Synthesis Acetylation of Glycerol Using Batch Reactor and Continuous Reactive Distillation Column

By Zahrul Mufrodi

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Article

Synthesis Acetylation of Glycerol Using Batch Reactor and Continuous Reactive Distillation Column

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Abstract. Biodiesel production from vegetable oil produces glycerol as by-product with the amount of about 10 wt% of its product. This excessive amount of glycerol needs to be converted into the higher valuable product. One of the prospective glycerol's derivatives is triacetin, a good bio-additive as anti-knocking agent. In this work 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 be used as a place of reaction and purification products in one place. Reactive distillation can separate water and acetic acid to 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%.

Keywords: Triacetin, bio-additive, reactive distillation.

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1. Introduction

As the demand and price of diesel fuel has been increasing rapidly over the past few years, the use of biodiesel as an alternative renewable fuel is receiving increased attention. Biodiesel is generally produced via the transesterification reaction, in which the triglycerides in vegetable oil react with alcohol converting into esters of fatty acids (biodiesel) and glycerol in the presence of either alkali or acid catalysts. Biodiesel can be made from a variety of plants such as palm oil [1], soybean oil [2, 3] and microalgae [4]. Glycerol is a byproduct of the biodiesel production and a very promising low-cost feedstock for producing a wide variety of value-added special and fine chemicals. Acetylation of glycerol can be a good alternative to utilize the glycerol produced by biodiesel process. Crude glycerol from biodiesel industry contains glycerol, alcohol and water. Crude glycerol need purification before is used in acetylation process. The purification use two column, the first column is used to separate alcohol then the second column is used to separate alcohol [5]. The products of glycerol acetylation are monoacetin, diacetin and triacetin (Fig. 1). They have great industrial applications. Triacetin is widely applied for pharmaceutical, cosmetics and fuel additive, while monoacetin and diacetin have been applied in cryogenic industry and as raw material for biodegradable polyesters manufacture [6-9].

Biodiesel that uses triacetin as additive, which is a cetane improver, has resulted in a lower NO emissions to a reasonable extent. Usage of this additive can decrease the engine exhaust smoke because of the reduction of carbon molecules in fuel mixture. Triacetin ($C_9H_{14}O_6$) is a good anti-knocking additive and it is easily soluble in biodiesel. Triacetin also has benefit to suppress engine knocking, improve the performance and reduce tail pipe emissions. Combination of biodiesel with 10% triacetin leads to the improvement of the engine performance in all aspects [10]. However, this great amount of glycerol can be utilized as raw material to produce several high value chemicals such as monoacetin, diacetin and triacetin by acetylation process as shown in equations 1 through 3.

