EFFECT OF PH AND GLYCEROL WASTE AMOUNT ON THE GLYCEROL RECOVERY

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ABSTRACT

The objective of this research is to obtain the highest recovery of glycerol based on pH and waste volume. Usually, glycerol residue will be dumped into landfill and can give effect to the environmental pollution. The recovered of glycerol will be produced more valuable product such as for medical, pharmaceutical and succinic acid production. The glycerol residue was taken from the by product of biodiesel production. In this research, the experiment has been run with nine different pH which are from pH 1 until pH 9 and five different amount of sample used which are from 80ml until 160ml. Result from the analysis using HPLC showed that the highest recovery of glycerol was at pH 5 and 140ml of sample used. Increased in pH (after pH 5.0) and glycerol residue (after 140 ml) resulted in decreased in glycerol recovery.

ABSTRAK

Objektif kajian ini adalah untuk mendapatkan gliserol daripada sisa gliserol yang diperolehi dari kilang.Kebiasaannya, sisa gliserol akan dibuang ke tempat buangan dan ini akan memberi kesan kepada pencemaran alam sekitar. Gliserol yang diperolehi daripada sisa boleh menghasilkan produk berharga untuk tujuan perubatan,farmaseutikal dan menghasilkan asid suksinik.Sisa gliserol yang digunakan dalam kajian ini adalah daripada kilang penghasilan biodiesel.Dalam kajian ini, experimen telah dijalankan dengan Sembilan pH iaitu dari pH 1 hingga pH 9 dan lima perbezaan jumlah sampel digunakan iaitu dari 80ml hingga 160ml.Daripada keputusan analisa HPLC menunjukkan keadaan maksimum kepekatan gliserol yang diperolehi adalah pada pH5.0 dan 140ml sampel yang digunakan.Peningkatan pH(selepas pH 5.0) dan sisa gliserol (selepas 140ml) menunjukkan penurunan dalam perolehan semula gliserol.

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LIST OF SYMBOLS/ABBREVIATIONS

g	-	gram
hr	-	hour
^{o}C	-	degree Celcius
ml	-	Mililiter
min	-	minute
L	-	Liter
eg	-	Example

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CHAPTER 1

INTRODUCTION

1.1 Background of study

Glycerol waste is a largely waste in Malaysia. Usually, glycerol waste is produce from by product of the oleo chemical and biodiesel industries are potentially useful and largely waste. So, it would advantageous if its valuable components can be recovered for customer usage. Usually, glycerol residue is dumped into landfill and it can be effected to the environmental pollution. Glycerol residue is produced from soap which are obtained by saponification of triglyceride from vegetable oils or animal fats. During the saponification, triglycerides are converted by alkaline hydroxides into salts of fatty acid (soap) and glycerol (Zajic, 1988). Glycerol residue contains 20.2% glycerol,6.6% fatty acids and 64.3% salt.91.9% of it is useful (Yong *et. al.*,2001). It is obviously advantageous, both environmentally and economically, to recover the glycerol in the waste (spent soap lye) for use.

Glycerol is an abundant and inexpensive carbon source generated as inevitable by-product during the production of biodiesel (Yazdani, 2007). The tremendous growth of the biodiesel industry has created a glycerol surplus that resulted in a dramatic 10-fold decrease in crude glycerol prices over the last 2 years (Yazdani, 2007). The use of glycerol as feedstock in fermentation processes has yet another advantages such as given the highly reduced nature of carbon atoms in glycerol, fuels and reduced chemicals can be produced from it at higher yields than those obtained from common sugars such as glucose or xylose (Yazdani, 2007).

