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# Feasibility Study of Crude Glycerol Purification Processes

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**Abstract—***Glycerol is produced as a by- product of the transesterification of vegetable oils and fats with methanol in the presence of a suitable catalyst (Biodiesel Production Process). In this study, the economic and environmental impacts of crude glycerol purification processes (i.e. vacuum distillation and membrane separation) are studied and compared. Aspen Plus v. 8.2 is employed to obtain mass and energy balance for crude glycerol purification processes. Based on the study, it is concluded that the processes are economically profitable, when the selling price of the purified glycerol is $ 1.98/kg. Membrane process is more profitable as compared to the vacuum distillation and has less environmental impact.*

## 1. INTRODUCTION

Biodiesel is one of the most promising renewable energy (diesel substitute fuel) of this century. Glycerol is one of the major by-products of biodiesel production process. Approximately, biodiesel production generates about 10% (w/w) glycerol as the main by-product [1]. The reaction scheme is shown in Fig. 1.

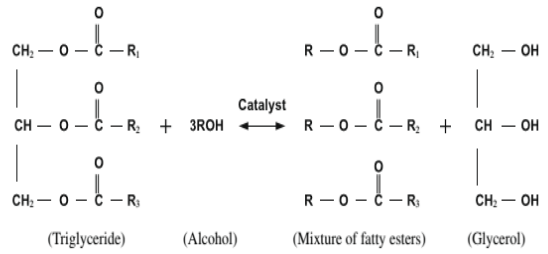


**Fig. 1: Transesterification Reaction**

Purified glycerol (>98%) are used in pharmaceutical, cosmetics and food industries. In addition, glycerol can be used in recently developed applications in the fields of animal feed, carbon feedstock in fermentations, polymers, surfactants, intermediates and lubricants. Thus, the biodiesel market economy can be improved by purifying glycerol and selling it as a valuable product. In this study, for the first time different crude glycerol purification processes are compared based on the process economics and ecological impacts.

## 2. COMPOSITION OF CRUDE GLYCEROL

A typical composition for a crude glycerol stream obtained from the biodiesel production process is as follows: 32.59 wt % methanol, 60.05 wt % glycerol, 2.62 wt % $NaOCH_3$, 1.94 wt% fats, and 2.8 wt % ash [2]. A crude glycerol extracted from sunflower oil biodiesel had a composition (w/w) of 30% glycerol, 50% methanol, 13% soap, 2% moisture, 2-3% salts (primarily sodium and potassium) and 2-3% other impurities [3]. Glycerol contents of 38 to 96% are reported by Hansen et al. [4] in a set of 11 crude glycerol samples collected from 7 different Australian biodiesel producers. Some of those samples are contained more than 14% methanol and 29% ash. Milligan Biofuels Inc. is one of the leading biodiesel producing company in Saskatchewan and also in Canada. Every year they produce approximately two million litres of crude glycerol. The typical composition of their crude glycerol is [5]: potassium hydroxide 10-30%, methanol 10-30%, glycerol 30-60%, fatty acid methyl esters 10-30%.

## 3. DEVELOPMENT OF PROCESS MODELS

Aspen Plus v. 8.2 is employed to obtain mass and energy balance for crude glycerol purification process using vacuum distillation and membrane separation. Thereafter a technical assessment is performed for the same system. All the unit operations, input conditions and operating conditions are specified during process flow sheet development. A typical crude glycerol composition of (glycerol 50%, methanol 35%, potassium hydroxide 10% and methyl oleate 5%) is used. The properties for all the components are collected from the Aspen library. As the simulation involves ionic species (Potassium hydroxide and sulphuric acid) and polar components (glycerol and methanol), electrolyte non–random two liquid (ENRTL) thermodynamic model is chosen as the base model for the simulation of the crude glycerol purification process. Since some of the binary interaction parameters are not available in the databank, they are estimated using the UNIFAC vapour-liquid equilibrium and UNIFAC liquid-liquid equilibrium. Plant capacity is specified at 6 million litres/year crude

glycerol purification. This translates to crude glycerol roughly 1000 kg/h for process configuration. The processes are designed to use vacuum distillation and membrane separation and to obtain a high quality glycerol. In all processes potassium hydroxide is neutralized using sulphuric acid. In the first process, crude glycerol is finally purified using vacuum distillation, whereas in the second process, crude glycerol is purified using the membrane separator. However, in both processes, methanol is separated using flash separation.

