Journal of Engineering Science and Technology
Vol. 11, No. 8 (2016) 1056 - 1072

PURIFICATION OF CRUDE GLYCEROL FROM INDUSTRIAL WASTE: EXPERIMENTAL AND SIMULATION STUDIES

WAN NOR ROSLAM WAN ISAHAK[1,*], JAMALIAH MD JAHIM[1],
MANAL ISMAIL[1], NURUL FITRIAH NASIR[2], MUNEER M. BA-ABBAD[1],
MOHD AMBAR YARMO[3]

[1]Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, Malaysia
[2]Faculty of Mechanical Engineering and Manufacturing, Universiti Tun Hussein Onn Malaysia, Batu Pahat, Johor, Malaysia
[3]School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia
*Corresponding Author: wannorroslam@ukm.edu.my

Abstract

In this study, the purification of crude glycerol as a by-product of transesterification reaction was investigated. The first purification stage of the crude glycerol was achieved by employing the neutralization method, followed by microfiltration using 0.45μm filter membrane. Only glycerol peak could be detected by high performance liquid chromatography analysis which indicating that the neutralization step enabled to removal of excess homogeneous catalyst as well as the unreacted free fatty acids from crude glycerol samples. However, the free ions from salt and catalyst were then eliminated through an ion exchange process using two types of Amberlite resins to produce higher glycerol purity up to 99.4%. The purity of glycerol was confirmed by the other analysis such as the Fourier transform infrared, United States Pharmacopoeia and American society for testing and materials methods. The simulation studies were applied using Super-Pro-Designer 7.0 software which can provide the data for scale up to industrial scale. The P2 and P5 simulation process gives a higher purity of pure glycerol of 98.35 wt. % and 99.27 wt%, respectively were generated after through several combinatorial purification steps. The combination between the experimental and simulation process showed a good way to investigate the laboratory experiment input for possible industry scale in future.

Keywords: Glycerol, Industrial scale, Ion exchange resin, Process design.

1. Introduction

Glycerol (IUPAC name 1,2,3-propanetriol, $C_3H_8O_3$) is typically produced from transesterification of vegetable oil with alcohol over an acid or base catalyst. In this process, crude glycerol is the principal by-product of biodiesel production [1-3]. Generally, 10% glycerol and 90% biodiesel would be produced from the transesterification process as shown in Fig. 1.

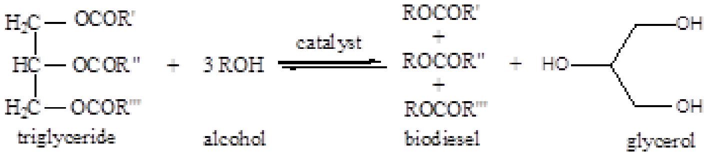

Fig. 1. Stoichiometric equation of the transesterification process for biodiesel and glycerol production.

Crude glycerol requires a series of purification steps before converting it into valuable products that is by removing the impurities such as excess catalyst, soap, free fatty acids and matter organic non-glycerol (MONG). Currently, purification technologies were deemed expensive and complex [4]. As a result, many researches have been conducted to produce cost-effective pure glycerol from the organic production using neutralization, filtration, evaporation, vacuum distillation and ion exchange resins among other processes [4, 5].

The combined method which is integration of two or more separation technique has gained much attention. Hydrochloric and sulfuric acids are commonly acids used in neutralization of crude glycerol to reduce the amount of soaps that adversely impact the separation which leads to a loss of yield [6]. Neutralized glycerol can be further purified to 99.5% using a combination of purification techniques such as adsorption, vacuum distillation as well as ion exchange processes [7]. After the removal of methanol by evaporation or vacuum distillation stage, the purity of glycerol reached to approximately 85%. The fatty acid salts and micro size particles in crude glycerol can be separated using microfiltration technique which working more efficient in pore size of filter in range of 1.10^{-6} to 1.10^{-8} m [5]. This purification technique would assist in producing high quality glycerol with a minimum loss of glycerol [8, 9].

In this study, the combinatorial methods were applied in the purification of crude glycerol from industrial wastes. The simulation studies were carried out for upscaling of laboratory data. The crude glycerol was neutralized by strong acid namely phosphoric acid to separate the fatty acid content and excess catalyst. The process followed by microfiltration and ion exchange steps. The effect of unit operation in purification system would be discussed on the basis of glycerol purity.

2. Materials and Methods

2.1. Materials

Crude glycerol (CG) based on homogeneous catalysts was collected from biodiesel plant located in west peninsular Malaysia. CG was initially treated to check for any existing methanol by running the sample in the evaporator. No methanol condensate appeared in the CG sample, therefore was concluded to be almost free from methanol. Pure glycerol reference material (PG) was purchased from Merck, Germany, with the purity content of 99.9%. The phosphoric acid (85% v/v) and methanol were supplied by Sigma Aldrich, Germany. Sodium hydroxide (NaOH) was purchased from SYSTERM.

2.2. Crude glycerol purification

2.2.1. Neutralization

A 5 mL of crude glycerol sample as a by-product of homogeneous catalytic transesterification was prepared in test tubes. The sample was titrated with phosphoric acid 85% (v/v) and monitored by pH meter until reached to 7 [10]. The amount of phosphoric acids necessary for crude glycerol neutralization was also recorded for each sample.

2.2.2. Filtration

The inorganic salts such as sodium phosphate from homogeneous reaction and other fatty acid salts that formed in neutralization stage were removed by 0.45 μm filter.