Figure 1.1 : Glycerol waste from biodiesel production process

Nowdays, the production of crude glycerol exceeds the present commercial demand for purified glycerol. Furthermore, the purification of glycerol that is generated during biodiesel manufacturing is not a viable option for the biodiesel company (Chi *et. al.*, 2007).Usually crude glycerol can be burnt, with the consequent energetic advantages, the setting up of biorefineries that co-produce products of higher economic value along with the biofuels has been proposed as a solution for the economic viability of this product. Several strategies based on chemical and biological transformation are being pursued to convert glycerol into more valuable products (Yazdani and Gonzalez,2007)

Usually, the applications of glycerol include in the manufacture of alkyd resins and flexible polyurethane for the plastic industry. It is also an important ingredient in cosmetics and adhesive manufacture. Many pharmaceutical preparations such as glycerol phenol mixture which serves as bacteriological culture medium and glycerol derivatives example is nitro glycerol used as tranquilizers utilize glycerol

Besides that, Converting glycerol into value-added products provides an alternative for glycerol disposal and for its surplus problems. Glycerol can be converted into propylene glycol and acetol (Dasari *et. al.*, 2005). It also can serve as carbon source in fermentation processes to produce various products such as 1,3 propanediol, lipid, and pigment . Anaerobic fermentation of glycerol by *E. coli* also generates a mixture of products such as ethanol, succinate, acetate, lactate, and hydrogen (Dharmadi *et.al.*, 2006).

Figure 1.2 : Purified glycerol

1.2 Problem statement

In order to avoid the by-product of the oleo chemicals and biodiesel industry in Malaysia are largely waste, it is potentially very useful to convert the large amounts of glycerol residue that are produced from glycerol refining from transesterefication process from biodiesel production to the crude glycerin. It also to avoid glycerol residue dumped into landfill and can effect to the environmental pollution such as water pollution. Besides that, glycerol residue also can cause illness and blindness. With the demand for methyl esters and biodiesel expected to increase greatly, the amount of glycerol residue generated will also rise. So, it would be convert to something that can be advantageous if its valuable components can be recovered for use. After the pre treatment process to convert to the glycerol, many valuable product can be produce such as succinic acid was produce by fermentation process of glycerol.

1.3 Research Objective

The main objective of this experiment to study the glycerol waste volume and effect of pH on the glycerol production.

1.4 Research Scope

In order to achieve the objectives, the following scopes have been identified:

i. Effect of pH at range pH1 to pH9 for highest production of glycerol recovered
ii. Effect of different volume of glycerol residue to produce maximum glycerol recovery

iii. To determine amount of glycerol waste that can be recovered from glycerol waste.

1.5 Rational and significant

This research use the by product of the industry which are very potentially useful. So, this waste of glycerol can convert another valuable component. If the glycerol waste does not treat, it can cause to environmental pollution. Another significant is, it will reduce the cost because of the price for glycerol residue are very cheap compare to commercial glycerol. Lastly, the pre treatment of glycerol waste can be increased the glycerol price because, the glycerol waste are not contain the high glycerol. So, if we purified the waste glycerol, it can increase the price in market depends on the purity. Besides that, many valuable product can be produced from the glycerol recovery such as succinic acid.

CHAPTER 2

LITERATURE REVIEW

2.1 Waste Glycerol from Biodiesel Manufacturing

The United States has been experiencing historic highs in energy prices and is now showing the desire to use greener fuels to become energy independent. Biodiesel as an alternative fuel has attracted increasing attention in recent years. While biodiesel is currently produced around the country, the process produces waste glycerol. If this waste stream can be utilized economically, the biodiesel production process will become more profitable and more prevalent.

2.2 Biodiesel

This research is based on by product of biodiesel production. Usually, biodiesel as an alternative fuel has attracted increasing interest worldwide in recent years. In the United States, for example, the biodiesel production capacity has increased sharply from less than 100 million gallon/year in 2005 to an expected 580 million gallon/year in 2007. During the biodiesel production process, oils/fats (triglycerides) are mixed with methyl alcohol and alkaline catalysts to produce esters of free fatty acids, with glycerol as a primary by-product.

