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The Effect of Recycle Stream on The Selectivity and Yield of The Formation of Triacetin from Glycerol

The Effect of Recycle Stream on The Selectivity and Yield of The Formation of Triacetin from Glycerol

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Abstract. Biodiesel is an alternative fuel that recently widely used to substitute fossil fuels. Biodiesel production from vegetable oil produces glycerol as by-product which is a very promising low-cost feedstock for producing a wide variety of special and fine chemicals. One of the potential glycerol derivatives is triacetin, a promising alternative chemical to be fuel additive. In this work, triacetin was synthesized using reactive distillation with recycle stream from bottom product to increase the conversion of monoacetin became diacetin and diacetin became triacetin. The effects of using catalyst and recycle stream are evaluated. The experiments showed recycle stream made contact between reactant were better. So the selectivity and the yield increased. The optimum recycle rate is 65.5 mL/men and the results are 98.38% of glycerol conversion and 9.00% of triacetin yield.

Keywords: Biodiesel, glycerol and catalyst.

1. Introduction

The development of alternative fuels from renewable natural resources becomes one option to overcome the needs of oil energy sources from fossil fuels that are increasing, while inventories are running low. Alternative fuels recently widely used is biodiesel. Glycerol is a byproduct of biodiesel production. A variety of value added special and fine chemicals as pharmaceutical, propellant binder, personal care, polyester, triacetin, alkyd resins, as an emulsifier, softener agent, stabilizer, wetting agent for bakery products, ice creams, tobacco, lotions and other countless pharmaceutical and cosmetic applications can be produced from glycerol [1], [2], [3].

One of several industrial synthesis alternatives for utilization of glycerol is the acetylation process of glycerol and acetic acid. The products of this process have great industrial applications i.e. triacetin has been used for pharmaceutical and cosmetics industry, while monoacetin and diacetin have been applied in cryogenic industry and used as raw material for biodegradable polyesters manufacture [2],[4],[5]. On the other hand, triacetin is a promising alternative chemical to be transformed into fuel additive [6],[7],[8]. Adding 10% (w/w) of triacetin to biodiesel can give better performance as compared to the pure biodiesel [9]. The reaction mechanism acetylation of glycerol and acetic acid can be seen in Figure 1:

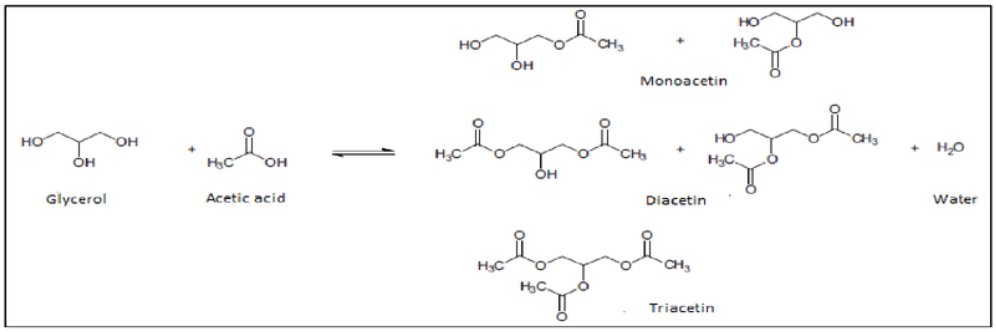

Figure 1. Acetylation of glycerol reaction mechanism

Acetylation of glycerol for triacetin production had been studied in reactor batch [10], kinetics reaction [11], continuous process[12], and comparation between batch and reactive distillation reactor [13]. As mentioned in [14] the selectivity of triacetin increased with an increase in the mole ratio of catalyst to glycerol. Increasing temperatures lead to increase selectivity of triacetin. It will decrease at the time of acetic acid has begun to evaporate. Synthesis of triacetin is an exothermic reaction, a higher reaction temperature will cause in shifting the balance toward the formation of reactants. This needs to be anticipated by taking one of the products so that the equilibrium shifting toward product formation.

The synthesis of triacetin from glycerol and acetic acid using sulfuric acid catalyst has been performed in batch reactor and reactive distillation continuous process. Triacetin was synthesized using batch reactor to give 96.30% of glycerol conversion. Reactive distillation can separate water and acetic acid in the reaction of distillate product around 75% of the main product of bottom results. The production using continuous reactive distillation resulted in glycerol conversion of 98.51% [13]. Continuous process for triacetin production had been studied. They made triacetin using Amberlyst-15 catalytic column. The dimension of the column is 1.5 cm in diameter and 44 cm in length. In this study, the ratio of glycerol to acetic acid was 2:9 and the flow rate was 0.3 cm3/minute. The acetic acid conversion obtained in this process was 50%. The synthesis of triacetin was done using continuous process by a fixed bed reactor at the temperature of 323 K with Amberlyst catalyst. The best result was obtained on the ratio of acetic acid to glycerol in 3:1 [14]. Triacetin was synthesized using reactive distillation. The continuous process has 98.50% of glycerol conversion with 8.98% of triacetin selectivity [12].