2.2.3. Ion exchange resins method

Ion exchange resins type Amberlite IRN-78 was purchased from SUPELCO and Amberlite 200C from Sigma Aldrich were added into the neutralized crude glycerol samples for free ions removal. Ion exchange process was performed by column technique where the resins were placed in a vertical column chromatography to form a bed. Silica beads were also packed inside the column to remove any excess moisture content in the sample. These two types of ion exchange resins would adsorb the free anions and cations in treated crude glycerol. After the ion exchanges process completed, the used resins were then regenerated by washing under a flow of diluted sodium hydroxide (NaOH) for Amberlite IRN-78 and diluted sodium chloride (NaCl) for Amberlite 200C. All purification steps of crude glycerol based on homogeneous catalyst were summarized in Fig. 2.

2.3. Characterization of glycerol stream

The purified crude glycerol samples were characterized using USP 26 and ASTM standard methods as follows: (1) USP 26: Determination of glycerol content [11] (2) ASTM D0482-03: Determination of ash (3) ASTM D0240-02: Test method for heat of combustion by Bomb Calorimeter (4) ASTM D 1093-98: Acidity test and (5) ASTM D4377-00E01: Determination of moisture content [12]. The high performance liquid chromatography (HPLC) was used to measure of glycerol purity. The HPLC column Dionex C18 type with mobile phase of acetone and acetonitrile, flow rate at 1 mL/min) which ELSD detector were applied for 30 min of run time.

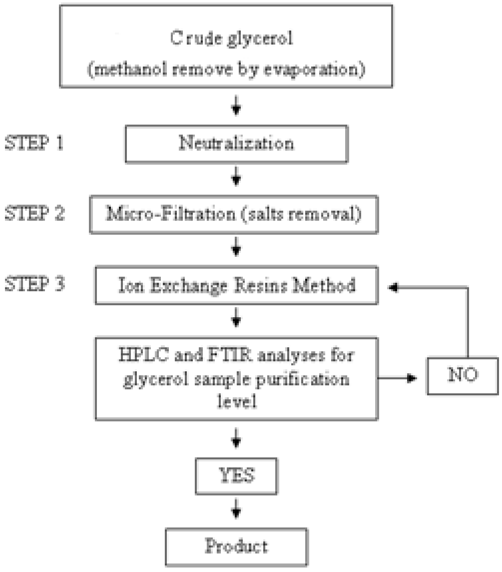

Fig. 2. Flow diagram of crude glycerol purification process.

2.4. Simulation studies

Simulation processes was conducted using Super-Pro-Designer 7.0 software focusing on crude glycerol purification process from transesterification reaction of vegetable oil. The procedures for developing of simulation process based on Super-Pro-Designer 7.0 simulator were selected with chemical components for the process. The proposed flowsheets for biodiesel and crude glycerol production, biodiesel purification and crude glycerol purification will be discussed in section 3.2.

2.4.1. Chemical components

Super-Pro-Designer 7.0 library contains information for the following components that wants to apply in the simulation: methanol, glycerol, sodium hydroxide, phosphoric acid and water.

2.4.2. Thermodynamic model

For each pure component, the SuperPro databank was provided the thermodynamic properties such as molecular weight, critical pressure and temperature, Acentric Factor, vapour pressure, density, specific heat, particle size, and etc. Note that a new component such as biodiesel is not listed in the library. However, it can be easily registered in the library by inserted the biodiesel main properties such as molecular weight and normal boiling point. Other that, the critical properties can be added such as the temperature, pressure, compressibility factor and Acentric Factor (ω). Besides that, other properties can be introduced for the new component such as density, saturated vapor pressure (Antoine data), heat capacity and heat of vaporization.

2.4.3. Plant capacity, unit operations and operating conditions

The Superpro has provided an easy way to simulate the plant processes. The users just need to give the inputs to unit procedures and fix their operating conditions based on the experimented process in the laboratory. The capacity of plant, feed and products stream was determined using this simulation software.

3. Results and Discussion

3.1. Glycerol characterization

Crude glycerol samples before, after purification and commercial pure glycerol (PG) were analyzed using HPLC. The single glycerol peak of chromatograms results for the purified crude glycerol compare to commercial PG was observed. The HPLC results showed only one peak detected which attributed that purify crude glycerol sample was free of impurities such as excess catalyst, free fatty acids, methyl esters, triglyceride, diglyceride and monoglyceride after neutralization stage. However, excess methanol in crude glycerol sample was removed by evaporation stage. Additionally, impurities in the neutralized glycerol samples were only contained inorganic salts and free ions from salts and catalyst. Removal of these impurities once microfiltration and ion exchange resins methods were also employed.

The crude glycerol (CG) before and after purification were also analyzed using FTIR to determine the functional groups and classes of glycerol compounds with their absorption frequencies in the infrared. In general there five stretches and bands detected in glycerol that included –OH stretch, -C-C-H bend, -C-H stretch, -C-O stretch and -CH_2-OH band were obtained for crude glycerol and commercial. FTIR analyses of commercial and crude glycerol before and after neutralization and filtration as well as after step 3 were carried out in range of wavelength 500 to 4500 cm^{-1} as shown in Fig. 3. In CG sample, -COO^- functional group was detected at frequency 1556.6 cm^{-1} which indicated the impurity comes from fatty acids salt traces as resulted from reaction of the catalyst with free fatty acid. As the sample underwent steps 1 and 2, such impurity could be minimized and subsequently fully removed once ion exchange resins method (i.e. step 3) was employed.

