Continuous Process of Reactive Distillation to Produce Bio-additive Triacetin From Glycerol

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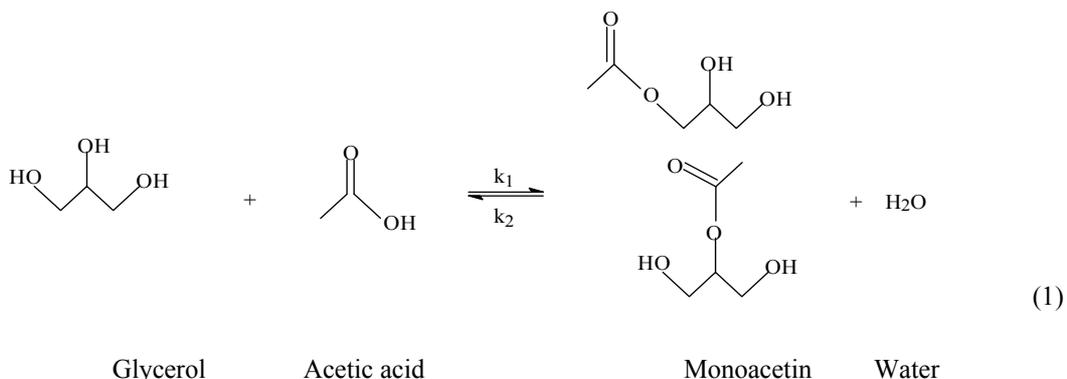
Abstract

Glycerol as byproduct of biodiesel production is a very promising low-cost feedstock for producing a wide variety of special and fine chemicals. This great amount of glycerol needs to be converted into higher valuable products. One of glycerol's derivatives potential is triacetin, a good bio-additive as anti-knocking agent. In previous work triacetin synthesis from glycerol and acetic acid using sulfuric acid catalyst has been conducted in batch and continuous process. In this work, triacetin was synthesized using reactive distillation. The continuous process has 98.50% of glycerol conversion with 8.98% of triacetin selectivity.
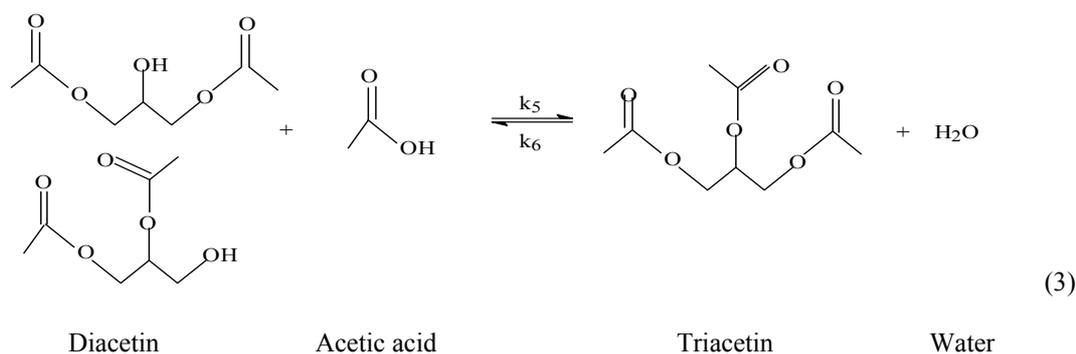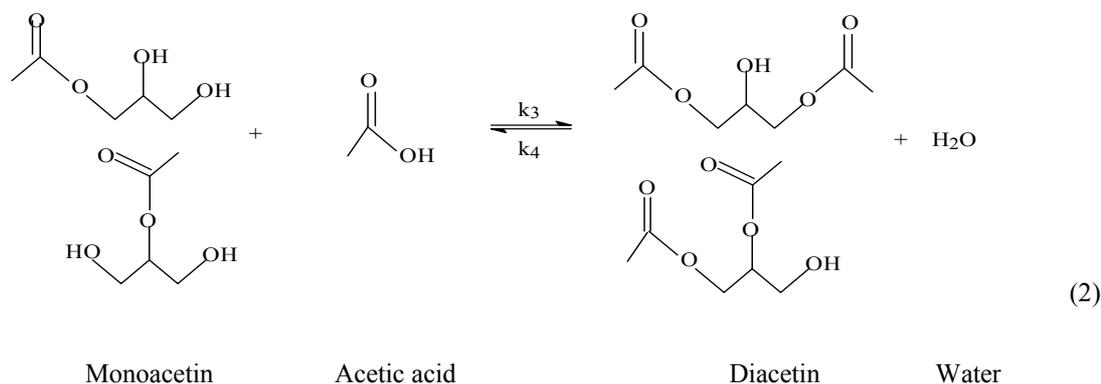
Keywords: Glycerol, triacetin, bio-additive, reactive distillation