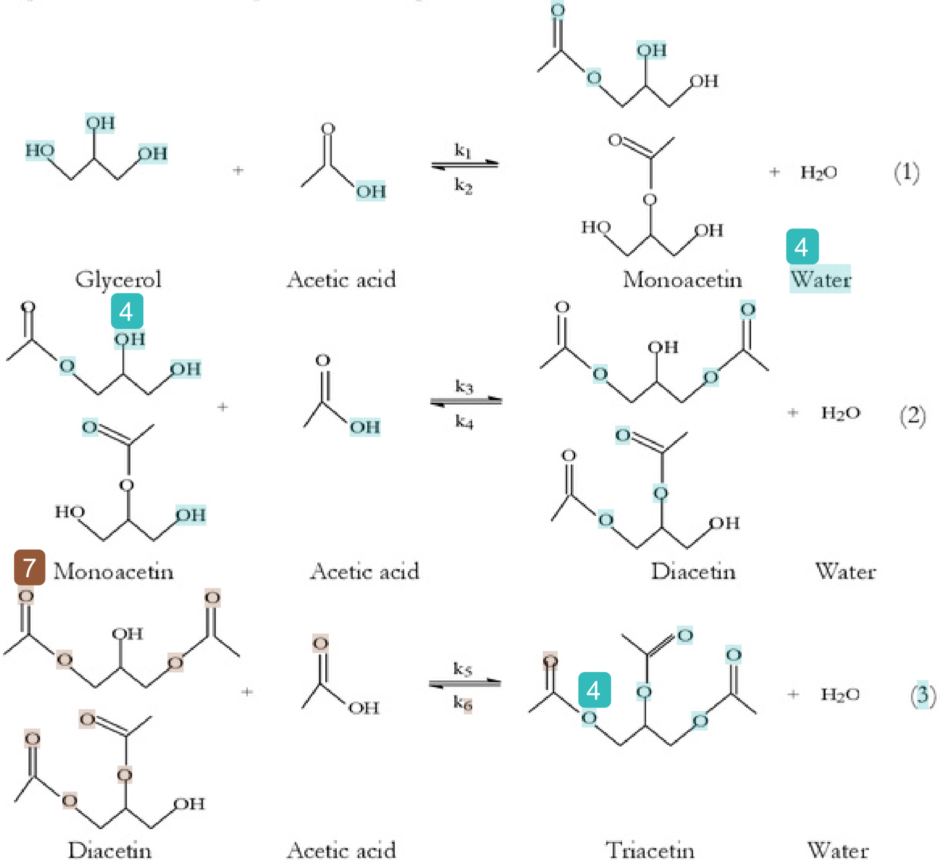

Fig. 1. Acetylation of Glycerol reaction mechanism.

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1.1. Batch Reactor

Synthesis of triacetin in the absence of catalyst was carried out in a stirred reactor at a pressure of 1070 kPa, 290 rpm of stirring speed, temperatures of 393 and 433 K [11]. Synthesis of triacetin has been previously conducted using various types of heterogeneous solid catalysts, such as aminosulphonate [12], phosphotungstic, mesoporous silica with sulfonic acid groups [13], p-toluensulfone [14], Amberlyst-15 or SAC-13 (Nafion-SiO2) [15] and SO4 $^{2-}$/ $ZrO^{2-}TiO_2$ [16], Amberlist-15, K-10, Niobic acid, HZMS-5 and HUSY [17], Amberlyst-35 [18], ZrO_2, $TiO^{2}–ZrO_2$, $WOx/TiO_2–ZrO_2$ and $MoOx/TiO_2–ZrO_2$ [19].

Others materials were studied as heterogeneous catalyst is niobic acid supported tungstophosphoric acid (TPA) [20], and dodecatungstophosphoric acid (PW) supported on activated carbon [21], $CeO_2–M$ and $SO_4^{2-}/CeO_2–M$ ($M = ZrO_2$ and Al_2O_3) [22], Amberlyst-15 [23], ion exchange resin [24] and $MoO_x/TiO_2–ZrO_2$ [21]. In addition to the solid catalyst, sulfuric acid as a homogeneous catalyst has also been applied by some researchers [25-28]. It was revealed that this catalyst has functionalized as the best one among several types of liquid catalysts [29].

1.2. Continuous Process

Continuous process for triacetin production had been studied [27]. 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 flow rate was 0.3 cm^3/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 ratio of acetic acid to glycerol of 3:1 [30].

The present paper aims at evaluating and comparing of two process technologies for acetylation of glycerol in batch and continuous reactive distillation column. The effect of temperature in batch reactor, height of packing and mole ratio acetic acid to glycerol for reactive distillation column towards conversion and product concentration are evaluated.

2. Materials and Methods

2.1. Reagents

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

2.2. Experimental Methods

2.2.1. Batch reactor

The reaction take place in a three-neck flask equipped with heating mantle, cooling system, mercury stirrer, thermometer and sampling equipment (Fig. 2). Reaction was running at mixing time until 30 minutes and speed of stirrer 235 rpm. The reaction was carried out with the following variables: molar ratio of catalyst to glycerol and temperature. Samples were taken every 5 minutes and were analyzed using gas chromatography (GC) and GCMS.

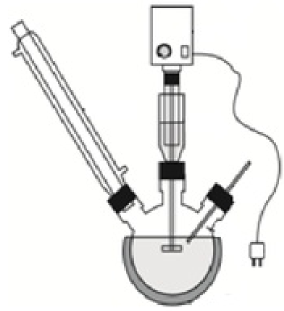

Fig. 2. Batch reactor.

2.2.2. Reactive distillation

Reactive distillation can be used as a place of reaction and purification products in one place. Reactive distillation column has been used dimensions of height 1.20 m, diameter of 4.5 mm and thickness of 2 mm. The column was insulated to reduce heat loss and equipped with total condenser and partial reboiler. Figure 3 shows the schematic of a reactive distillation for triacetin production. Acetic acid and glycerol feed to F_2 and F_1. The column is operated at atmospheric pressure, the temperature of acetic acid feed streams is 391 K and glycerol feed streams is 373 K.