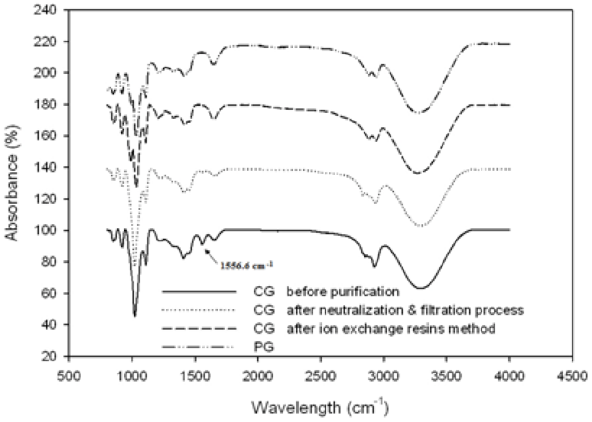

Fig. 3. Analysis of FTIR for CG sample before and after purification steps.

The fatty acids salt, detects in CG sample in step 1 and step 2 at frequency 1557.2 cm^{-1} and at a very low absorbance percentage of 2 % was totally eliminated after step 3. This result was due to the fact fatty acids salt traces in glycerol were presented by adsorbs at the anion exchange resins. In addition, the free ions from inorganic salts were also adsorbed by cation exchange resins.

3.1.1. Acid and ion exchange resins usage

The volume and weight of phosphoric acid and ion exchange resins are needed in purification of CG was shown in Table 1. About 32% of phosphoric acid used to neutralize the basic components in CG samples. There were 2.5g of ion exchange resins can be exchange of free ions in the samples as well. It was included anionic and cationic resins works to purify and remove the free cations and anions from catalyst leaching during the stirring process in reaction and acid treatment.

Table 1. Volume and weight amount of phosphoric acid and ion exchange resins required in CG purification process.

Quantity	Values
H_3PO_4 (mL)	1.6
Ion exchange resins (g)	2.5

3.1.2. Standard test method for glycerol characterization

Other characterization tests including ASTM and USP methods were carried out to determine the viscosity, pH value, free fatty acid value [13], moisture content, ash content and MONG percentage of CG before and after purification. All of these characterizations were compared with commercial pure glycerol (PG) as summarized in Table 2. The pH value of CG is dissimilar to PG sample due to neutralization of basic excess or leaches catalyst in the sample.

The results also showed the CG contains high ash content. By applying the filtration method, the value was decrease significantly as well as MONG content [4]. It could also be deduced from Table 2 that purified CG showed nearly achieve the technical grade as PG based on the physical properties according to the standard methods. Silica beads enabled the reduction of moisture level in the crude glycerol of 25 % to 0.25 % of the final level of purified glycerol.

3.2. Process design and simulation studies of glycerol purification process

To achieve technology suitability, mass and energy balance, a complete simulation process of purification was conducted. Simulation processes involves Super-Pro-Designer 7.0 software was focused on CG recovery from transesterification reaction process. The suitable unit operation uses in the simulation were selected based on the carried out experimental. The important parameters such as reaction temperature, inlet flow rate and reaction time were applied as similar to experimental conditions. The same mass composition for CG in experimental was used in simulation processes as given in Table 3.

Table 2. Characterization of CG before and after purification and the comparisons to a commercial PG.

Parameters	Before	After	Commercial PG
Glycerol content (%)	77.400	99.400	99.800
Viscosity (dP) at 40 ºC	50.500	99.600	105.500
Free fatty acid value (%)	0.840	0.100	0.050
Moisture (%)	2.500	0.250	0.150
Density at 27 ºC (g/mL)	1.230	1.250	1.260
Ash content (%)	2.400	0.007	0.002
pH value	11.120	6.740	6.70
MONG* (%)	17.700	0.300	0.050
Gross energy (cal/g)	3685.000	5810.300	5832.500

*MONG: matter organic non-glycerol. Defined as 100-[glycerol content (%) + water content (%) + ash content (%)].

Table 3. Mass composition of input flow for crude glycerol.

Input flow	Mass composition (%)
Biodiesel	1.97
Glycerol	19.24
Methanol	76.94
Palm oil	0.10
Sodium hydroxide	1.75

3.2.1. Simulation unit operation

The selected unit operation such as glycerol storage tank, neutralization reactor, microfiltration, ion exchange resin column, centrifuge and distillation column were used in the simulation. The operation condition for all unit operation was set up before mass equivalent balances.

3.2.2. Biodiesel and glycerol production

Two new molecules that create in the simulation, namely palm oil and biodiesel were added to the process. The properties of palm oil and biodiesel as raw material and product respectively, were reported in Table 4.

Table 4. Properties for hypothetical molecules creation.

Properties	Substances	
	Palm Oil	Biodiesel
Molecular weight (g/mol)	885.46	296.49
Critical temperature (K)	1366.83	490.85
Critical pressure (bar)	4.70	12.36
Compressibility Factor	0.1070	0.2140
Acentric factor (omega)	-	1.0494

In addition, the unit operations of biodiesel and glycerol synthesis processes were included of pump, materials storage tank, mixer, flow separation, heating, two reactor and centrifuge. The parameters and condition data of the simulation process were shown in Table 5. In Fig. 4, the transesterification reaction was conducted in CSTR reactor and catalyzed by sodium hydroxide (NaOH). After 3 hours reaction, the biodiesel conversion is around 99.54 wt.%. From reactor 2, the biodiesel was successfully recovered by 98.1% with final purity of 99.8%, while, the CG was recovered from both reactor (reactor 1 and 2) with the relatively high purity of 77%.

Table 5. Summary of unit operating condition for biodiesel and CG production.

