# REVIEW: GLYCEROL RESIDUE AND PITCH RECOVERED FROM OLEO CHEMICAL AND BIODIESEL WASTE INDUSTRIES

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**Abstract**

The pretreatment process to recovered glycerol is a pretreatment method has been recognized as a method for environmental protection. This paper highlights the pretreatment methods to recovered the glycerol from two types and sources of glycerol waste i.e. glycerol residue from oleo chemical and glycerol pitch from biodiesel industries by pretreatment process. The purpose of this study is to explore the pretreatment potential use in glycerol waste pretreatment process. The general characterization of glycerol waste, application of glycerol waste recovered and pretreatment with operational parameters in terms pH, temperatures, ratio of solvent are thoroughly discussed in the paper. The data obtained and researchers discussed about the kinetic studies of the various pretreatments, thus giving maximum awareness about glycerol waste for further research. The future aspects for research needs are also outlined.

*Keywords*: Glycerol; Glycerol residue, Glycerol pitch, Recovered glycerol production; Glycerol waste pretreatment, pretreatment process.

## 1.0 Introduction

Currently, the development to convert agricultural wastes; oil palm wastes as energy resources are widely investigated in Malaysia. In 2008, Malaysia was the second largest producer of palm oil with 17.7 million tonnes, or 41% of the total world supply (MPOB, 2008). On the other hand, palm kernel oil normally used as a raw material for the production of oleochemicals via transesterification to produced methyl esters. By its plantation and derivative, oleochemcials industry generates by products formation including glycerol residue (Ooi *et al*., 2004b). Because of the availability of oil palm wastes or distillation bottom contained of glycerol residue, it seems to be a very promising alternative source of renewable energy.

On the other hand, the biodiesel production increasing dramatically, and it will be significantly increased quantity surplus (Lee *et al.*, 2000) of crude glycerol, significantly increase the waste for the environmental (Manosak *et al.*, 2011) and significantly increased the landfill for waste. In order to avoid the glycerol waste dumped into landfill, it will be benefits to treat the waste and produce something valuable. Consequently, the waste from biodiesel (glycerol pitch) can give indirect effects such as cause illness and blindness. Production cost is a major problem to refine crude glycerol (Johnson *et al.*, 2007). On the other hand, by recovered the glycerols from waste are low cost compare with refine crude glycerol which is affected by small and medium plant (Johnson *et al.*, 2007). Normally, glycerol waste is produced from oleo chemical industries as known as glycerol residue from bottom distillation process and from biodiesel industries as known as glycerol pitch.

Ooi *et al*., (2004) have been demonstrated, in glycerol residue contain about 20.2% glycerol and Chi *et al*., (2007) proving that from biodiesel waste, 10 % glycerol can be recovered. As a result, it is potentially benefits to produce something valuable from waste (glycerol residue) which can be converted to valuable products (crude glycerol). On the other hand, the glycerol can be converted to succinic acid by fermentation process which is by using microorganism with environmental friendly (Lee *et al*., 2001, 2002). Furthermore, the biodiesel made from vegetable oil and it is biodegradable, non-toxic, and produces low emissions of polluting gasses balance cycle on agriculture, economic and environmental need (Jansri *et al*., 2011).

In the transition to a more sustainable renewable energy usage, glycerol can be recovered from glycerol residue has attracted wide attention across the world. Glycerol residue is a promising alternative waste source to recovered glycerol with by pre-treatment method, which can be reduced the waste of industries producer.

## 2.0 Benefit and Application of Glycerol

To focus the pretreatment process to recovered glycerol from glycerol residue, the parameters are involved in the pretreatment will be considered to study the effect on the glycerol recovers from glycerol residue. Manosak *et al.*, (2011) first researcher who using activated carbon by adsorption process to remove the colour of the crude glycerol. From the studies, they get the clear colour of glycerol and this will increased the purity of the glycerol (96.2 wt %). Beside that, the recycle system of the polar solvent should be developed in order to save the cost of chemical substance utilized in chemical stage (Manosak *et al.*, 2011). In addition, the environmental costs of the disposal of the waste components and costs of acid-alkali rounds plus chemical extraction need to be explored (Kongjao *et al.*, 2010, Ooi *et al.*, 2001).