Nowdays, the production of biodiesel has recently received much attention worldwide. Because of the world energy crisis (Korbitz, 1999) ,many countries have started to take a series of measures to resolve this problem(Ryan *et. al.*, 2006).Finding alternative energy resources is a pressing mission for many countries, especially for those countries lacking conventional fuel resources. In the 1930s and 1940s, vegetable oils has been used as diesel fuels in the emergency situation. With the rapid development of the modern industry, the demand for energy has been greatly increased in recent years, and therefore alternative energy sources are being explored. Thus, the term ‘‘biodiesel” has appeared very frequently in many recent reports (Fischer and Schrattenholzer., 2001).

The world total biodiesel production was estimated to be around 1.8 billion liters in 2003. Although there was no increase in biodiesel production between 1996 and 1998, a sharp increase in biodiesel production was observed in the past several years. It is speculated that the production of biodiesel will be further tremendously increased because of increasing demand for fuels and ‘‘cleaner” energy globally.

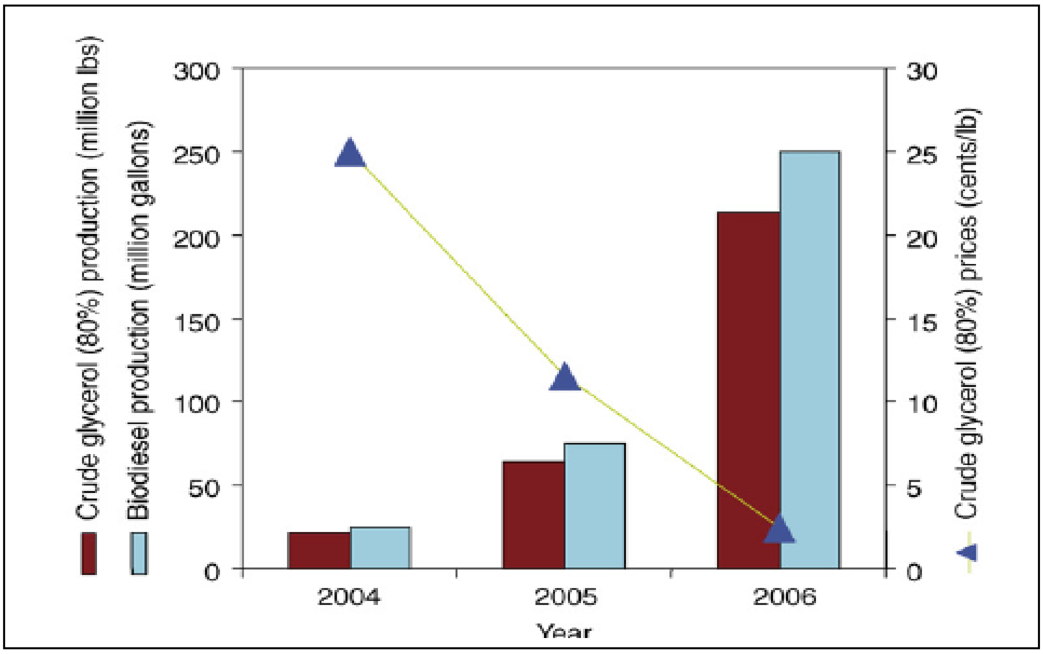


Figure 2.1 : Biodiesel production and its impact on crude glycerol prices.

Biodiesel is produced by chemically reacting a fat or oil with an alcohol, in the presence of a catalyst. The product of the reaction is a mixture of methyl esters, which are known as biodiesel, and glycerol, which is a high value co-product. The process is known as transesterification.