1. Introduction

1.1 Introduce the Problem

Glycerol is byproduct of biodiesel process and it is now regarded as a waste product due to tremendous growth of biofuel industry. Stoichiometrically, biodiesel production will generate 10% (w/w) glycerol. In other words, every gallon of biodiesel produced generates approximately 1.05 pounds of glycerol. This indicates a 300-million-gallon-per-year plant will generate about 115,000 tones of 99.9 percent pure glycerin. 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.

$$\text{Glycerol} \qquad \text{Acetic acid} \qquad \qquad \text{Monoacetin} \qquad \text{Water}$$

(1)

(2)

Monoacetin   Acetic acid   Diacetin   Water

(3)

Diacetin   Acetic acid   Triacetin   Water

There are several industrial synthesis alternatives for utilization of glycerol, one of them is acetylation process of glycerol and acetic acid. The products of this process has great industrial applications, such as 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 (Galan et al., 2009; Reddy et al., 2010; Rahmat et al., 2010). Besides, triacetin is a promising alternative chemical to be transformed into fuel additive (Rao & Rao, 2011; Ferreira et al., 2009; Hou et al., 1998). Mixing 10% (w/w) of triacetin to biodiesel can give better performance as compared to the pure biodiesel (Zang & Yuan, 2001).

1.2 Catalyst for Reaction

Traditionally, the reaction of glycerol and acetic acid is carried out using homogeneous catalysts, such as sulphuric acid (Gelosa et al., 2003; Mufrodi et al., 2010; Mufrodi et al., 2012) and acidic functional ionic liquid (Li et al., 2009), H_3PO_4, HCl, HNO_3 and H_2SO_4 (Khayoon & Hameed, 2011). This process has advantages including high activity (complete conversion within short time) and mild reaction conditions (from 100 to 120 °C and atmospheric pressure). However, researchers have started to study heterogeneous catalyst for this reaction, due to its advantages.

Several heterogeneous solid catalysts for synthesis of triacetin from glycerol and acetic acid has been explored, such as aminosulphonate (Liu et al., 2007), phosphotungstic, mesoporous silica with sulfonic acid groups (Melero et al., 2007), $SO_4^{2-}/ZrO^{2-}TiO_2$ (Wu et al., 2007), Amberlist-15 15 (Zhou et al., 2013), K-10, Niobic acid, HZMS-5 and HUSY (Goncalves et al., 2008), Amberlyst-35 (Liao et al., 2010), ZrO_2, TiO_2-ZrO_2, WOx/TiO_2–ZrO_2 and MoOx/TiO_2-ZrO_2 (Reddy et al., 2010). However, heterogeneous catalyst has complicated catalytically sites, i.e., chemically and geometrically for improving selectivity to a certain product.

So far, homogeneous catalysis is widely used over heterogeneous in industry for the following reasons:

a. Access to the reagents for homogeneous catalyst is easier since it is in solution, so there is improved activity and milder reaction conditions can be used.

b. The heat transfer in homogeneous phase for highly exothermic or endothermic reactions is not a problem.

c. Mechanisms are better understood.