## 4. PROCESS DESIGN

The Vacuum distillation process flowsheet is shown in Fig. 2. The process is described with the help of stream numbers and equipment name and numbers mentioned in Fig. 2. Both Crude Glycerol/Feed and $H_2SO_4$ enter the process at atmospheric pressure and room temperature and are neutralized in a mixer tank. The reaction mixture (stream no.101) is then heated to 130$^o$C by passing through a heat exchanger. The stream is then sent to a flash separator (Flash1) and methanol and water are flashed out as vapour. The main stream (stream no. 103) is sent to a vacuum flash separator (Flash 2) to separate salt from the mixture. The stream (GLY+FAME) is then sent to a vacuum distillation column where glycerol is produced as a top product (stream no. 104). The highly pure glycerol (104) is cooled down to 25$^o$C through a cooler and then pumped through a PUMP to obtain the desired pressure of 1 atm (Table 1).

The Membrane separation process flowsheet is shown in Fig. 3. The process is described with the help of stream numbers and equipment name and numbers mentioned in Fig. 3. Both Crude Glycerol/Feed and $H_2SO_4$ enter the process at atmospheric pressure and room temperature and are neutralized in a mixer tank. The reaction mixture (stream no.201) is then heated to 130$^o$C by passing through a heat exchanger. The stream is then sent to a flash separator (Flash1) and methanol and water are flashed out as vapour. The main stream (stream no. 203) is sent to a vacuum flash separator (Flash 2) to separate salt from the mixture. The top stream (GLY+FAME) is then passed through a cooler to bring the reaction mixture into the liquid phase and then pumped through a pump to obtain the desired pressure of 5 atm. The stream (205) is brought to room temperature and then passed through a membrane separator. The top stream of the separator is rich in biodiesel and the bottom stream is rich in glycerol.

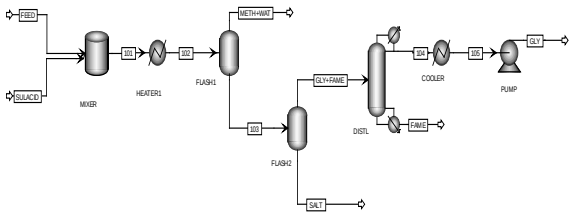


**Fig. 2: Flowsheet for Vacuum Distillation process**

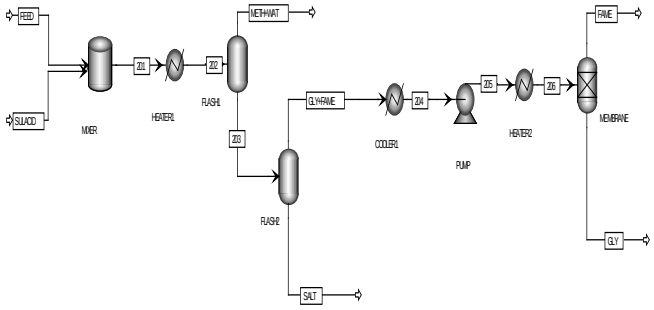


**Fig. 3: Flowsheet for membrane separation process.**

**Table 1: Feed and product stream information for the vacuum distillation process**

| | Crude Glycerol | Sulfuric acid | Product Glycerol |
|---|---|---|---|
| Temperature (°C) | 25 | 25 | 25 |
| Pressure (kPa) | 101.32 | 101.32 | 101.32 |
| Molar flow (kmol/h) | 24.10 | 10.99 | 4.76 |
| Mass flow (kg/h) | 1200 | 283.78 | 436.90 |
| Component mass fraction | | | |
| Methanol | 0.35 | 0 | 0.00047 |
| KOH | 0.1 | 0 | 0 |
| $H_2SO_4$ | 0 | 0.37 | $3.60\times10^{-8}$ |
| Glycerol | 0.5 | 0 | 0.99 |
| Water | 0 | 0.63 | 0.00072 |
| FAME | .05 | 0 | $3.61\times10^{-8}$ |

**Table 2: Feed and product stream information for the membrane separation technology**

| | Crude Glycerol | Sulfuric acid | Product Glycerol |
|---|---|---|---|
| Temperature (°C) | 25 | 25 | 25 |
| Pressure (kPa) | 101.32 | 101.32 | 101.32 |
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## 5. ECONOMIC ASSESSMENT