Parameters	Conditions data
Catalyst	Sodium hydroxide (NaOH)
Reactor	CSTR
Reaction temperature (°C)	64.75
Pressure (psi)	64.696
Molar ratio methanol to oil	15:1
Residence time (hR)	3
Conversion (%)	99.54

3.2.3. Crude glycerol purification

The CG purification section was carried out in the packed reactor with mixing of three sources of glycerol. There were three major stages applied in glycerol purification process which were included of neutralization using phosphoric acid, centrifugation/filtration and ion exchange resins chromatography. The purity of glycerol was achieved in P5 simulation process which was up to 99.27 wt.%, because combination of three steps during purification process. It was noted that the combination steps of purification glycerol (PG) could be achieved the high purity level of glycerol. The PG is considered higher than develop universal method including saponification, phase separation and biphasic extraction as reported by Xiao et al. [14]. The units operating conditions for all process (P1 to P5) were summarized in Table 6.

Table 6. Summary of units operating conditions for different process design of glycerol purification.

Parameters	P1	P2	P3	P4	P5
Recovery (%)	92.36	92.36	92.72	89.75	99.98
Product stream flowrate (MT/year)	89.75	533.10	535.28	508.19	577.08
Total mass flow (MT/year)	91.25	541.15	614.37	532.90	581.35
Final purity (%)	98.35	98.35	87.13	97.22	99.27

For simplification purposes the process was split into five different simulations for glycerol purification processes such as P1, P2, P3, P4 and P5 process as shown in Fig. 5 to 9. A Super-Pro section is simply a set of unit procedures (processing steps) of production and purification process. The process flow diagram for crude glycerol purification from transesterification reaction in lab scale (P1) is depicted in Fig. 5. The scale up of purification process to industrial scale with six times enlargement (P2) was designed as shown in Fig. 6. Same simulation equipment's were used in P1 and P2 process. The conventional purification process (P3) includes combination of centrifugation, neutralization and vacuum distillation process were given the lower purity of glycerol as 87.13 wt% which the process shown in Fig. 7.

Figure 8 showed (P4) the upgrading of conventional process with a suggestion of microfiltration technique was significantly to increase the glycerol purity up to 97.22 wt%. It means that the microfiltration showed the good ability to separate the micro size sediment or inorganic impurities from glycerol. Furthermore, from P5 simulation process as in Fig. 9, the purity of glycerol was achieved up to 99.27 wt.% of mass composition. It was influenced by combination of three steps such as centrifugation, ion exchange resin and vacuum distillation. From simulation studies, the amount of glycerol was 3000 MT/year for purification process. Indeed, the plant capacity for products stream was about 581 MT/year of purified glycerol and recovery of methanol with 2303 MT/year.

From overall, P4 process gives a lower recovery of glycerol with 87.75 wt.% which indicates that glycerol was loose during centrifugation and microfiltration. From stream S-106 (Fig. 8) and S-115 in Fig. 7, about 7.27% and 3% of glycerol was loss, respectively. Also P5 process could be gave a higher purity of glycerol after purification process with higher recovery of 99.98%.

3.2.4. Methanol recovery

For methanol and water removal purpose, the simulation processes of P3, P4 and P5 which using distillation column were compared with that using evaporator in P1 and P2 process. For methanol distillation in P5 process gives the higher recovery as 99.79% of methanol with high product stream flowrates of 2303.35 MT/year. Effects of column pressure on methanol recovery under different unit operating conditions with stage efficiency of 80% for all process were summarized in Table 7.

Table 7. Summary of unit operating conditions for methanol recovery in P3, P4 and P5 processes.

Parameters	P3	P4	P5
Reflux ratio	0.125	0.125	1.700
Number of theoretical stages	12	12	5
Column pressure (psi)	14.7	14.7	15.00
Recovery (%)	92.6	92.6	99.79
Product stream (MT/year)	2138.1	2138.1	2303.35
Percent in distillate (%)	99.90	99.90	99.99
Stage efficiency (%)	80	80	80