1.3 Continuous Process

Current triacetin productions are mostly using batch-tank reactor. For a small capacity, batch system is very versatile, but for mass production, this process is tedious, labor intensive and low in productivity. However,

continuous acetylation processes are preferred over batch processes in commercial production. The basic advantages of continuous-flow process are a greater productivity and a consistent product quality.

Continuous acetylation of glycerol was studied as early as the 196s by Morrissette (1964). In this system, synthesis of triacetin from glycerol was conducted in 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. Then, recently Fukumura et al. (2009) improved the process by using Amberlyst-15 in catalytic column. By 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%.

2. Method

2.1 Materials and Dimension of Reactive Distillation Column

The materials used in this experiment are glycerol of 93% purity (production of P & G Chemicals), acetic acid of 98% purity (production of Petrochemical Chang Cun) and sulfuric acid as catalyst (Merck Index No. 016-020-00-8).

Reactive distillation (RD) column with dimensions of height as 1.20 m, diameter as 45 mm and the wall thickness as 2 mm. The column contains glass raschig rings with dimensions out diameter as 0.5 mm, length as 8.5 mm and wall thickness as 0.85 mm. The column was insulated to reduce heat loss and equipped with total condenser and partial reboiler. Figure 1 shows the schematic of a reactive distillation for triacetin production. Acetic acid and glycerol was fed to F_2 and F_1. The column was operated at atmospheric pressure. The temperature of acetic acid feed streams was 391 K and glycerol feed streams was 373 K.
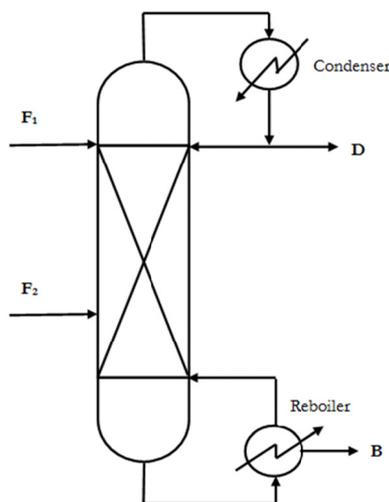

Figure 1. Reactive distillation (RD) column

2.2 Sampling Procedures

Experiment begun by heating glycerol and acetic acid feed. Glycerol (F1) entered from the top of the column and acetic acid (F2) on 2/3 height of the upper part 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 a result and certain amount returned to the column as reflux. The bottom product stream used a partial reboiler where the vapour raised in the reboiler was re-introduced into the unit at the bottom of the column and liquid removed from the reboiler was taken as the bottoms (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 gas chromatograph.

2.3 Samples Analysis

Gas chromatograph (GC) was used for the analysis since it was proved to provide good results in monoacetin, diacetin and triacetin analysis (Morrissette & Link, 1964; Ogawa et al., 1988; Lu, 1991; Uematsu et al., 1997).

GC analyses were performed using an Agilent 6890N MSD 5975B with the specification of HP-5ms column 5% Phenyl methyl siloxane, Model Number: Agilent 19091S-433, the injector temperature of 548 K, the temperature at the detector: MS Quad was 523 K, injection volume of 1 micro liter, injector pressure of 3.27 psi. Materials GC standard are triacetin of 99% purity from Kanto Chemical Co. Inc. (Cat. No. 40224-30), diacetin of 97% purity from Kanto Chemical Co. Inc. (Cat. No. 10018-32) and monoacetin of 99% purity from Kanto Chemical Co. Inc. (Cat. No. 25371-32) and glycerol more than 99% purity from Waco Pure Chemical Industries Ltd. (Reff. No. 079-00614).