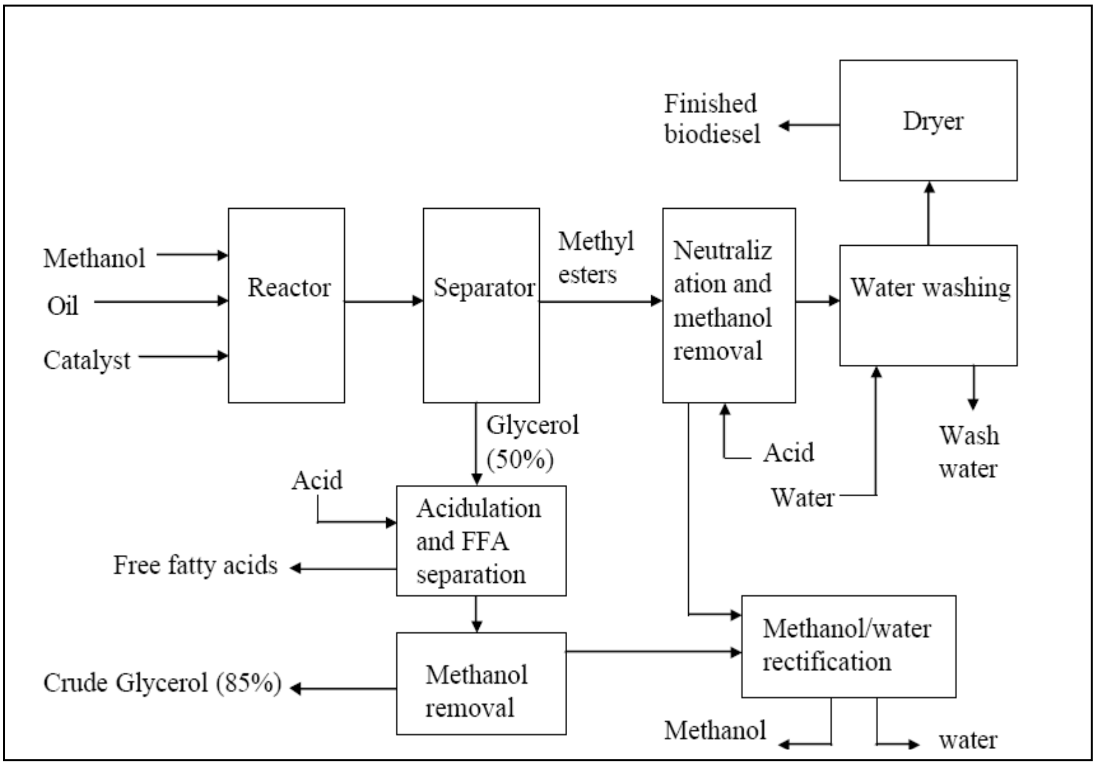
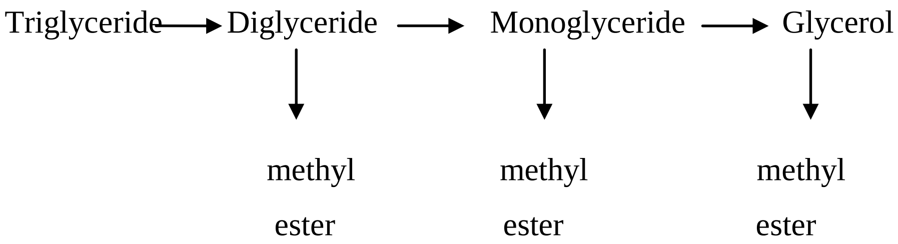


Figure 2.2: Process flow for biodiesel production

2.3 Production Process Factor

The most important issue during biodiesel production is the completeness of thetransesterification reaction. The basic chemical process that occurs during thereaction isindicated by the following sequence of events :



Firstly, the triglycerides are converted to diglycerides, which in turn are converted to monoglycerides, and then to glycerol. Each step produces a molecule of a methyl ester of a fatty acid. If the reaction is incomplete, then there will be triglycerides, diglycerides, and monoglycerides left in the reaction mixture. Each of these compounds still contains a glycerol molecule that has not been released. The glycerol portion of these compounds is referred to as bound glycerol. When the bound glycerol is added to the free glycerol, the sum is known as the total glycerol.