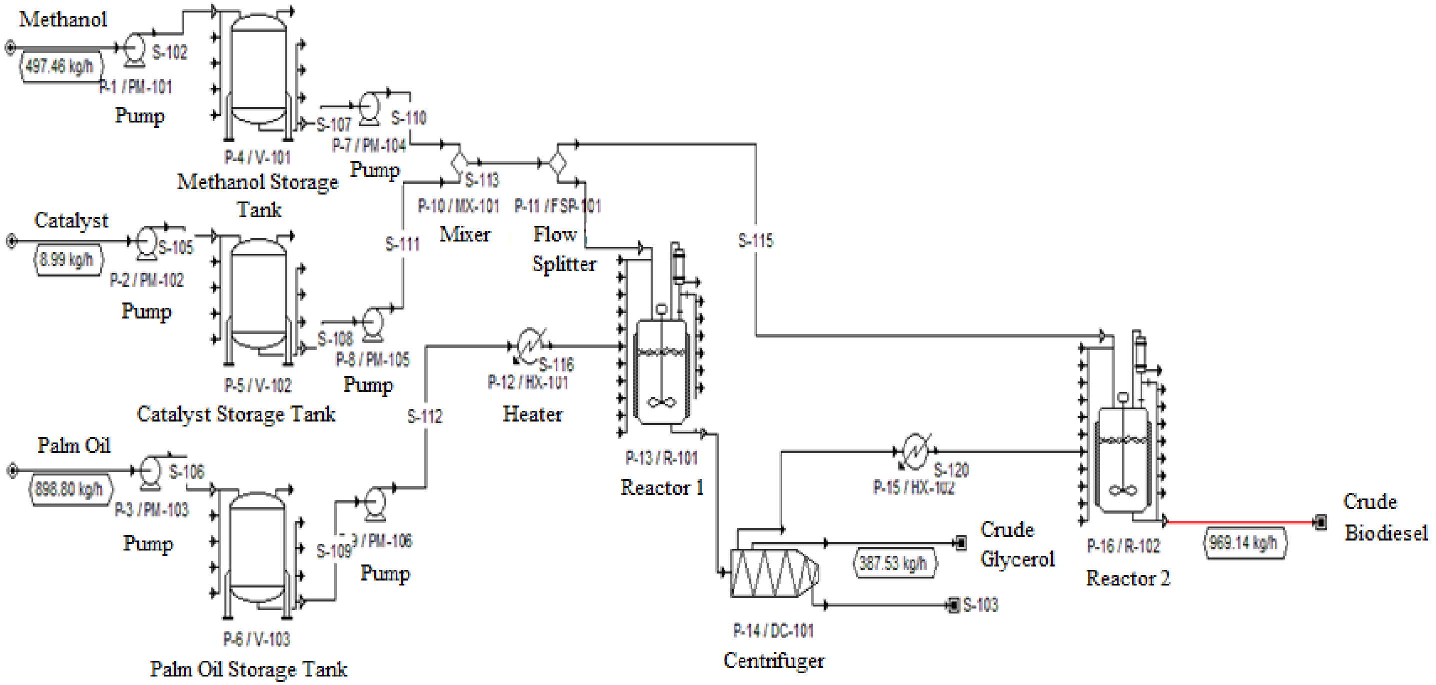

Fig. 4. Process flow of crude biodiesel and glycerol production from transesterification reaction.

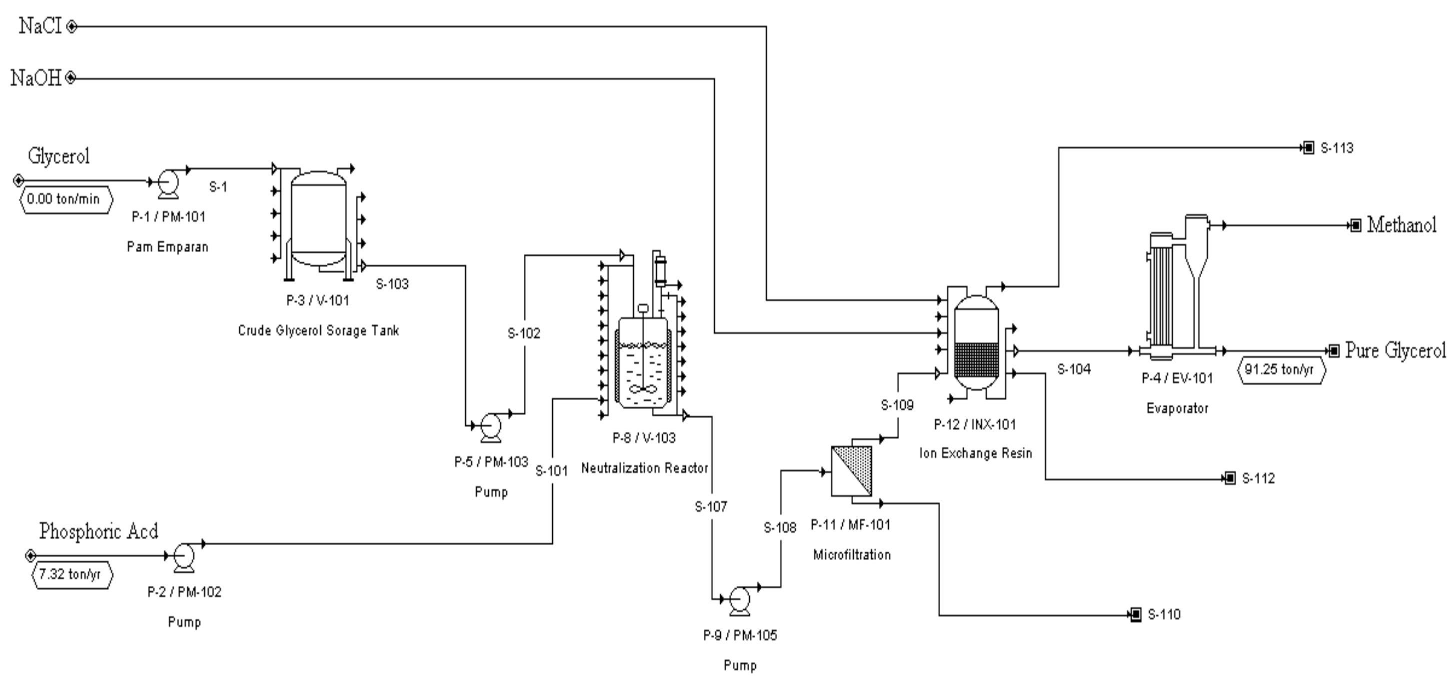

Fig. 5. Simulation of crude glycerol purification process based on transesterification palm oil at lab scale (P1).