3. Results and Discussion

3.1 Effect of Packing Height

The height of column is responsible for contact time between glycerol and acetic acid in reaction zone of RD column. That's why knowledge of the packing height is essential for design of RD column to get the best optimizing performance of packing. The effect of the packing height to the concentration of monoacetin, diacetin and triacetin are shown in Figure 2. It shows that the increase of the height of packing would increase the concentration of the diacetin and triacetin. But the monoacetin concentration was decreased. It means that monoacetin was converted into diacetin and triacetin due to excessive contact time because of the height of column. The larger the contact area leads to the better reaction. Increasing of packing height as 19.5 cm would cause an increase diacetin and triacetin of 3.81 and 4.95% while monoacetin decrease of 3.39%.
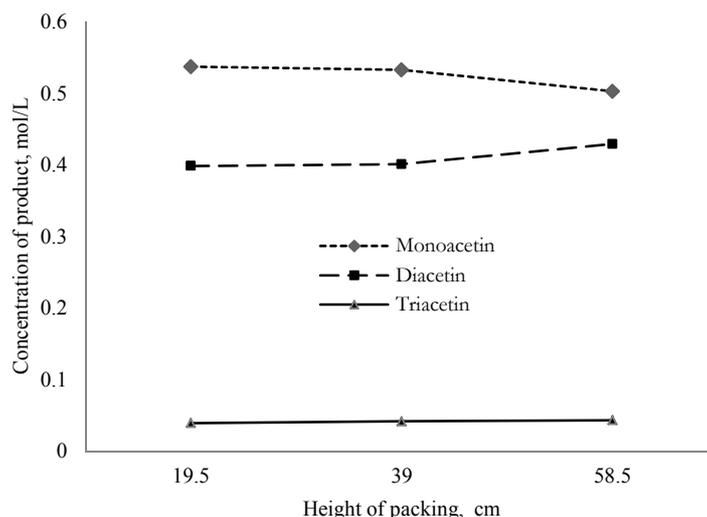

Figure 2. Concentration monoacetin, diacetin and triacetin as function of height of packing

Glycerol conversion increased linearly with the packing height. The effect of packing height on the glycerol conversion is shown in Figure 3. The effect of packing height resulted in an increase concentration of triacetin as product. Triacetin conversion was increased as 0.0077% at 19.5 cm interval of packing height. Maximum conversion of glycerol in this process was 97.50%.
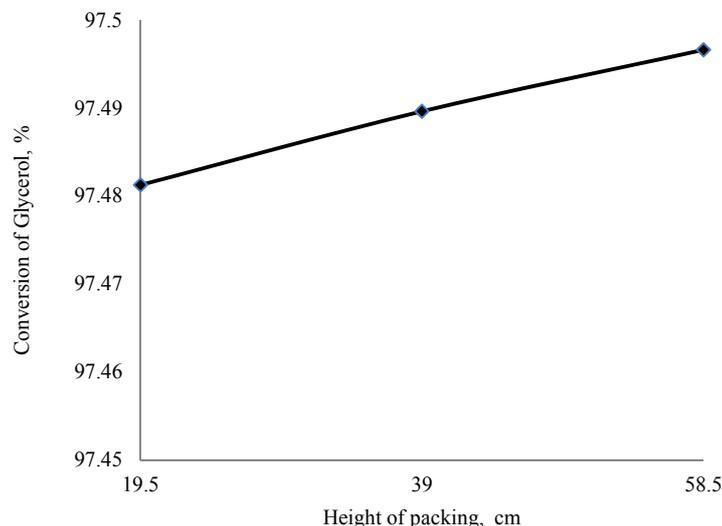
Figure 3. Conversion of glycerol as function of height of packing

