligomers (Martin A).

Name	Molecular formula/weight (g/mol)	Refractivity (η_D^{20}) (-)	Density (g/cm^3)	Boiling point (^{o}C)/(Pa)	Hydroxyl number (mg KOH/g)
Glycerol	$C_3H_8O_3$ 92	1.4720	1.2560	290	1830
Diglycerol	$C_6H_{14}O_5$ 166	1.4897	1.2790	205/133	1352
Triglycerol	$C_9H_{20}O_7$ 240	1.4901 (40°C)	1.2646 (40°C)	>250/13.3	1169
Tetraglycerol	$C_{13}H_{26}O_9$ 314	1.4940 (40°C)	1.2687 (40°C)	69-73 (melting point)	1071

As the molecular weight of the oligomer increases, the density increases correspondingly with the addition of glycerol units in the chain.

The hydroxyl number generally decreases with increasing number of glycerol units. This equally results in variations to polarity, solubility, viscosity and colour from water clear to dark yellow (Martin A, 2011).

A main potential market for this substance is its ability to be transformed into polyglycerol ester. This is used as an emulsifier in the cosmetic/food and plastic industries, also another market potential of this product is that it could be used as non-ionic surfactant (Nek Mat Din NSNM, 2010). Other synthetic emulsifier that is made up of polyglycerol esters, sucrose esters and polyglycerol polyricinoleate is expected to be another market driver for emulsifiers (Zahra Gholami, 2014). But it is seemingly difficult to ascertain accurate future prices due to the rapid increase of palm oil and other vegetable oil prices (Zahra Gholami, 2014).

In the global food emulsifier market, Europe generated maximum revenue, but in the global market segment, US leads. North America is the second largest market of the segment. In the Asia-pacific market, China is the major driver with the highest annual growth rate globally. In the European market, Germany generated maximum revenue followed by Italy. Considering the rest of the world, the emulsifier market led by Brazil is given a boost by the promising growth in South Africa and the Middle East (Food emulsifiers market worth $2858.6 million by 2018, 2012).

According to this new market report, the food emulsifier market will grow from an estimated rate of $2108.9 million in 2012 to $2858.6 million by 2018, the annual growth rate being 5.2% from 2013-2018 (Food emulsifiers market worth $2858.6 million by 2018, 2012).

4.2 Diglycerol

This is clear and viscous and very similar to glycerol, but with less volatility and higher molecular weight. Its properties are more desirable than that of glycerol. Additionally, they possess some properties that are more applicable and valuable in many uses. Different methods can be adopted in the production of pure diglycerol. This could be either from glycerol itself or from other substances. All the processes that have been reported have disadvantages as they need some intermediate steps that yield much salt as by-products (Barrault J C. J.,

2004) (Zahra Gholami, 2014). The methods involved consist mostly of non-catalytic processes like allylation, hydroxylation and hydrolysis. Methods of catalysed glycerol oligomerization have been developed. Diglycerol synthesis process has equally improved with the application of some techniques which includes the use of affordable materials and equipment.

IV. CONCLUSION AND FURTHER RECOMMENDATIONS

✓ **Processes of value-added products production from glycerol**

The availability of glycerol has increased significantly as a result of the growth in the production of biodiesel (Ruppert AM, 2008). The equivalence of glycerol production is about 10% by weight of the entire biodesel produced (Khayoon MS, 2012). Consequently, this situation has given rise to surplus yield of glycerol which has adversely affected the market and drastic fall in the price of glycerol (Melero JA & Morales G, 2012). The conversion of surplus glycerol to value-added product is vital so as to utilize effectively the abundant potentials of this compound without wasting it. This would create more applicable opportunities for the compound thereby building on its green credentials, and to effectively implement this, a new, innovative and greener catalytic process is required (Zahra Gholami, 2014).

Processes involved include: Further esterification of glycerol and catalytic etherification using acid, alkali, or metal oxide base catalysts for the production of polyglycerols.

Submerged and solid state fermentation processes by combining glycerol with some other carbon sources can yield Polyhydroxyalkanoates (PHA), it could also be produced by Fermentation of hydrolysed whey permeate and glycerol liquid phase using a highly osmophilic organism (Corma A, 1998) (Abro S, 1997).

✓ **Scarce Market Sources**

One of the biggest challenges encountered is the unavailability of free and comprehensive market information. We were only able to get hold of

incomplete works, in most cases samples which were not up to date.

There is limited market information available for glycerol due to its relative small scale against the global basis and also the constantly changing and small market make it difficult to predict glycerol prices in the future resulting in lack of reliable economic analysis of its application (Zahra Gholami, 2014) (Muhammad Ayoub, 2012).

Therefore, I recommend more sustainable agro practices at homes, schools and research organisations. It would facilitate this effort.

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