Both the processes are capable of purifying glycerol to a same level, so an economic assessment is done to determine process viability and determine which one is advantageous over the another. The processes are evaluated based on the profit, net present value (NPV), internal rate of return (IRR) and payback period. The assessment performed in this work is classified as a “study estimate”, with a range of expected accuracy from +30% to – 20% [6]. All the economic calculations are done within the CAPCOST spreadsheet. All parameters necessary to

determine material and energy costs are imported to a spreadsheet from the flowsheet. Costing equations are incorporated directly into the spreadsheet as well. Table 3 gives the breakdown of the capital investments of two processes. The equipment prices are estimated using Bare module method [6]. The fixed capital cost, working capital and the total capital investment are estimated using the procedure mentioned earlier [7]. The bare module cost of membrane is $\$23/m^2$ [8].

**Table 3: Equipment costs, total fixed capital costs and total capital investments ($ in millions) of the two processes**

| Equipment | Vacuum Distillation | Membrane |
|---|---|---|
| Mixer | 0.21 | 0.21 |
| Heater_1 | 0.122 | 0.122 |
| Heater_2 | - | 0.116 |
| Flash1_heat exchanger | 0.122 | 0.122 |
| Flash2_heat exchanger | 0.117 | 0.117 |
| Vessel_1 | 0.07 | 0.07 |
| Vessel_2 | 1.3 | 1.3 |
| Condensor_Distl | 0.21 | - |
| Reboiler_Distl | 0.21 | - |
| Tower | 0.092 | - |
| Cooler1 | 0.122 | 0.15 |
| Pump | 0.024 | 0.024 |
| Membrane | - | 0.0016 |
| Total bare module cost, $C_{BM}$ | 2.59 | 2.23 |
| Contingency fee, $C_{CF}$=.18 $C_{BM}$ | 0.46 | 0.4 |
| Total Module Cost, $C_{TM}=C_{BM}+C_{CF}$ | 3.05 | 2.63 |
| Auxiliary facility cost, $C_{AC}$=.3$C_{BM}$ | 0.77 | 0.67 |
| Fixed Capital Cost, $C_{FC}=C_{TM}+C_{AC}$ | 3.82 | 3.3 |
| Working Capital, $C_{WC}$=.15 $C_{FC}$ | . | |
| Total Capital Investment, $C_{TCI}=C_{FC}+C_{WC}$ | 57 | 0.49 |
| | 4.39 | 3.79 |

The capital cost for the equipments (Table 3) shows that biodiesel distillation column is the most expensive equipment. Direct manufacturing expenses are estimated based on the price and consumption of each chemical and utility. The chemical and utility prices are presented in Table 4 and material flow information is obtained from HYSYS process flowsheet. The operating labour cost has been estimated based on the number and types of equipments [6]. The detailed direct and indirect manufacturing costs are estimated following the method described elsewhere [7]. The net annual profit after tax is calculated assuming an income tax of 42%. The estimated project life is 20 years and the estimated construction period is 2 years. Based on the profit, net present value (NPV), and discounted cash flow rate of return (DCFROR) or internal rate of return (IRR), it can be concluded that membrane separation process is more economically favourable.

**Table 4: Total manufacturing cost and profit after tax of the processes**

| | Distillation | Membrane Separator |
|---|---|---|
| **Direct Manufacturing costs** | | |
| Total raw material cost ($ in millions) | 1.08 | 1.08 |
| Total utility cost ($ in millions) | 0.26 | 0.21 |
| Cost of operating labours ($ in millions) | 0.16 | 0.16 |
| Waste Treatment cost ($ in millions) | 0.06 | 0.06 |
| Maintenance and repair(M&R), 6% of $C_{FC}$ | 0.2256 | 0.1936 |
| Operating supplies, 15% of M&R | 0.03384 | 0.02907 |
| Lab charges, 15% of operating labour | 0.024 | 0.024 |
| Patents and Royalties | 0.11 | 0.11 |
| **Indirect Manufacturing costs** | | |
| Overhead packaging and storage | 0.096 | 0.096 |
| Local taxes, 1.5% $C_{FC}$ | 0.0564 | 0.048 |
| Insurance, 0.5% $C_{FC}$ | 0.0188 | 0.016 |
| Depreciation, 10% | 0.376 | 0.323 |
| Administrative costs | 0.024 | 0.024 |
| Distribution and selling | 0.38 | 0.38 |
| R&D | 0.19 | 0.19 |
| Total Manufacturing costs ($ in millions) | 3.09 | 2.94 |
| Revenue from sales ($ in millions) | 7.58 | 7.58 |
| Net annual profit ($ in millions) | 4.48 | 4.63 |
| Annual taxes, 42% | 1.885 | 1.94 |
| Net annual profit ($ in millions) | 2.60 | 2.69 |
| Discounted Payback Period (DPBP) (years) | 1.6 | 1.4 |
| Net Present Value (NPV) (millions) | 15.32 | 16.31 |
| Internal rate of return (IRR)% | 51.12 | 58.76 |