There is various glycerol application in industries reported from researchers. Table 1 shown the applications glycerol in cosmetic, pharmaceutical, automotive, food, pulp and paper, and textile industries.

**Table 1:** Application of glycerol in industries

| Application | References |
|---|---|
| **Cosmetic**<br>Polyglycerol is a useful derivative of glycerol which is extensively employed in controlled drug release and in cosmetics | Liang *et al*.,2010,<br>Wang *et al*.,2000,<br>Johnson *et al*.,2007 |
| **Pharmaceutical**<br>Propylene glycol (propanediol) which has a high global demand is a monomer for the production of polyesters. It is also used as an anti-freeze fluid, and additive in cosmetics, food and pharmaceutical formulations to cite some of its uses | Liang *et al*.,2010,<br>Wang *et al*.,2000,<br>Johnson *et al*.,2007 |
| **Automotive**<br>Epychlorohydrin is another major resin ingredient compound that is already being prepared from glycerol, by its chlorination and epoxidation. This compound is a reagent in the synthesis of epoxy resins which are useful coating materials for marine appliances, in automotive industry. | Wang *et al*.,2000 |
| **Food**<br>Monoglycerides are widely used as emulsifiers in food and cosmetic industries due to their active surfaces | Wang *et al*.,2000,<br>Johnson *et al*.,2007 |
| **Pulp and paper**<br>Glycerol used in wrapping papers to give flexibility without brittleness. | Wang *et al*.,2000 |
| **Textile industries**<br>Glycerol is used as a lubricant in various operations in the textile industry, and can be mixed with sugar to make nondrying oil. | Wang *et al*.,2000 |

### 3.0 Characterization of Glycerol Waste

Malaysia is the world's largest palm oil and palm kernel oil (Ooi *et al*., 2004). Glycerol residue was obtained from a local oleochemicals company, the waste from glycerine refining in palm kernel oil methyl ester plant resulted in bottom distillation column (DB) (Ooi *et al*., 2004). Glycerol also can obtain from the synthesis process (Song and Lee., 2006) but it would be advantageous if its valuable components can be recovered for use from pre-treatment process to recovered glycerol from waste. Glycerol residue contains 20.2% glycerol, 6.6 % fatty acids (as soap) and 64.3% salt (Ooi *et al.*, 2001). Ooi *et al.*, (2001) have found that the methyl ester plant is a good source of glycerol and rich with fatty acid which is contained C8:0 (30.3%), C10:0 (9.4%) and C12:0 (40.8%). On the other hand, that showed besides the high glycerol content (average about 20.2 %), glycerol residue can also provide a good source of short and medium chain of fatty acids.

**Table 2**: The British Standard Specification of Crude Glycerol

| Variables | Bs 2621:1979 Soap Iye Crude Glycerol | BS 2622:1979 Hydrolyser crude glycerol |
|---|---|---|
| Glycerol % | 80.0 | 88.0 |
| Ash % (max) | 10.0 | 1.0 |
| MONG % (max) | 2.5 | 1.5 |
| Water % (max) (Karl Fischer method) | 10.0 | - |
| Propane 1,3 diol (TMG)% (max) | 0.5 | 0.5 |
| Arsenic (ppm or mg $kg^{-1}$) | 2.0 | 2.0 |
| Sugars (max) | Nil | Nil |

Sources: Journal of Palm Research 13(2)