2.4 Free Glycerol

Free glycerol refers to the amount of glycerol that is left in the finished biodiesel.Glycerol is essentially insoluble in biodiesel so almost all of the glycerol is easily removed by settling or centrifugation. Free glycerol may remain either as suspended droplets or as the very small amount that is dissolved in the biodiesel. Alcohols can act as cosolvents to increase the solubility of glycerol in the biodiesel. Most of this glycerol should be removed during the water washing process. Water-washed fuel is generally very low in free glycerol, especially if hot water is used for washing.

2.5 Properties of glycerol

Glycerol is an organic compound, also called glycerin or glycerine. It is a colorless, odorless, viscous liquid that is widely used in pharmaceutical formulations. Glycerol has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature. The glycerol substructure is a central component of many lipids. Glycerol is sweet-tasting and of low toxicity.

Glycerol has a specific gravity of 1.261, a melting point of 18.2°C and a boiling point of 290°C under normal atmospheric pressure, accompanied by decomposition. At low temperatures, glycerol may form crystals which melt at 17.9 °C.

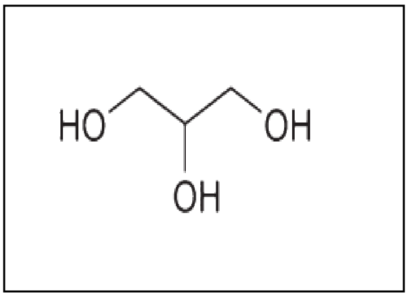


Figure 2.3: Structure Of Glycerol

Table 2.1 : Physicochemical Properties of Glycerol at 20°C

NO	ITEM	DESCRIPTION
1	Chemical Formula	$C_3H_4(OH)_3$
2	Molecular mass	92.09382 g mol^{-1}
3	Density	1.261 g cm^{-3}
4	Viscosity	1.5 Pa.s
5	Melting point	18.2°C
6	Boiling point	290°C
7	Food energy	4.32 $kcal.g^{-1}$
8	Flash Point	160°C
9	Surface tension	64 mNm^{-1}
10	Temperature coefficient	-0.0598 $mN(mK)^{-1}$

2.6 Traditional Application of Glycerol

Glycerol is used as an additive or as a raw material, range from its use as a food, tobacco and drugs additive to the synthesis of trinitroglycerine, alkyd resins and polyurethanes.

Currently, the amount of glycerol that goes annually into technical applications is around 160 000 tonnes and is expected to grow at an annual rate of 2.8% of the glycerol market, pharmaceuticals, toothpaste and cosmetics account for around 28%, tobacco 15%, foodstuffs 13% and the manufacture of urethanes 11%, the remainder being used in the manufacture of lacquers, varnishes, inks, adhesives, synthetic plastics, regenerated cellulose, explosives and other miscellaneous industrial uses. Glycerol is also increasingly used as a substitute for propylene glycol