3.2 Effect of Acetic Acid to Glycerol Mole Ratio

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 of triacetin. In these experiments, the molar ratios of acetic acid to glycerol were varied 3, 4, 5 and 6. Le Chatelier's principle stated that if a system in chemical equilibrium changes (concentration, temperature, volume or partial pressure), it will cause the equilibrium shifts to counteract the change. Consequently, the new equilibrium will be established. Changes in the concentration of reactant will shift the equilibrium to the side reactions that reduce the concentration. This case means the addition of one of the reactants will result in a shift towards product formation. Here, effect of ratio mol acetic acid to mol glycerol resulted in an increase concentration of triacetin as product. Increasing of one mole ratio of acetic acid to glycerol would cause an increase triacetin of 28.06%.
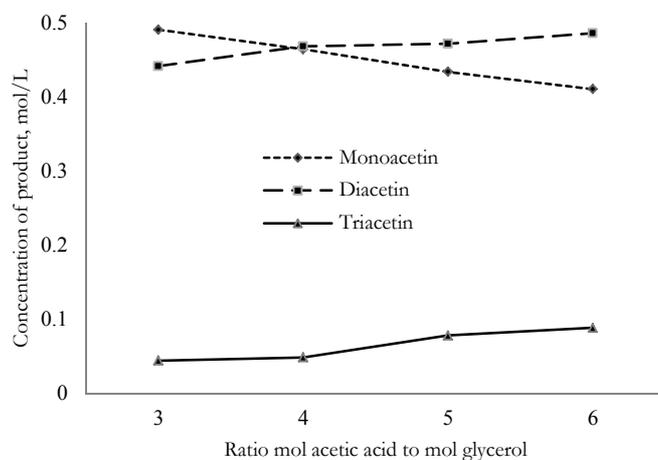

Figure 4. Concentration monoacetin, diacetin and triacetin from bottom product as function of ratio mol acetic acid to mol glycerol

The effect of ratio mol acetic acid to mol glycerol on the glycerol conversion is shown in Figure 5. Triacetin conversion was increased by 0.2941% at 1 mol acetic acid addition. In this process, the maximum conversion of glycerol obtained was 98.51%. It was higher than glycerol conversion using the same catalyst in batch reactor that was 96.30% (Mufrodi et al., 2012).
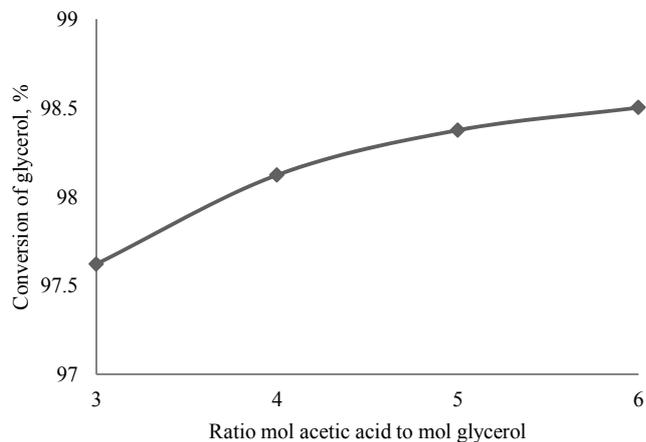
Figure 5. Conversion of glycerol as function of ratio mol acetic acid to mol glycerol