The present paper aims to evaluate of process technologies for acetylation of glycerol in continuous reactive distillation column with recycled stream. The bottom was recycled to the top of the column to increase the conversion of monoacetin became diacetin and diacetin became triacetin. The effect of using catalyst and recycle stream are evaluated.

2. Methodology

2.1. Materials

Triacetin was made from 98 % of acetic acid (production of Petrochemical Chang Cun) and 93 % of glycerol (production of P & G Chemicals) using sulfuric acid as catalyst (Merck Index No. 016-020-00-8).

2.2. *Instrumentation*

Reactive distillation can be used as a place of reaction and purification products in one place. The dimensions of reactive distillation column which has been used are diameter of 5 mm, thickness of 2 mm and height of 1.20 m. The column was insulated to reduce heat loss and equipped with total condenser and partial reboiler. Figure 2 shows the schematic of a reactive distillation for triacetin production.

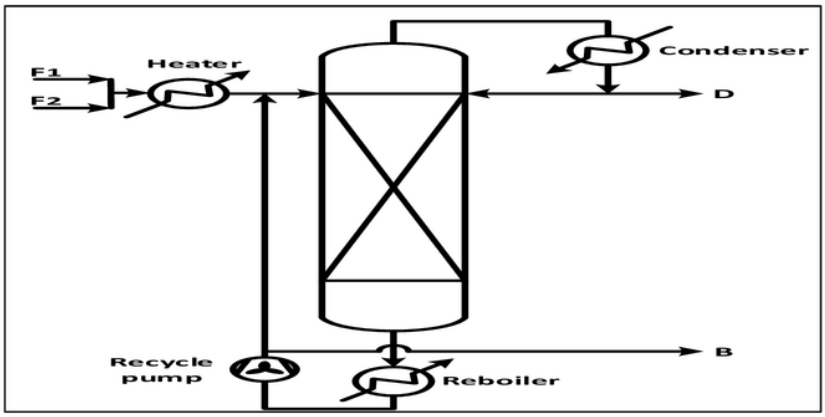

Figure 2. Reactive Distillation (RD) column with recycle from reboiler.

2.3. *Procedure*

Glycerol and acetic acid were heating. Then, glycerol (F1) and acetic acid (F2) entered from the top of the column. Glycerol and acetic acid discharged in accordance with the variation of the velocity which would be observed. Residual acetic acid and water would rise to the top of the column and then flowed through the total condenser. Product stream exiting the top divided into distillate (D) taken as result and certain amount returned to the column as reflux. The bottom product stream used a partial reboiler where the vapor raised in the reboiler was re-introduced into the unit at the bottom of the column and liquid removed from the boiler used recycle pump and was taken as the recycle and the bottom (B). This B product contains monoacetin, diacetin, triacetin, sulfuric acid catalyst and small amount of acetic acid and glycerol. Then, after reaching the steady operating conditions, samples at various specified were taken and analysis with chromatograph.

2.4. *Analysis*

Gas chromatograph (GC) was used for the analysis to provide good results in monoacetin, diacetin and triacetin analysis [15]. The GC specification used for analysis was GC Agilent 6890N MSD 5975B, Model Number: Agilent 19091S-433, HP-5ms column 5 % Phenyl methyl siclohexane, the injector temperature of 548 K, the temperature at the detector: MS Quad 523 K, injection volume of 1 micro liter, injector pressure of 3.27 psi. External standards were used for analysis : glycerol 99% (production of Waco Pure Chemical Industries Ltd., reff. No. 079-00614), monoacetin 99% (production of Chemical Co. Inc., cat. No. 25371-32), diacetin 97% (production of Kanto Chemical Co. Inc, cat. No. 10018-32), and triacetin 99% (production of Kanto Chemical Co. Inc., cat. No. 40224-30). Based of data, the conversion of glycerol and selectivity were calculated.

3. Results and Discussion

3.1. Effect of Recycle

Reaction between glycerol and acetic acid is a series-parallel reaction with triacetin as the main product. At the previous research, performance between batch process and reactive distillation were compared. The acetylation of glycerol is reversible reaction so that one of the ways for the reaction to shift to the right is to take one of the products. Therefore, reactive distillation which used has two functions: reaction and separation. Water is separated as the top product with the consideration that the boiling point of water is the lowest among other products. The glycerol conversion in reactive distillation is greater than in batch process, however triacetin selectivity is lower than using a batch process [13]. At this work, a recycle stream is used to increase the selectivity of triacetin. In this experiment recycle flow rate from reboiler design from 53.5 to 71.5 ml/min and the bottom product flow rate is 69.5 ml/min. The recycle stream causes changes in feed composition with the presence of monoacetin, dicetin and triacetin in the feed. Recycle stream affect contact between glycerol and acetic acid, monoacetin and acetic acid, and diacetin and acetic acid in reactive distillation column. The impact is an increase in glycerol conversion and increased selectivity of diacetin and triacetin (see figure 3 and figure 4). Figure 3 shows the effect of variable recycle flow rate of glycerol conversion. The data can similar with equation $y = -0.1665\ x^2 + 21.985\ x - 627.91$. The optimum recycle is achieved at recycle flow rate of 66.021 mL/min.