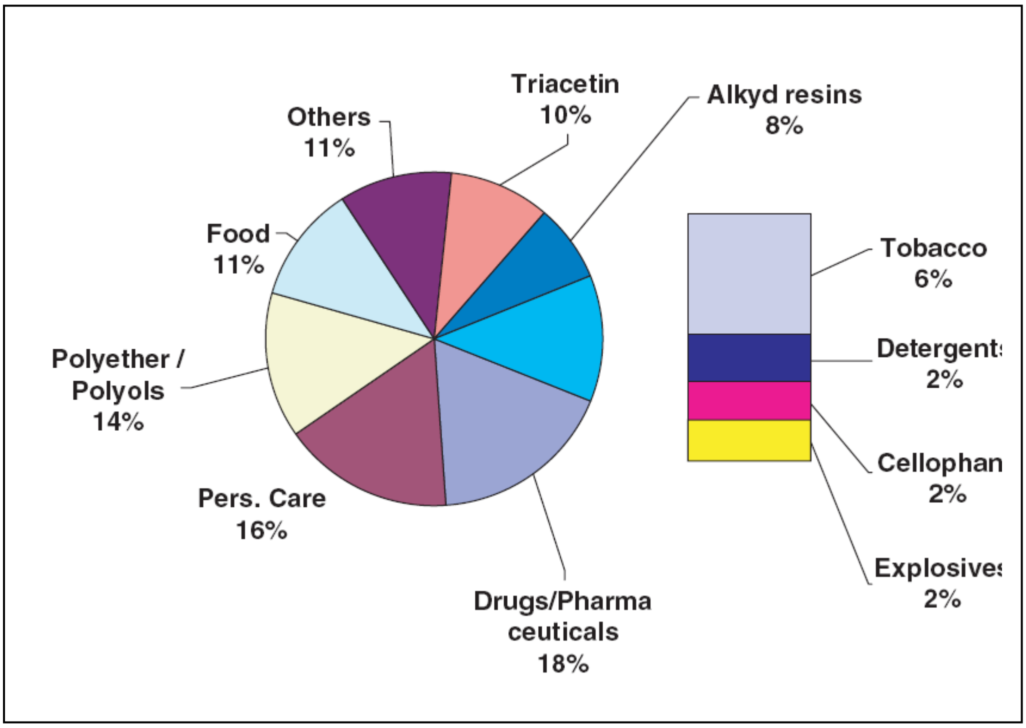


Figure 2.4: Market for glycerol (volumes and industrial uses)

Besides that, Glycerol is widely used in alkyd resins and regenerated cellulose as a softener and plasticizer to impart flexibility, pliability and toughness in surface coatings and paints.

Another application of glycerol is it can draw water from its surroundings and the heat produced by the absorption makes it feel warm. Due to this property, glycerol is added to adhesives and glues to keep them from drying too rapidly. It also acts as a solvent, sweetener, and preservative in food and beverages, and as a carrier and emollient in cosmetics. The effectiveness of glycerol as a plasticizer and lubricant gives it wide applicability, particularly in food processing, because it is nontoxic. Glycerol is also used in alkyd resin manufacture to impart flexibility.

In medical and pharmaceutical Glycerol is used as a means of improving smoothness, providing lubrication and as a humectants, that is as a hygroscopic substance which keeps the preparation moist. Glycerol helps to maintain texture and adds humectancy, controls water activity and prolongs shelf life in a host of applications. It is also widely used as a laxative and, based on the same induced hyperosmotic effect, in cough syrups (elixirs) and expectorants.

Figure 2.5: Glycerin soap

In personal care products, glycerol serves as an emollient, humectants, solvent, and lubricant in an enormous variety of products such as toothpaste, where its good solubility and taste give it the edge on sorbitol. It is because, toothpastes are estimated to make up almost one-third of the personal care market for glycerol. Related applications include mouthwashes, skin care products, shaving cream, hair care products and soaps. It is for example a component of ‘‘glycerin soap’’ (Figure 2.5), which is used by people with sensitive, easily irritated skin because its moisturizing properties prevent skin dryness.

2.7 New use of Glycerol

Chemically glycerol is a tri-basic alcohol and more correctly named 1,2,3-propanetriol. Most of the larger biodiesel producers purify and refine this crude glycerol by several steps including vacuum distillation for sale in the commodity glycerol market. Many smaller plants simply discard the glycerol by-product as a waste. A primary reason for discarding the glycerol is because refining the crude glycerol which contains residual catalysts, water and other organic impurities is too complex and expensive to handle for small scale producers in their available limited facilities. Hence, 50% of the total crude glycerol by-product that is generated is disposed of and only the remaining is sold at a very minimal price.

