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Process Simulation of Glycerol Conversion to Formic Acid Using Hydrothermal Oxidation

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***Abstract*—Biodiesel as alternative fuel is widely produced from various source of vegetable oil. The production of biodiesel also generates large number of by-products, such as glycerol. The limitation of glycerol market, make glycerol the best candidate to propose as feedstock for chemical production because the many possible chemical derivative. Glycerol can be converted to many kinds of chemical products, one of them is formic acid. The oxidation of glycerol with hydrogen peroxide will produced formic acid and water. The simulation process was designed using Aspen Hysys. The reactor feed consists of pure glycerol and hydrogen peroxide 30%. The mole ratio of glycerol and hydrogen peroxide was set to 1:15. The oxidation process was simulated using conversion reactor with conversion 99% at temperature 250C and 170 atm. The process was continued with formic acid purification via distillation and extractive distillation using SULFOLANE. The extractive distillation needed because the azeotrope characteristic of water 22.4%-w and formic acid 77.6%-w. The simulation indicates that from 100 kg/h glycerol can be produced around 113 kg/h formic acid with purity 92%.**

Keywords—formic acid, glycerol, process simulation, oxidation

I. INTRODUCTION

The production of biodiesel as alternative renewable fuel is rapidly increase all over the world. From biodiesel production via transesterification large quantity of glycerol also produced (10%-wt) as by product [1]. In the previous studies, it was shown that glycerol can be produced as by product of transesterification of corn oil [2], but from hydrodeoxygenation propane was produced as by product using crude palm oil as raw material [3]. The limitation of glycerol market, make glycerol the best candidate to propose as feedstock for chemical production because the many possible chemical derivative [4]. From various available processes that use glycerol as raw material to produce value- added chemical products, the most promising one is hydrothermal process, because water as the reaction medium has exceptionally good properties at high temperature and pressure [5]. From environmental aspect water has been proven by many studies to be an environmental friendly medium for various type of biomass conversion [6-8]. Glycerol conversion using hydrothermal conditions into formic acid is quite efficient [9-11].

As chemical feedstock formic acid mostly used as a commercial product or as a synthetic precursor in many industries like agriculture, leather and dye industries. At conventional process, toxic carbon monoxide and water used to mainly produce formic acid via carbonylation of NaOH at raised pressure and temperature. The process production of formic acid from renewable source like glycerol is safer, more sustainable and more environmentally friendly also likely to be rapidly developed in comparison with the traditional route [12].

The Conversion of glycerol into formic acid can be occurred via two oxidation methods hydrothermal oxidation [12] and electrocatalytic oxidation [13]. It also can be done using heterogenous catalyst [14].

II. METHODS

Aspen Hysys was used to design the process simulation. The assumptions in this simulation as the basis for simulate the process of formic acid production are the glycerol conversion process into formic acid and its by-products mainly take place via hydrothermal oxidation. The conversion of glycerol is set to be 100%. It was assumed on all production process equipment there are no heat loss. The pressure drop that occurs in the heat exchanger is 1.5 psi. The number of pressures drops due to fluid flow along the pipe is assumed to be zero. The feed consists of glycerol 100% and H_2O_2 30%. The glycerol conversion to formic acid process diagram illustrated in Figure 1.

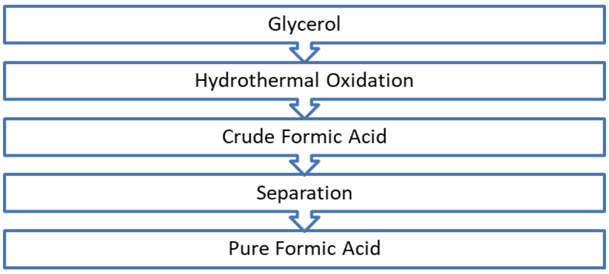

Fig. 1. Block flow diagram of formic acid production.