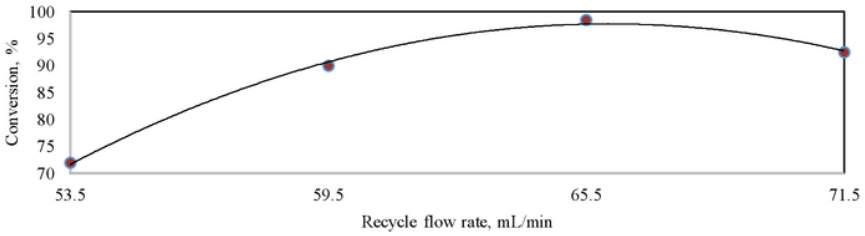

Figure 3. Conversion of glycerol as function of recycle flow rate.

Reaction between glycerol and acetic acid produces three products i.e. monoacetin, diacetin dan triacetin. In general, the use of catalysts will increase conversions. Figure 4 informs the yield of diacetin is highest than the others. From figure 4, we can also notice that yield product triacetin is increasing recycle flow rate from 53.5 to 65.5 ml/min. After that yield of product is decreasing.

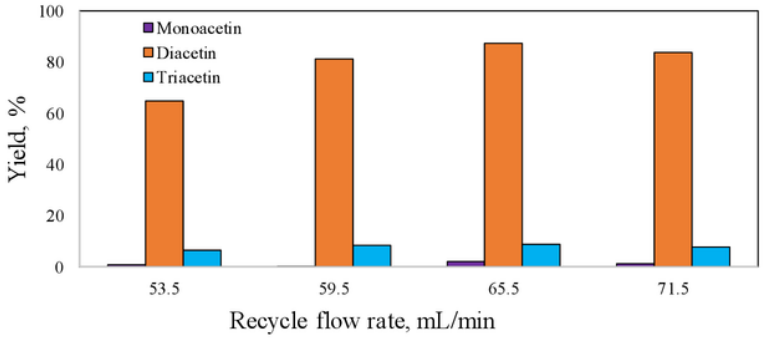

Figure 4. Yield of products as function of recycle flow rate

3.2. Effect of Catalyst

The catalyst is added in a reaction to speed up the reaction. The use of the catalyst will not affect the equilibrium constant of the reaction, but it act to accelerate both forward and reverse reactions. It causes new route to make product by forming an intermediate product, with a lower energy barrier [16]. This research used sulphuric acid as catalyst. The temperature of acetic acid and glycerol feed streams is 373 K at atmospheric pressure. The column operates at atmospheric pressure, the temperature of the top of the column is 373 K is and the temperature of the bottom of the column is 393 K. The recycle flow rate is 65.5 mL/min. The influence of catalyst to the yield and selectivity of monoacetin, diacetin and triacetin is shown on Table 1.

Table 1. the effect of Catalyst to the yield and selectivity

Product	**without catalyst**		**with catalyst**	
	Yield, %	*Selectivity, %*	*Yield, %*	*Selectivity, %*
Monoacetin	1.2867	1.8048	0.2521	0.2803
Diacetin	64.3954	90.3264	81.2217	90.3118
Triacetin	5.6097	7.8686	8.4608	9.4077

Table 1 demonstrates that using catalyst increase the yield and selectivity of triacetin significantly. The using of catalyst increases the selectivity by 1.5 times compared without catalyst and increases the yield 1.2 times. In this process, the use of the catalyst increases glycerol conversion reaches 26%. Luque et al [17] also used sulphuric acid as catalyst in acetylation of glycerol with batch process. The result were the glycerol conversion of 85% with monoester selectivity of 43%, diester selectivity of 32% and triester selectivity of 25%. Compared with that study, this work obtained higher glycerol conversion but triacetin selectivity was lower. In batch process, reaction time was longer than in reactive distillation which increased chance of collision between diacetin and acetic acid.

4. Conclusions

Triacetin was synthesized using reactive distillation with recycle from bottom product to increase the conversion of monoacetin became diacetin and diacetin became triacetin. The contact of monoacetin, diacetin and acetic acid is better using recycle stream. The optimum recycle rate is 65.5 mL/men. This process has 98.38% of glycerol conversion and 9.00% of triacetin yield.

5. Acknowledgment

The authors would like to thank to The Ministry of Research Technology and Higher Education of the Republic of Indonesia for financial support of this work through scheme Competitive Research Grant of Pasca Doctor 2017 project no. 118/SP2H/LT/DRPM/IV/2017.

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