

Glycerine Purification Methods research for

iLive Sustainable Development Holdings Pty (Ltd)

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# Introduction

Glycerine produced during biodiesel production is laden with methanol and caustic chemicals. This glycerine is known as crude glycerine and usually has a purity of 40-80% w/w (Raissi, 2009) (Thompson & B., 2006), the balance being water, methanol and soap.

This means that for every 100 litres of biodiesel produced 20-25 litres of crude glycerine is produced of which approximately 25% is methanol. This crude glycerine must thus be treated as a hazardous waste at all times. (Raissi, 2009). Purification of this glycerine could be an acceptable solution however it is predicted that there may be soon be an oversupply and dramatic price drop for glycerine due to an international increase in the production of biodiesel (and thus glycerine). (DT & KA, 2007)

A number of options have been investigated with regards to using glycerine for the production of different chemicals by using catalysts and biocatalysts such as 1,2-propanediol. In the past using glycerine as the primary feedstock for ethanol production as well as the production of soaps and cosmetics was limited as glycerine was expensive, yet due to the abovementioned increase in supply and decrease in price the use of glycerine for these products has become much more feasible. (DT & KA, 2007)

# The Glycerine Market

Glycerine produced in the production of biodiesel can either be purified or sold in its crude form but since purification can prove to be expensive many manufacturers opt for the latter option and sell crude glycerine to large refineries for upgrading. However due to the increased supply of crude glycerine the market price has decreased. (Wen, 2012)There have been some slight increases in certain countries due to biodiesel endeavours failing in those countries and thus they need to import glycerine for general use. Examples of this are Malaysia and Indonesia where imports of crude glycerine have seen a drastic increase in the past 2 years.

The following graph shows the average international selling prices of crude glycerine per unit (in kg) for the past 2 years converted to ZAR.

Figure 1: Graph of Crude Glycerine Selling Price Fluctuations

Purified Glycerine can however be sold at a higher price and a Biodiesel plant that is able to add the purification process to the cycle of the plant will be able to sell Glycerine in its purified form. The purification can be done in various ways the most common being distillation and ion-exchange techniques. Distillation is the most commonly used method for purifying glycerine and is an established technology that produces high-purity glycerine in high yield. Because glycerine has a high heat capacity a higher energy input is needed for vaporisation to take place, this means that the distillation of glycerine is an energy-intensive process. The Glycerine produced in biodiesel production generally has a high salt content which makes classical ion-exchange techniques highly uneconomical and thus not the preferred option for a biodiesel plant. (Lancrenon & Fedders, 2008)

The following graph shows the average international selling prices of refined glycerine per unit (in kg) for the past 2 years converted to ZAR.

Figure 2: Graph of Refined Glycerine Selling Price Fluctuations

As can be seen from the above graphs the selling price of refined glycerine was double that of crude glycerine in September this year and thus a much greater profit stands to be made if a biodiesel plant can find a way to refine glycerine at a reduced cost to the plant. Refined glycerine is also easier to transport and store as it doesn’t have the high levels of methanol found in crude glycerine so the advantages of refining the glycerine before sale is clear.

Due to said transport and storage issues with regards to crude glycerine it recommended that the sale of glycerine should be handled through a broker such as HBI. These glycerine brokers identify market trends in different countries and also understand the regulations associated with glycerine sales in the said countries and would thus provide a commercial advantage in the long run and take some strain off of the plant with regards to selling both crude and refined glycerol. (Heming)

# Glycerine Refining Processes

## Purification using acidification

Crude glycerine in its gel-like state at room temperature is melted at 55⁰C in a stirring unit while acid is added. The ideal pH should be as low as possible as the purity of the refined glycerol is increased as pH is decreased. Once at the desired pH the solution should be left to stand while 3 layers form, the best acid for use during this process is phosphoric acid as it has the lowest phase separation and precipitation times and phosphate salts obtained at the end of the process can be sold as fertiliser. (MR *et al.*, 2014)

The three layers that are formed are fatty acids at the top, glycerine in the middle and inorganic slat at the bottom. The bottom phase is removed by decanting and the fatty acid phase can be removed by funnelling through a separator funnel. (MR *et al.*, 2014)

The extracted glycerine is then neutralised using 12M KOH solution followed by evaporation at 110⁰C to remove water, the remaining precipitated salts are then removed by filtration. The end result of this process is refined glycerine of 96-98% purity. (MR *et al.*, 2014)

The following table show the expected costs and income associated with this process with operational costs excluded.

|  |  |  |  |
| --- | --- | --- | --- |
| Products formed | Price per unit (R/t) | Amount of products produced (t) | Income (ZAR) |
| Refined glycerine | 9028.8 | 1 | 9028.8 |
| KH2PO4 | 16416 | 0.4 | 6566.4 |
| K2HPO4 | 15048 | 0.8 | 12038.4 |
| Total |  |  | 27633.6 |
|  |  |  |  |
| Raw materials used | Price per unit (R/t) | Amount of raw materials used (t) | Costs (ZAR) |
| Crude glycerine | 684 | 6.67 | 0 |
| H3PO4 | 10944 | 1.07 | 11710.08 |
| KOH | 12312 | 0.2 | 2462.4 |
| Methanol | 5472 | 1.33 | 7277.76 |
| Activated carbon | 10260 | 0.07 | 718.2 |
| Total |  |  | 26730.72 |
| Gross Profit | |  | 5465.16 |

Figure 3: Table of Income and Expense associated with Purification process

The cost of crude glycerine is recorded at R0 as we assume the crude glycerine is obtained from the biodiesel production process. Methanol and activated carbon obtained from the process can be reused in the biodiesel production and glycerine refining processes.