Today, with plenty of glycerol available to the world market, prices and U.S. exports have declined. Prices in the glycerol market will continue to drop with an over saturated market and new supplies of glycerol coming into the market from the burgeoning biodiesel industry. The price of glycerol is already (2005) about half the price of past averages in Europe where biodiesel production exceeds 400 million gallons per year. Increased biodiesel production is expected to further suppress glycerol prices. In addition, glycerol can be a platform chemical that serves as an important biorefinery feedstock, and so, conversion of glycerol to other commodity chemicals is desirable.

By converting glycerol to propylene glycol is one of the potential solutions to this problem. Propylene glycol demand is not only twice that of glycerol demand, but also the opportunity exists to market propylene glycol in the antifreeze market as an alternative to ethylene glycol. This technology also could be used in biodiesel production plants to increase profitability. The preferred technology would be to convert crude natural glycerol with high selectivity to propylene glycol at moderate temperatures and pressures.

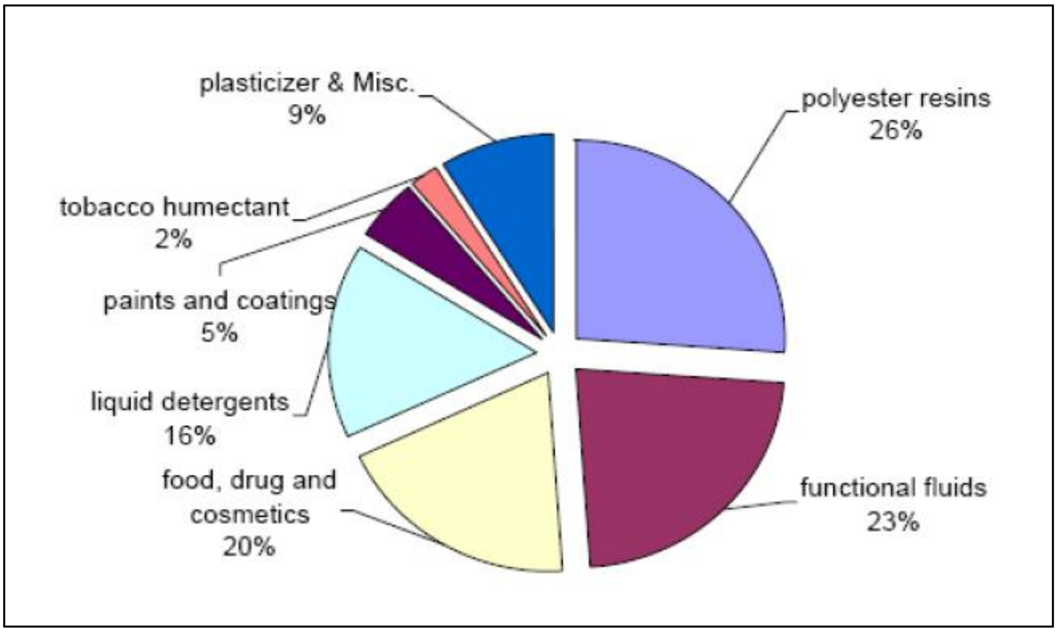


Figure 2.6 : Breakout of propylene glycol use

2.8 Glycerol residue

The oleochemicals industry in Malaysia is expanding strongly and producing an increasing array of products. However, the by-products of the industry, although potentially useful, are largely wasted. In the production of palm kernel oil methyl esters, large amounts of glycerol residue are produced from glycerol refining - about 1 t day-1 by a particular plant alone. With the demand for methyl esters and fatty alcohols expected to increase greatly, the amount of glycerol residue generated will also rise. As most of this residue is dumped in landfills, it would be advantageous if its valuable components can be recovered for use.(Yong *et. al.*, 2001).

Usually, from the research glycerol residue has been reported to contain 20.2% glycerol, 6.6% fatty acids (as soap) and 64.3% salt1. Thus 91.1% of it is potentially useful. It is obviously advantageous, both environmentally and economically, to recover the glycerol in the waste (spent soap lye) for use. The present work is aimed at practically exploiting these wastes materials from soap