A. General Description of Hydrothermal Oxidation

Formic acid can be produced via glycerol hydrothermal oxidation [12,15]. For this process hydrogen peroxide used as oxidant with excess amount. These both reactions can be produced formic acid as main product and by product in formed of oxalic acid and water. The process occurred in high temperature and pressure around 250 ºC and 170 bar. Before entering distillation stage, the excess hydrogen peroxide and oxalic acid separated from product stream by using membrane.

$$C_3H_5(OH)_3 + 4H_2O_2 \rightarrow 3HCOOH + 5H_2O \quad (1)$$

$$C_3H_5(OH)_3 + 5H_2O_2 \rightarrow HCOOH + (COOH)_2 + 7H_2O \quad (2)$$

The production of formic acid from glycerol, occurred in two steps. First, glycerol was oxidized, then decomposed into formic acid and oxalic acid. The present of oxalic acid was indirectly contributed to the amount of formic acid formation from glycerol, because it can be acted as a retardant to prevent formic acid further oxidation [12]. The production of formic acid from glycerol oxidation using catalyst $Ru(OH)_4$/r-GO and $FeCl_3$ in aqueous solution, result in high yields of formic acid [16].

B. General Description of Formic Acid Separation Process

Water and formic acid have azeotrope properties (22.4% and formic acid 77.6%). In order to produce higher purity formic acid it is not enough to only using conventional distillation, further separation is needed. The most common option like altering the operating condition (pressure) or adding an entrainer substance. The option of pressure alteration only economical for mixtures which have high sensitivity to pressure change. Another alternative method that can be used to get formic acid with higher purity, are azeotrope distillation and extractive distillation [17]. The extractive distillation of water-formic acid system can be used SULFOLANE as solvent [18]. The extractive distillation consists of two stages. The first stage is extraction of formic acid from water and continued with solvent regeneration. Extractive distillation to separate azeotropic mixture of formic acid- water can also be done by using Li-Br as a salt [19]. Liquid-liquid extraction also can be used to separate formic acid from aqueous solution, by making ternary system with 2-methylpropyl ethanoate [20].

III. Results and Discussion

The overall simulation flowsheet is shown in Figure 2. The process simulation stages are feed preheating, hydrothermal reaction, distillation, extractive distillation with SULFOLANE, and solvent generation.

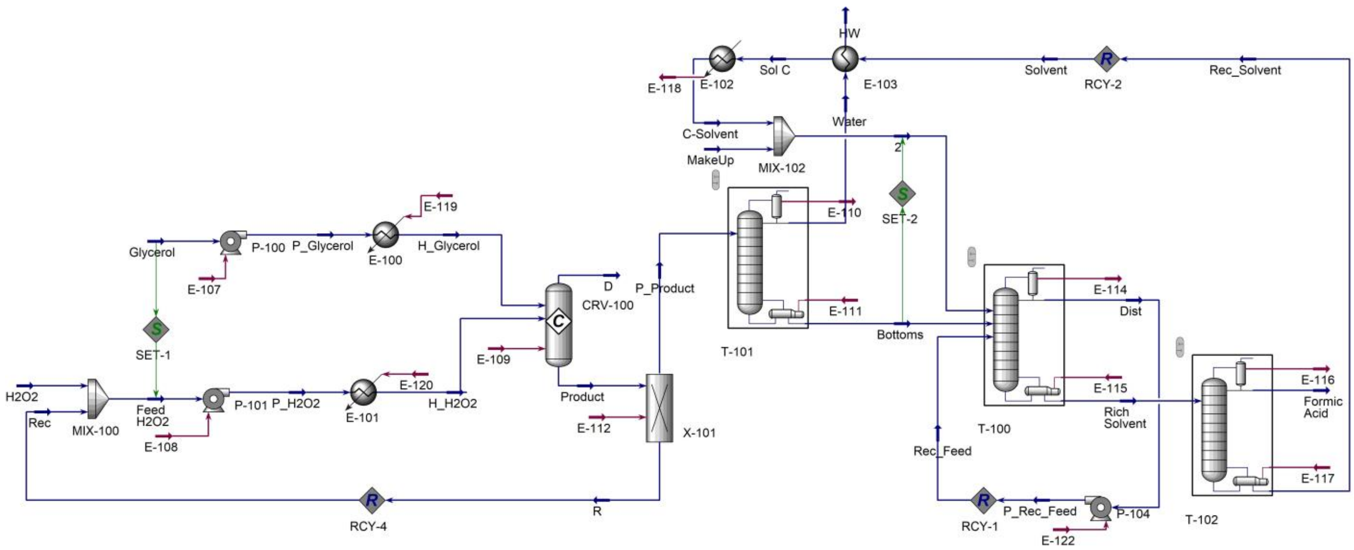

Fig. 2. Formic acid production from glycerol simulation flowsheet.