From the above table we see that the company can expect an income of R 5465.16 for every ton of refined glycerine produced, one still needs to take operational costs into consideration before a final decision is made with regards to this process.

## Vacuum Distillation

Vacuum distillation is currently the most popular method of glycerine purification at an industrial level with modern equipment allowing for distillation at pressures below 10 mbar, thus bringing the boiling point of glycerine to less than 160⁰C. Although this method gives a high purity grade of pure glycerine the equipment is very expensive and has very high operating costs which has resulted in plants using a series of these distillation units rather than a single, robust distillation column as the method of using a series of columns results in a lower specific energy consumption. (Kovács, 2011)

Figure 4 shows a typical vacuum distillation system for fluid reclamation. Such a system typically consists of the following components:

1. Positive displacement pumps- transfer fluid to and from vaporiser. In cases where a vacuum is used to draw fluid into a unit the need for an input fluid pump is eliminated. This method reduces the fluid control capabilities and is not preferred in most large scale processes.
2. Incoming filter- removes solid contaminants and keeps distillation columns clean. Discharge filtration is often used for the final removal of solid contaminants.
3. Heating in cases where inlet fluid is not high enough to facilitate vaporisation a heat source is added to the system.
4. Distillation column- separates volatile liquids and gasses from fluid. High surface area is created with contaminated fluid allowing ready effervescent vaporisation to take place.
5. Condense- convert vapour to liquid and cools to prevent re-evaporation.
6. Vacuum pump- exhausts trace amounts of non-condensed vapour and non-condensible gasses to atmosphere (or containment for safe disposal). A variety of vacuum pumps are used depending on the properties of fluid and contaminants.
7. Gauges- for monitoring and control of the system. (Fitch, 2001)

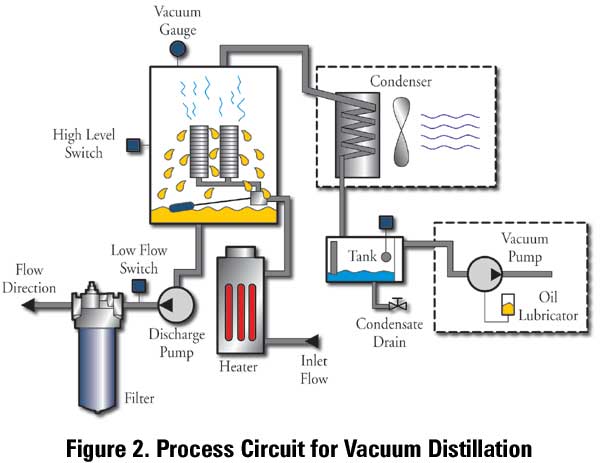


Figure 4: Process circuit for vacuum distillation

## Purification with EET corporation process

EET Corporation has developed a glycerine purification process based on High Efficiency Electro-Pressure Membrane (HEEPM™ ) technology. HEEPM™ technology uses patented and patents pending membrane units called High Efficiency Electro dialysis (HEED®) membrane units. These units are operated in integrated configurations with nanofiltration and/or reverse osmosis units in a single synergistic unit operation as seen in Figure 3. EET corp. claims that this process technology can effectively refine glycerine up to USP grade 99.7. (EET Corporation, 2011)Their process also allows for the production pf lower cost, intermediate purity grades for direct use in other processes and avoids many of the issues associated with standalone evaporation and distillation such as foaming, contamination, corrosion, limited recovery and high costs. (EET Corporation, 2011)

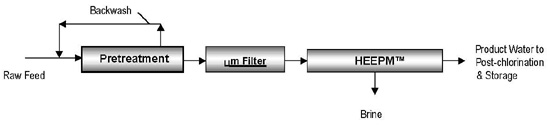


Figure 5: single synergistic unit operation for a water desalination application

HEED® maintains or lowers the feed to nanofiltration/reverse osmosis membrane elements in the HEEPM™ integrated arrangement. The result is a high permeate quality even at high overall recoveries. In addition the recycle streams from the nanofiltration/reverse osmosis membranes maintain the HEED® feed at levels providing the most efficient current utilisation and separations. (EET Corporation, 2011)

EET’s technology can be applied before or after methanol removal over a range of feed compositions. The process can purify:

* Neutralised glycerol streams containing methanol
* Neutralised glycerol streams with no methanol
* Refined glycerol which has been distilled or evaporated but still needs more treatment.

EET’s glycerine purification process begins with pre-treatment of glycerine to remove solids and fouling organics, it also partially removes colouring organics. The desalting of crude glycerine with the HEEPM™ system then results in a colourless liquid with low salt content. (EET Corporation, 2011)

The following table compares EET’s process with the popular method of vacuum distillation:

(EET Corporation, 2011)

|  |  |
| --- | --- |
| **Vacuum Distillation** | **EET Process** |
| * Well established technology for glycerine * Low recovery/yield * High capital cost * Energy intensive * Only suited to operations >30 tons/day * High maintenance * Sensitive to feed stream variations | * Production proven technology for glycerols/glycols * 95%+ recovery * Lower capital cost * Low energy use * Scalable process * Low maintenance * Tolerates feed stream variations |

Figure 6: comparison between Vacuum distillation and the EET process

# Conclusion

Refining crude glycerine shows a lot of financial potential as refined glycerine has many more buyers (a larger market) than unrefined glycerine and can also be sold at a higher price. However the potential profits vs losses have to be considered when a method of purification is selected. My assessment of the available technologies is that most of them stem from the acidification and vacuum distillation methods which are very costly, provide new problems in terms of chemical and energy waste and are not always as effective as desired. New technologies such as EET corporation’s membrane technology shows a lot of potential, would be easy to set up (the company does it for you) and may work out to be cheaper than the alternative methods.

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