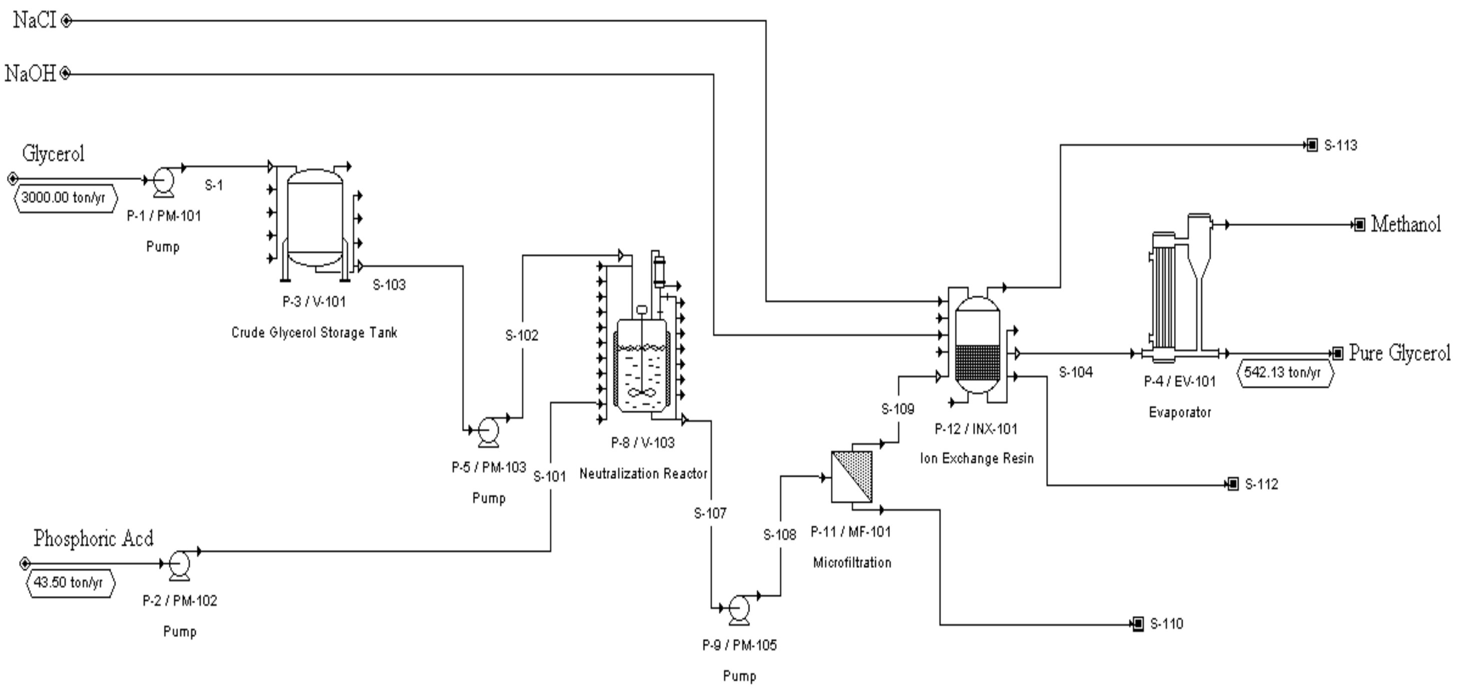

Fig. 6. Simulation of crude glycerol purification process based on transesterification palm oil at industrial scale (P2).

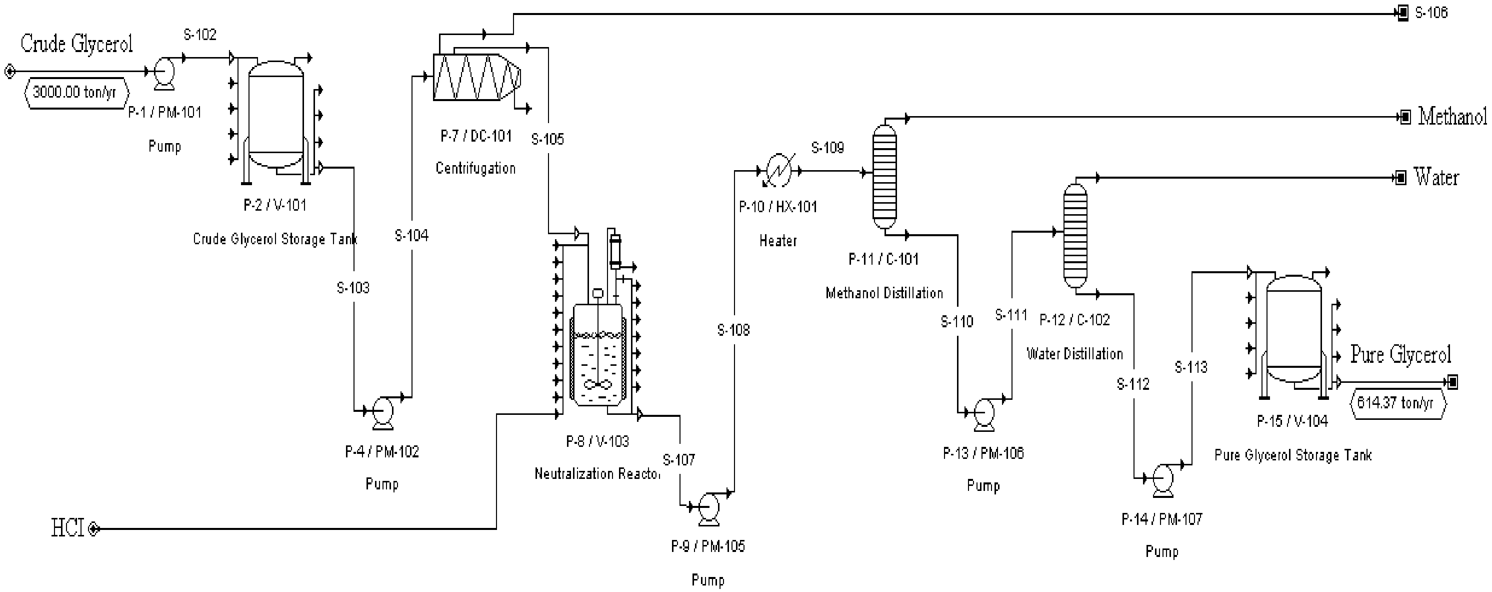

Fig. 7. Simulation for crude glycerol purification process based on transesterification palm oil at industrial scale (P3).