A. Hydrothermal Reaction Process

The hydrothermal reaction operating condition was simulated based on study by Zhang, et al [12]. Before entering the reactor both feed streams are preheated to 250ºC. The mole ratio of glycerol and H_2O_2 30% was set to 1: 15. The reactor (CRV-100) operating condition was 250ºC and 170 bar and glycerol conversion was set to 100% After the reaction complete around 130 kg/h of formic acid produced from 100 kg/h of glycerol. Oxalic acid was produced as by product with insignificant amount. The product stream also consists of water and excess H_2O_2. The excess H_2O_2 and oxalic acid was separated using membrane from product stream (X-101). In Zhang, et al the highest yield of formic acid from the glycerol hydrothermal reaction was around 31.0% [12]. The formic acid and water continued to further separation. Figure 3 shown the formic acid production stage.

B. *Formic Acid Separation Process*

Water and formic acid have azeotrope characteristic that make further separation stages needed. The product stream of water and formic acid enter the distillation column (T-101) and exit the column with distillate stream rich of water and the bottom product has azeotrope composition of formic acid and water. To obtain higher purity of formic acid, the bottom product undergoes the extractive distillation. SULFOLANE is the most common solvent to separate this azeotrope combination. The SULFOLANE mass flow was set 10 times from the bottom product stream. The extractive distillation occurred in column T-100. The rich solvent stream then enters solvent regeneration process in column T-102. Around 113 kg/h formic acid 92% was produced. The solvent then recycled to column T-100. The azeotrope and extractive distillation shown in Figure 4.

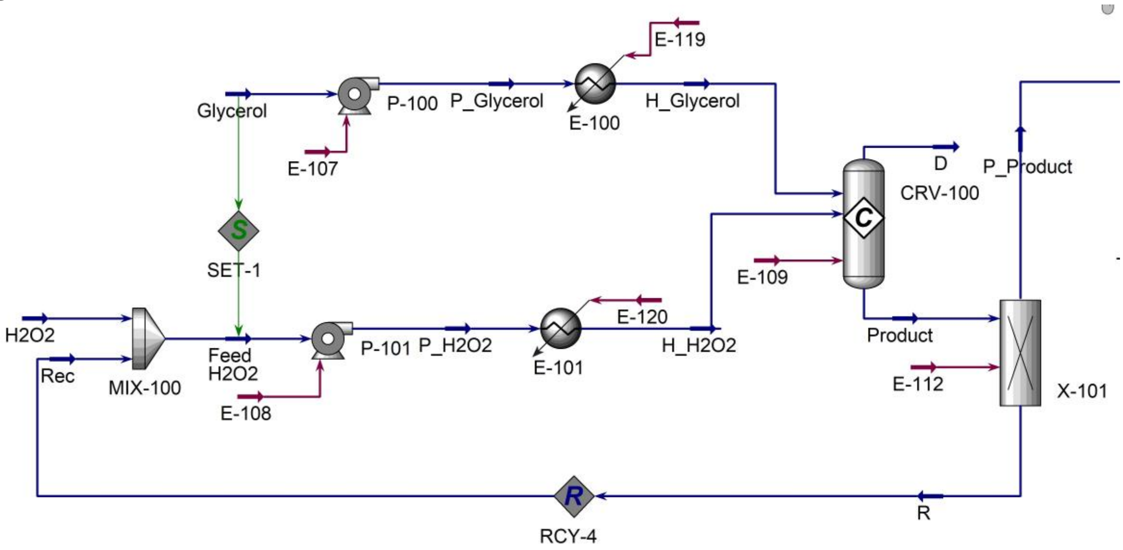

Fig. 3. Formic acid production stage simulation flowsheet.