The selected parameters to determine the characteristic glycerol waste were the contents of glycerol, ash, moisture and matter organic non-glycerol (MONG) and pH. As a results, the glycerol waste from biodiesel is dark brown liquid (Manosak *et al.*, 2011; Kongjao *et al.*, 2010), high pH (Manosak *et al*., 2011; Kongjao et al., 2010), low density and viscosity (Kongjao *et al*., 2010), high content of ash, water and MONG contaminant (Kongjao *et al*., 2010). Commonly the ash content composed of organic matter (Manosak *et al*., 2011). Beside that the glycerol waste also contain various compounds such as fatty acid, methyl oleate, methyl palmitate, palmitic acid, methyl stearate, oleic acid, methyl taurate, methyl myristate, methyl palmitoleate and others component of vegetable oil (Manosak *et al*., 2011).

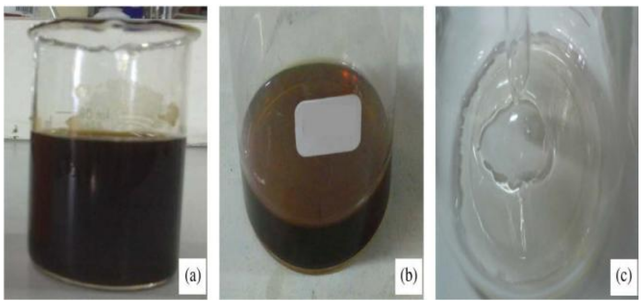


**Figure 1**: A: Crude glycerol obtained from biodiesel plant, B: Refine crude glycerol after second stage, C: Refine crude glycerol after third stage which is adsorption process using activated carbon to remove color. (Sources: Manosak *et al*., 2011)

Glycerol residue obtained from oleochemical plant which is by-product of glycerol refining from a palm kernel oil methyl ester plant, was characterized using standard test methods. It was found to contain, on average, 20.2% glycerol, 64.3% ash, 3.0% moisture, 12.4% MONG at pH 12.8. Fatty acids (6.6%) were isolated and comprised mainly C8:0 (30.3%), C10:0 (9.4%) and C12:0 (40.8%) (Yong *et al*., 2001). Yong *et al*., (2001) was using vacuum distillation to recover the glycerol from glycerol residue. The results successfully showed 141.8 g or about 14.2 % distillated glycerol was recovered from 1 kg glycerol residue. The characteristic of the distillated glycerol contained about 96.6 % glycerol, 0.03% ash, 1% water, 2.4 % matter organic non-glycerol (MONG) and pH 3.5. The physical appearance for glycerol residue was dark brown solid contain in distillated bottom.

## 4.0 Pretreatment Potential of Glycerol Waste

Glycerol waste normally from palm-based oleochemical and biodiesel industry which is growing rapidly about 70 % glycerol can be easily recovered by conventional chemical treatment from biodiesel waste (Yong *et al*., December 2001). Furthermore, esterification seems to be one of the pretreatment for glycerol waste (Hayyan *et al*., 2008) in order to reduce free fatty acid in oils and fats followed by transesterification reaction by using alkali-catalyzed to converted to biodiesel. Nevertheless, less attention had been paid to pretreatment of agricultural wastes. In fact, limited data have been found for pretreatment of oleochemicals waste. In the present study, the pretreatment of glycerol residue will be explored using rotary evaporator and vacuum distillation equipments. Table 3 has shown the comparison results from researchers to purified crude glycerol.

**Table 3:** Comparison of purified crude glycerol properties from oleochemical and biodiesel industries.

| Sources | Glycerol (%) | | Ash(%) | | MONG(%) | | Water(%) | | References |
|---|---|---|---|---|---|---|---|---|---|
| | A | B | A | B | A | B | A | B | |
| Transesterification of waste used-oil (Biodiesel) | 36.7±0.49 | 96.2±0.03 | 4.31±0.0027 | 2.08±0.06 | 44.0±0.44 | 1.50±0.07 | 14.7±0.90 | 0.06±0.02 | Manosak *et al*., 2011 |
| Transesterification of palm kernel oil (Oleochemical) | 17.7 | 51.4 | 58.7 | 13.8 | 5.9 | 8.9 | 17.7 | 25.9 | Ooi *et al*., 2001 |
| Transesterification of waste used-oil (Biodiesel) | 28.56 | 93.34 | 2.65 | 0.00045 | 56.13 | 5.16 | 6.7 | 1.5 | Kongjao *et al*., 2010 |
| Palm kernel oil (Oleochemical) | - | 20.2 | - | 64.3 | - | 12.4 | - | 3.0 | Yong *et al*., 2001 |