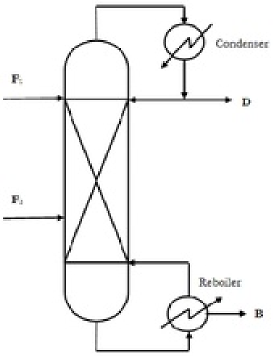

Fig. 3. Continuous reactive distillation column.

2.3. Analysis Instrument

The instrumentations used for analysis was gas chromatography GC Agilent 6890N MSD 5975B, HP-5ms column 5 % Phenyl methyl siclohexane, Model Number: Agilent 19091S-433, 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. The data obtained was interpreted to obtain the reaction rate constants. The mixture of compounds that contains glycerol, acetic acid, monoacetin, diacetin and triacetin can be separated easily in gas chromatography so all compounds were identified with GC [31]. The analyzed result can be seen in Fig. 4.

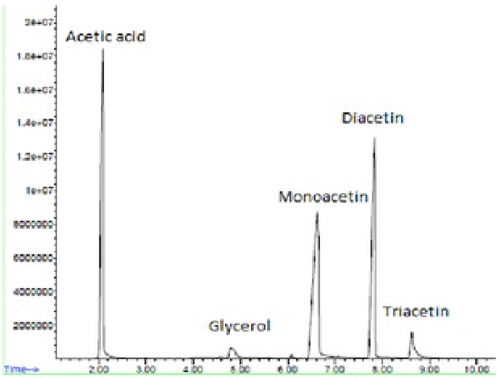

Fig. 4. Cromatogram of mixture of acetic acid, glycerol, monoacetin, diacetin and triacetin.

3. Results and Discussion

3.1. Batch Reactor

The reaction of the triacetin synthesis was carried on the mole ratio of sulfuric acid as catalyst to glycerol at 2.5. The effect of temperature on the acetylation of glycerol with acetic acid was studied from 373-393 K Higher reaction temperature increases the conversion of the glycerol at temperature of 373-393 K. It was due to the fact that at the temperature below 388 K, all reactants and products (except water) were in the liquid phase. When the temperature was higher than 391 K, some acetic acid began to evaporate. It consequently reduced the conversion of the glycerol (Fig. 5).

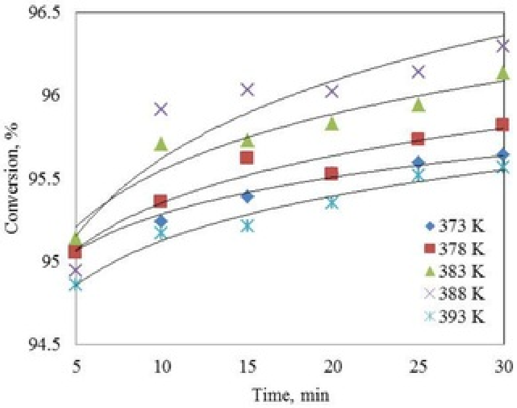

Fig. 5. Conversion of glycerol as function of time.

Figure 6 shows the effect of increasing temperature on glycerol and acetic acid reaction, Effect of increasing temperature resulted in increased monoacetin, diacetin and triacetin selectivity. Increasing temperature 5 K will increase triacetin selectivity of 1.96 %. The highest selectivity of triacetin is 13.69 % at temperature 388 K. After the temperature, selectivity of triacetin will decrease as 12.93 %. It is effect of some acetic acid began to evaporate.

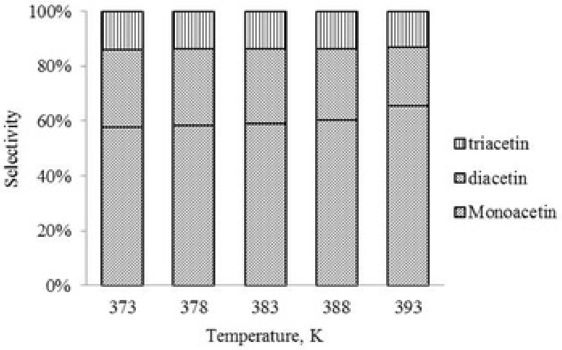

Fig. 6. Selectivity of produc as function of temperature.