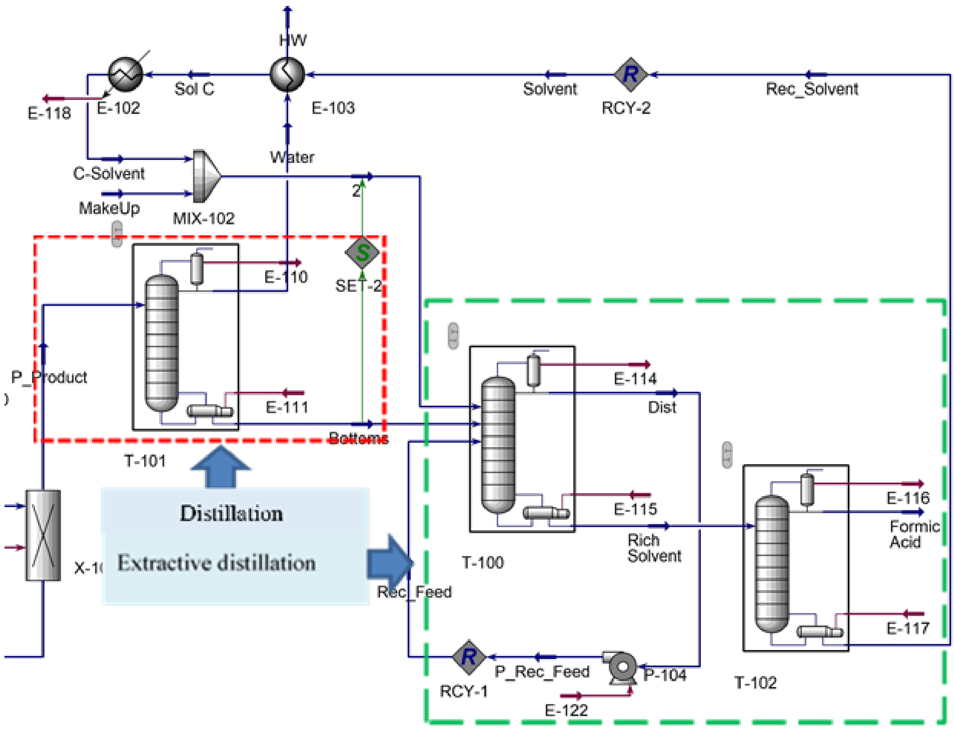

Fig. 4. Formic acid separation simulation flowsheet.

C. Estimation of Utilities Consumption

The utility consumption for the hydrothermal oxidation of glycerol to produced formic acid based on simulated process was estimated and shown in Table 1. The utility needed consists of electricity, heating utility, and cooling utility. Electricity was needed for powering pump for reactor feeding and extractive distillation distillate recycle. The heating utility can be supply using steam and for cooling utility, water already sufficient to use in this process. Extractive distillation column (T-100) consumes the highest utilities supplies. For condenser, the cooling water need is around 22 thousand kW. For reboiler heating was needed steam around 22 thousand kW. The extractive distillation column needs high heating and cooling utilities because the large number of stream flow that need to heating and cooling, in total around 7 m3/h. The hydrothermal reaction is exothermic energy, in order to maintain the operating condition large amount of cooling utilities was needed around 354 thousand kW.

TABLE I. UTILITIES CONSUMPTION ESTIMATION

Type	Equipment	Consumption (kW)	Total (kW)
Electricity	E-107	0.48	2.76
	E-108	2.06	
	E-122	0.22	
Heating utility	E-111	1,746	24,189
	E-115	22,130	
	E-117	207.3	
	E-119	21.74	
	E-120	84.11	
Cooling utility	E-109	354,200	378,203
	E-110	1,738	
	E-112	121.6	
	E-114	21,980	
	E-116	51.53	
	E-120	112.4	

IV. CONCLUSION

The hydrothermal oxidation of glycerol operating condition was 250ºC and 170 bar. The simulation results indicated that from 100 kg/h glycerol will be produced around 130 kg/h crude formic acid. Because of the azeotrope properties of formic acid-water, extractive distillation was chosen to obtain high purity formic acid with SULFOLANE as solvent. After separation process, the recovery of formic is 85.18% or around 113 kg/h formic acid with purity 92%. The estimation of utilities consumption is electricity (2.76 kW), steam (24,189 kW), and cooling water (378,203 kW).

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