**A:** Initial content of glycerol and impurities in the crude glycerol
**B:** Final content of glycerol and impurities in the refined crude glycerol

Hazimah *et al.*, (2000) was using the chemical and physical treatment to recovered the glycerol from glycerol pitch which is involved extraction, filtration and distillation. Vacuum distillation is a simple process to recover the glycerol from glycerol residue (Yong *et al.*, 2001).

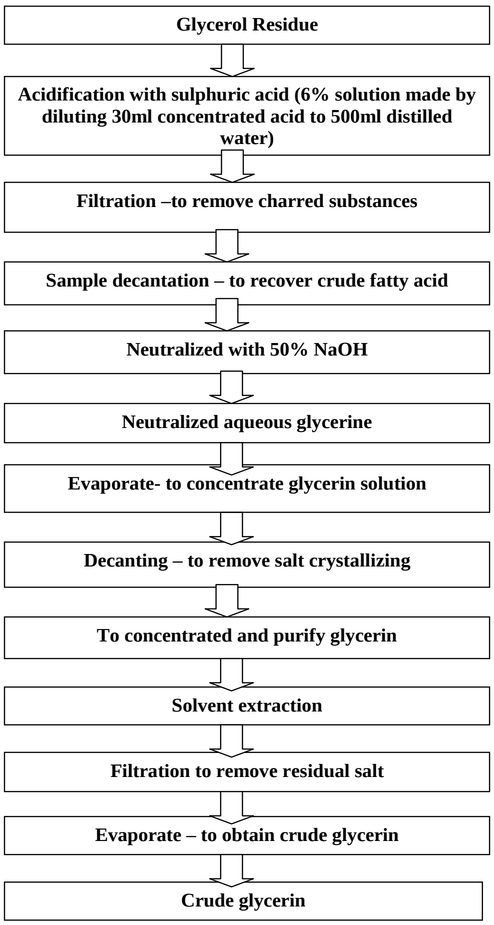


**Figure 2:** Step for Pretreatment process (sources: Malaysian Palm Oil Board (MPOB), 2001)

## 5.0 Parameters Involve in Pretreatment of Glycerol Waste

### 5.1 pH

Pre-treatment is a process to remove the contaminating substances that affecting the samples during its post-depositional history by chemical and mechanical methods. The methods are choosing are depending on size and material of the samples, the types of soiled to be removed and the performance of the sample requirements (finished product). The researchers were studies that pH (Ooi *et al*., 2001) can affect the production of glycerol from glycerol residue. The pH is an important factor that affects pretreatment process. Many researchers have been investigating the effect of pH on the pretreatment process. Increasing the pH of the acidification step led to an increased yield of the glycerol-rich layer and decreased amount of inorganic salt and free fatty acids phase. Under strong acid conditions, large quantities of fatty acid and salt in the glycerol-enriched fraction were eliminated. (Kongjao *et al*., 2010, Ooi *et al*., 2001).

Ooi et al., (2001) proving the same results with others researcher which is chemical treatment at low pH (1-2) was better as it increased the glycerol and reduced the ash contents in the recovered crude glycerol. However, the MONG content was slightly increased and the treatment also increased the recovered salt and reduced the crude glycerol but did not affect the recovery of crude fatty acids. At pH 1, high purity glycerol (~93.34%) with relatively low contaminant levels (0.00045% (w/w) ash and 5.16% (w/w) MONG) was obtained (Kongjao *et al*., 2010).