3.2. Reactive Distillation

Synthesis of triacetin from glycerol was done in 2 stages, reaction stage and purification stage. Both of stages can be simplified in reactive distillation column. Reactive distillation was used to separate the water which has the lowest boiling point for distillate products.

3.2.1. Effect of height of packing

Contact between glycerol and acetic acid in reactive distillation column occurs along the column that will be affected by the height of packing. The higher packing materials cause contact between the two reactants better than before. The effect of higher packing materials on the glycerol conversion is shown in Fig. 7. Effect of higher packing materials resulted in an increase concentration of triacetin as product. Triacetin conversion will increase by 0.0077% at 19.5 cm interval of stuffing materials. Maximum conversion of glycerol in the process is 97.49663%.

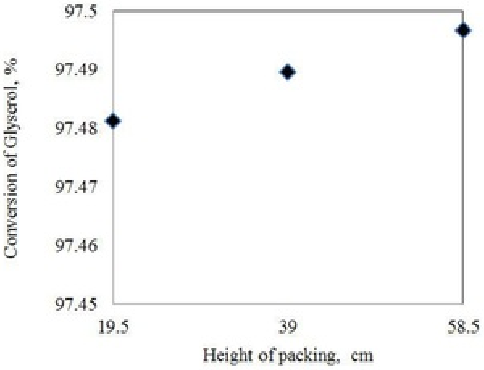

Fig. 7. Conversion of glycerol as function of height of packing.

The effect of the packing height to the concentration of all the compounds of the reaction mixture is depicted on Fig. 8.

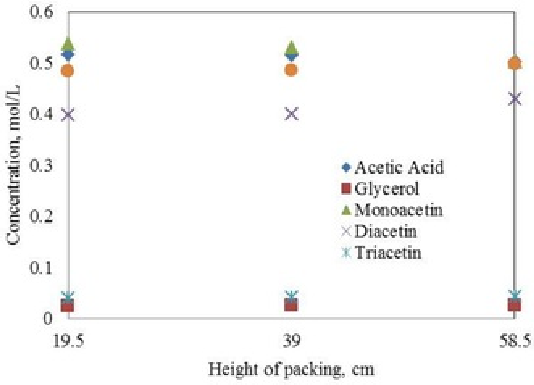

Fig. 8. Concentration of reactans and products as function of height of packing.

The effect of the packing height to the selectivity monoacetin, diacetin and triacetin can be seen in Fig. 9. It was shown that the increase of the height of packing will increase selectivity of the diacetin and triacetin but selectivity of monoacetin will decrease. This condition is caused by the fact that the higher packing height, the greater contact time of reactants.

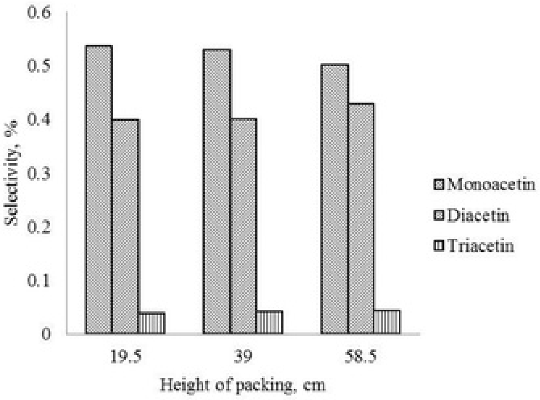

Fig. 9. Selectivity monoacetin, diacetin and triacetin as function of height of packing.

3.2.2. Effect of mole ratio acetic acid to glycerol

One common way to increase the reaction rate is using the excess amount of one of the reactants. Based on the stoichiometric calculation, 3 moles of acetic acid requires one mole glycerol to produce one mole triacetin. In these experiments, the molar ratio of acetic acid to glycerol was 3, 4, 5 and 6. The effect of mole ratio on the glycerol conversion is shown in Fig. 10. Effect of mole ratio resulted in an increase glycerol conversion. Glycerol conversion will increase by 0.2941% at added 1 mol acetic acid. Maximum conversion of glycerol in the process is 98.5043%.