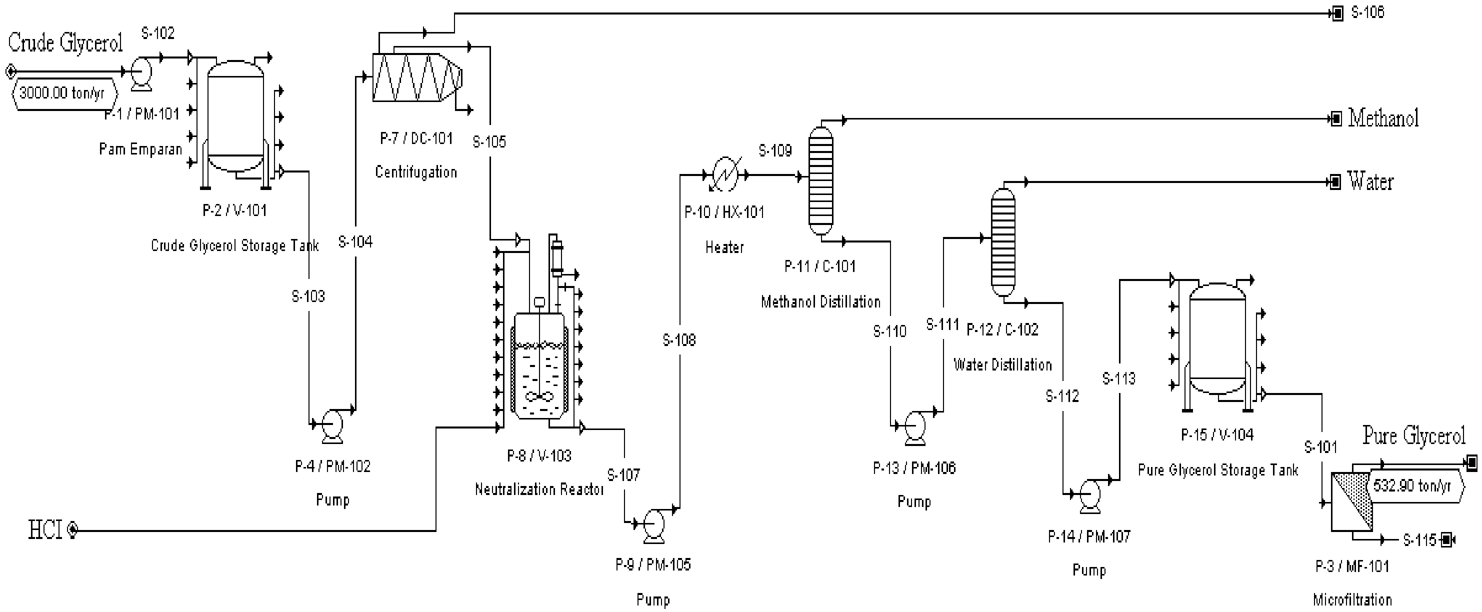

Fig. 8. Simulation of crude glycerol purification process based on transesterification palm oil at industrial scale (P4).