## 6. ECOLOGICAL IMPACT ASSESSMENT

Ecological impact of the two processes was assessed and compared based on the potential environmental impact index (PEI) and the process efficiency. The PEI index provides a relative indication of the environmental friendliness or unfriendliness of the process across the system boundary. The WAR software is used to calculate the PEI indexes and the PEI indexes with lower score indicates more environmental friendliness. The impact analysis indicates that membrane process is more environmentally friendly compared to vacuum distillation (Table 5).

**Table 5: Toxicity Index comparison of the two processes**

| | Vacuum Distillation | Membrane Separator |
|---|---|---|
| Human Toxicity Potential by Ingestion (HTPI) | 2.26 | 1.75 |
| Human Toxicity Potential by Exposure (HTPE) | 0.52 | 0.0014 |
| Terrestrial Toxicity Potential (TTP) | 2.26 | 1.75 |

| | | |
|---|---|---|
| Aquatic Toxicity Potential (ATP) | 0.87 | 0.30 |
| Global Warming Potential (GWP) | 0.63 | 0.22 |
| Ozone Depletion Potential (ODP) | $6.62\times10^{-06}$ | $2.33\times10^{-06}$ |
| Photochemical oxidation potential (PCOP) | 10.3 | $8.12\times10^{-05}$ |
| Acidification Potential (AP) | 19.5 | 6.87 |
| **Total (PEI/h)** | 36.3 | 10.9 |

The process energy efficiency is calculated by dividing the raw materials energy to product energy.

$$Energy\ Efficiency = \frac{\text{Energy of the Products}}{Energy\ of\ the\ raw\ materials\ + Input\ Energy} \times 100\%$$ The Process Efficiency obtained from the vacuum distillation and membrane separation is 30% and 35.20 % respectively.

## 7. CONCLUSIONS

From the process simulations and economic and environmental impact study of the two processes: Vacuum distillation and Membrane Separation, it is obtained that membrane separator is more profitable. It is also more environmental friendly as its toxicity index is the lowest and more energy efficient than vacuum distillation.

## 8. ACKNOWLEDGEMENTS

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## REFERENCES

[1] Sdrula, N. (2010). Desalination. 250, 1070–1072.

[2] J.A. Posada, C.A. Cardona, Validation of glycerin refining obtained as a by-Product of biodiesel production, Ingeniería y Universidad, 14, pp. 2-27 (2010).

[3] Hansen, C.F., Hernandez, A., Mullan, B.P., Moore, K., Trezona-Murray, M., King, R.H. and Pluske, J.R. A chemical analysis of samples of crude glycerol from the production of biodiesel in Australia, and the effects of feeding crude glycerol to growing-finishing pigs on performance, plasma metabolites and meat quality at slaughter. Anim. Prod.Sci., 49: 154-161 (2009).

[4] Isahak, W.N.R.W., Ismail, M., Yarmo, M.A., Jahim, J.M. and Salimon, J. Purification of crude glycerol from transesterification RBD palm oil over homogeneous and heterogeneous catalysts for the biolubricant preparation. J. Appl. Sci., 10: 2590-2595 (2010).

[5] MSDS sheet, Crude unstrapped glycerol, Milligan Biofuels Inc. Canada

[6] R. Turton, R. C. Bailie, W. B. Whiting, J. A. Shaeiwitz, D. Bhattacharyya, Analysis, Synthesis, and Design of Chemical Processes, 4th ed. Prentice Hall, Upper Saddle River, New Jersey, USA, pp. 164-310 (2012).

[7] A. H. West, D. Posarac, N. Ellis, Assessment of four biodiesel production processes using HYSYS. Plant, Bioresouce Technology 99 6587-6601 (2008)

[8] J. Arvid Lie, T. Vassbotn, M. Hagg, D. Grainger, T. Kim, T. Mejdell. Optimization of a membrane process for $CO_2$ capture in the steelmaking industry. International Journal of Greenhouse Gas Control, 1(3), 309-317 (2007)