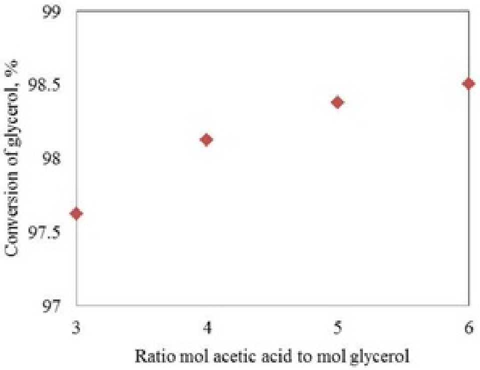

Fig. 10. Conversion of glycerol as function of ratio mol acetic acid to mol glycerol.

Effects of mole ratio of the reactants to products concentration in reboiler is demonstrated in Figs.11 and 12.

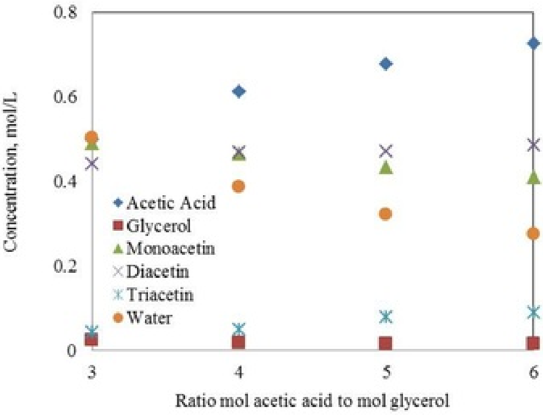

Fig. 11. Concentration of reactans and products as function of Ratio mol acetic acid to mol glycerol.

Figure 12 shows the effect of influence mole ratio of acetic acid to glycerol. Increasing mole ratio acetic acid to glycerol will increase of diacetin and triacetin selectivity but decrease the selectivity of monoacetin. Due to more concentration of acetic acid at higher acetic acid to glycerol molar ratios, the selectivity towards di- and triacetin are high and vice-versa.

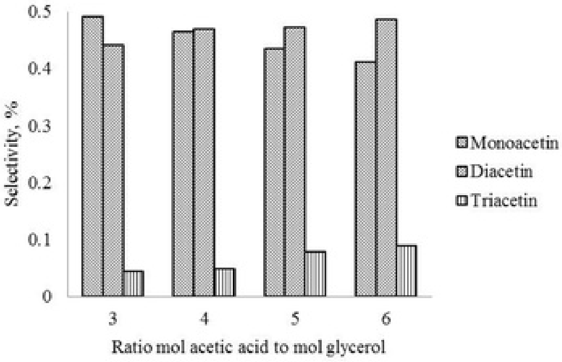

Fig. 12. Selectivity mono, di and triacetin as function of Ratio mol acetic acid to mol glycerol.

Table 1 shows the comparison conversion of glycerol and selectivity to monoacetin, diacetin and triacetin for batch reactor and continuous process of reactive distillation. It proves that the synthesis of triacetin in reactive distillation produce higher glycerol conversion than that resulted by batch reactor. On the other hand selectivity of monoacetin and triacetin decrease, while selectivity of diacetin increases.

Table 1. Conversion of glycerol and selectivity of product.

Reactor	Conversion, %	Selectivity, %		
		Monoacetin	Diacetin	Triacetin
Batch	96.30	60.49	25.81	13.69
Reactive distillation	98.51	41.67	49.35	8.98

The conversion of the process which was conducted using reactive distillation is greater than batch process because of the continuous removal of a product (water) which has the lowest boiling point as the distillate product. The continuous removal of one product will shift the equilibrium to the right. On the other hand, triacetin selectivity is lower because the mixing in reactive distillation is less favorable than a batch reactor. Reactive distillation can separate water and acetic acid to the reaction of distillate product around 75% of the main product of bottom results.

The next paper will learn about reactive distillation simulation with expand the range of variables i.e. height of packing and mole ratio of acetic acid to glycerol based on the results of experiments that have been done. The aim of simulation is to get the maximum selectivity of triacetin.

4. Conclusions

This paper takes comparative study of acetylation of glycerol by two processes of batch reactor and continuous reactive column. It seen from the results that acetylation by reactive column can be used to increase the conversion of glycerol. Synthesis acetylation of glycerol using reactive distillation make equilibrium reaction tends to shift in formation of products. It can be seen in the increasing of diacetin and triacetin. Increasing of mole ratio of acetic acid to glycerol and increasing of height of packing cause increase of triacetin selectivity.

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