### 5.2 Operating Temperatures

To date, however, the temperatures resulted on the pretreatment process from the glycerol residue or glycerol pitch has not been reported but Hayyan *et al.*, (2011) have reported the effects of reaction temperatures in sludge palm oil via acid catalyst for biodiesel production by an esterification process, followed by the basic catalyzed transesterification process. As a results, the optimum temperatures is 60°C was found with reduction of high content of free fatty acid in sludge palm oil (reduce from 23.2% below 2%). Conversely, Jansri *et al.*,(2011) was found that the temperatures not affected the rate of free fatty acid conversion to Methyl Ester. Darnoko *et al.*, (2000) also gave same results when they studied the kinetics of methyl ester produced by the transesterification of palm oil with methanol using KOH as the catalyst. The results are when the temperatures up to 60 °C did not reduce the time to reach the maximal conversion of the rate of transesterification in a batch reactor. Foon *et al*., (2004) studied the kinetics of the base-catalyzed transesterification of palm oil based on the molar ratio of methanol to oil, the amount of catalyst, and the reaction temperature to optimize the conversion rate. Their findings showed that the reaction was carried out at 60 °C, using a 1:10 molar ratio of oil to methanol, and catalyzed by 0.125 mol $kg^{-1}$ oil NaOH to obtain the rapid formation of palm oil methyl esters (rate constant of 0.163 l mol $min^{-1}$). From the studies, the best temperatures to recovery high glycerol is at 60 °C and the implication of operating at lower temperatures does not gave the affect on the medium and the reaction and the implication at higher temperatures can make the medium changed in term of quality, pH, other control parameters and production of salt while the recovery of glycerol.

### 5.3. Ratio of Solvent

The types of solvent are affect the recovery process of glycerol. For Examples, Manosak *et al*., (2011) was using waste used-oil methyl ester plant or waste from biodiesel production to studies the effect of ratio solvent on glycerol recovers and by using three different types of polar solvent which is methanol, ethanol and propanol. As the results, they have found that at ratio 2:1 (solvent: glycerol), the glycerol-rich layer obtained after acidification stage and the best solvent gave high recovery of glycerol is propanol. On the other hand, increasing the polar solvent ratio led to slight increased in the glycerol content in the refined crude glycerol. However Hayyan *et al*., (2011) have proven that molar ratio of solvent used in the treated the sludge palm oil will reduced the free fatty acid from 23.2 % to less 2% free fatty acid using molar ratio of methanol to oil is 8:1 for 60 minutes reaction time. Otherwise the yield of ester for transesterification is 83.72 % with the process conditions of molar ratio of methanol to sludge palm oil 10:1. Similarly with Jansri *et al*., (2011) which is studied the kinetics of methyl ester production from mixed crude palm oil by using acid-alkali catalyst based on molar ratio methanol to free fatty acid (10:1), the amount of catalyzed and the reaction temperatures to optimize the conversion rate. As a results, they found that molar ratio 10:1 methanol to free fatty acid is the best ratio with reducing about (8-12 wt %/wt oil) reducing high free fatty acid in methyl crude palm oil in esterification process but for tranesterification process they found about 6:1 molar ratio methanol to the triglyceride was different compared by Hayyan *et al*., (2011) studied.

## 6.0 Conclusions

By synthesis plant process, this may lead to a situation whereby the world would be threatened by the potential hazard and environmental pollution of synthesis plants. In concern to the adverse biological effects of glycerol residue and its potential reusability, 3R (Reuse, Recycling and Reduce) concept can be implemented to overcome the issues. In addition, using the waste to produce something valuable and reduce the cost is a reasonable for researcher to overcome these valuable benefits. For example is pretreatment process from glycerol waste to recover the glycerol. In this respect, there is a promising technique to produce glycerol in one process to reduce energy and natural resources consumption simultaneously as well reducing emission and glycerol waste in form of pretreatment process.

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