3.3 Effect of Reflux Ratio (R)

Reflux is an important part in the process of distillation. In this work, reactive distillation's vapor at the top of the column output is condensed in the total condenser. Then the condenser discharge flow partly as distillate and returned to the RD column as reflux. Reflux ratio is the ratio between the amounts of fluid that is returned in the column compared with the distillate. Increase the reflux ratio can be generated by adding heat to the reboiler. Effect of reflux ratio also affects the results obtained. Figure 6 shows that the increase in reflux ratio of 0.1 would increased diacetin and triacetin as 1.162% and 1.2% while monoacetin decreased as 2.085%.
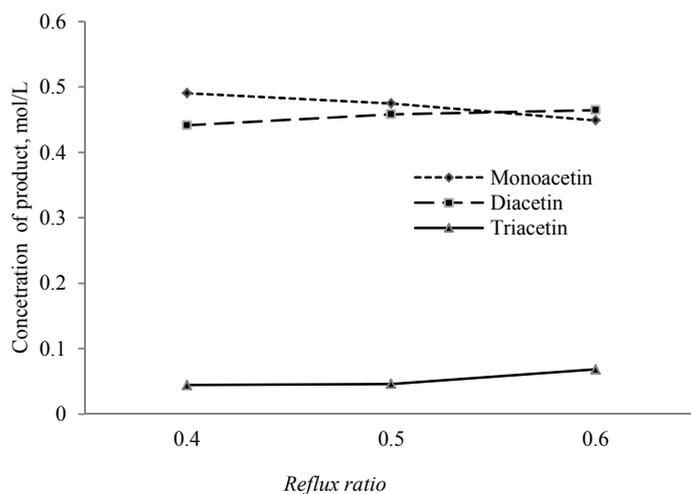

Figure 6. Concentration monoacetin, diacetin and triacetin from bottom product as function of reflux ratio

The higher reflux ratio, R would lead to greater contact time between the reactants, resulting in the better product. The increasing of reflux ratio would increase the conversion of glycerol on the results. The average increasing of reflux ratio of 0.1 causes the increasing in conversions as 0.27747% (see Figure 7).
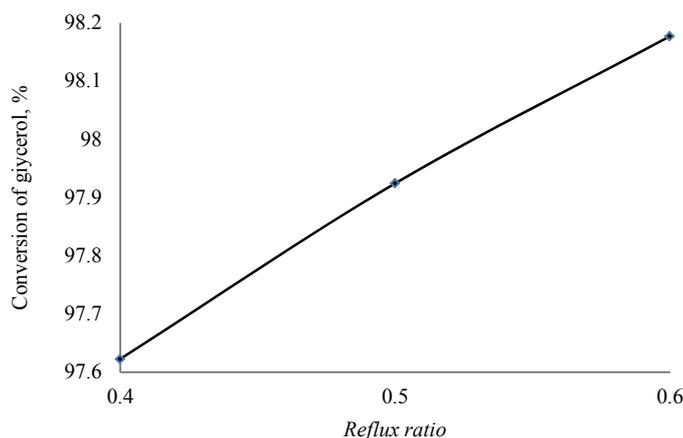
Figure 7. Conversion of glycerol as function of reflux ratio

Table 1 shows the effect of variables to selectivity of monoacetin, diacetin and triacetin using continuous process of reactive distillation. The most affecting variable to the selectivity was the mole ratio of acetic acid to glycerol. The less affecting variable was the packing height.

Table 1. The effect of packing height, mol ratio of acetic acid to glycerol and reflux ratio

Variables		Selectivity, %		
		Monoacetin	Diacetin	Triacetin
Height of packing, cm	19.5	55.090	40.868	4.042
	39.0	54.619	41.105	4.276
	58.5	51.557	43.992	4.451
Mol ratio of acetic acid to glycerol	3	50.2622	45.2166	4.5212
	4	47.3289	47.7309	4.9402
	5	44.1129	47.9439	7.9431
	6	41.6773	49.3450	8.9777
Reflux ratio	0.4	49.8031	44.1414	4.4137
	0.5	49.0219	45.8355	4.5875
	0.6	47.2429	46.4658	6.8142

This paper only uses three groups' tests for each variable. The next paper will discuss about reactive distillation simulation with expand the range of variables i.e. height of packing, mol ratio of acetic acid to glycerol and reflux ratio. The aim of simulation is to get the maximum selectivity of triacetin.

4. Conclusion

This paper studies acetylation of glycerol in continuous reactive column. The results show that acetylation by reactive column can be used to increase the conversion of glycerol and selectivity to triacetin. Adding acetic acid, increasing height of packing and reflux ratio resulted in an increase of triacetin selectivity.

Acknowledgements

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