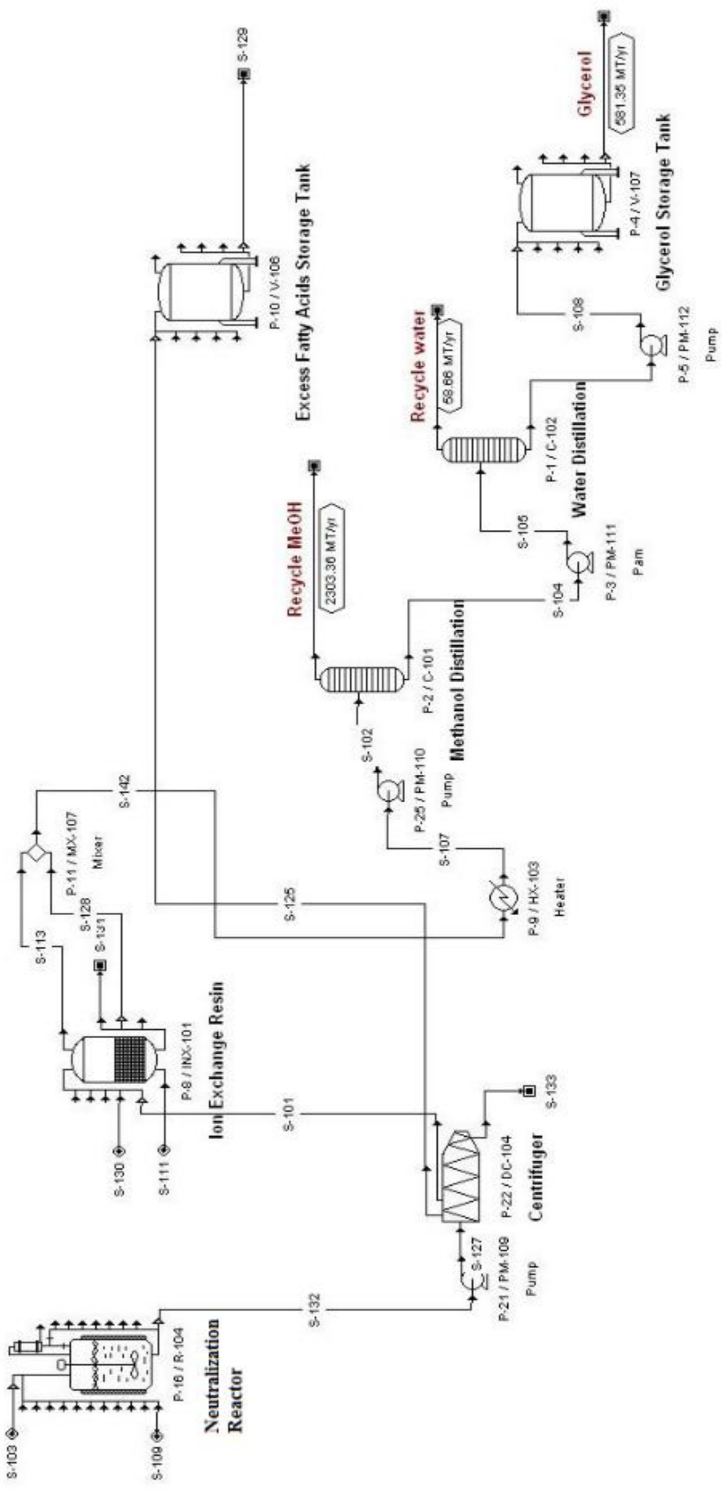

Fig. 9. Simulation of crude glycerol purification process with the presence of ion exchange and distillation column (P5).

3.2.5. Water recovery

The P3, P4 and P5 process were carried out with water distillation process to remove remaining water or moisture from crude glycerol samples. Data from Table 8 shows that higher recovery up to 100% and product stream flowrates with 22.48 MT/year were obtained from distillation process of P5 simulation. It was higher with compared to P3 and P4 process which attributed to higher reflux ratio and percent in distillate of column.

Table 8. Summary of units operating conditions for water recovery process.

Parameters	P3	P4	P5
Reflux ratio	0.125	0.125	1.70
Number of theoretical stages	10	10	5
Column pressure (psi)	14.7	14.7	15
Recovery (%)	91.71	91.69	100
Product stream (MT/year)	19.74	19.74	22.48
Percent in distillate (%)	99.90	99.90	99.99
Stage efficiency (%)	80	80	80

4. Conclusions

Purified glycerol as a considerable grade can be produced from the crude glycerol by-product of a transesterification reaction. This consideration exhibited high quality glycerol by combination of 3 purification steps namely (1) neutralization process, (2) microfiltration and (3) ion exchange resins chromatography method. However, only a small weight amount of amberlite ion exchange resins were needed to sufficiently adsorb and exchange free cations and anions from the salts formed during neutralization. The crude glycerol (CG) samples were analyzed in the HPLC and FTIR to check on the purity level. Both types were free from any impurities as only glycerol peaks and bandwidths were detected. Additionally, it was found that the viscosity, pH value, free fatty acid value, moisture content, ash content and MONG percentage of the purified CG were not closed to the PG properties. Nevertheless, crude glycerol after purification (CG2) was almost closed to physical properties values of PG which show it better product of crude glycerol samples in this work. Simulation studies were carried out to scale up the experimental work to industrial scale. The purity of glycerol after P5 simulation process by three steps of purification was produced higher glycerol purity as 99.27%. From this work, the results showed a very efficient combination process to produce higher recovery of glycerol at high purity of 99.98%.

Acknowledgement

The authors gratefully acknowledge the financial support given for this work by GGPM-2015-014 and FRGS/1/2015/SG01/UKM/02/2 from Universiti Kebangsaan Malaysia and Ministry of Higher Education, Malaysia, respectively.

References

1. Ma, F.; and Hanna, M.A. (1999). Biodiesel production: A review. *Bioresource Technology*, 70, 1-15.
2. Gerpen, J.V. (2005). Biodiesel processing and production. *Fuel Processing Technology*, 86, 1097-1107.
3. Thompson, J.C.; and He, B.B. (2006). Characterization of crude glycerol from biodiesel production from multiple feedstocks. *Applied Engineering in Agriculture*, 22, 261-265.
4. Isahak, W.N.R.W.; Ramli, Z.A.C.; Ismail, M.; Jahim, J.M.; and Yarmo, M.A. (2015). Recovery and purification of crude glycerol from vegetable oil transesterification. *Separation and Purification Reviews*, 44(3), 250-267.
5. Buenemann, T.; Oudejans, J.C.; Gambe, P.; and Rampi, A. (1991). *Process for purifying crude glycerol*. Patent No. 4990695.
6. Chuang, W.C.; Dasari, M.A.; Sutterlin, W.R.; and Suppes, G.J. (2006). Removal of residual catalyst from simulated biodiesel’s crude glycerol for glycerol hydrogenolysis to propylene glycol. *Journal of Industrial and Engineering Chemistry Research*, 45, 791-795.
7. Knothe, G.; Gerpen, J.V.; and Krahl, J. (2005). *The biodiesel handbook*. Illinois: AOCS Press.
8. Isahak, W.N.R.W.; Ismail, M.; Jahim, J.M.; Salimon, J.; and Yarmo, M.A. (2012). Characterisation and performance of three promising heterogeneous catalysts in transesterification of palm oil. *Chemical Papers*, 66(3), 178-187.
9. Isahak, W.N.R.W.; Ramli, Z.A.C.; Ismail, M.; and Yarmo, M.A. (2014). Highly selective glycerol esterification over silicotungstic acid nanoparticles on ionic liquid catalyst. *Industrial & Engineering Chemistry Research*, 53(25), 10285-10293.
10. Addison, K. (2006). *Separating glycerin/FFAs*. Homemade Project, Journey to Forever.http://journeyforever.org/biodiesel_glycerin.html.
11. Hitz; T. (2009). *Glycerin content determination according to USP 26 standard method*, pp 867.
12. American standard testing material. (2016). *Annual Book of ASTM Standards*, Vol 05.
13. Lubrizol standard test procedure. (2006). *Test procedure AATM* 109-01; 1-3.