Glycerol Esterification Using Reactive Distillation for Selective Production of Mono-, Di-, or Tri-acetin

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Highlights

- Valorization of glycerol to mono-, di-, and tri-acetin via glycerol esterification with acetic acid
- Reactive distillation was employed for selective production of mono-, di-, or tri-acetin
- Suitable design parameters and operating condition were determined.

1. Introduction

Glycerol is used in the synthesis of a variety of high-value chemicals. Comprehensive reviews [1,2] explored the catalytic esterification of glycerol into value-added products. Among them are mono-, di- and tri-acetin. Tri-acetin is a solvent commonly employed in personal care and pharmaceutical manufacturing products like creams, lotions, and ointments [3]. Di-acetin serves as a flavor and fragrance component in the food and beverage industries, contributing a sweet, fruity taste to items like candies, beverages, and dairy products [4]. Mono-acetin has antimicrobial and antioxidant activities, positioning it as a crucial player in medicine and pharmaceuticals, potentially aiding in inflammation-related diseases. Reactive distillation (RD) proves particularly suitable for the production of tri-acetin via the consecutive and reversible esterification of glycerol with acetic used. Due to the growing demand for di-acetin and mono-acetin in pharmaceuticals, food and beverages, solvents, and personal care, this work aims at designing the RD for selective production of mono-, di-, or tri-acetin. A parametric analysis of design and operating parameters, such as acetic acid to glycerol ratio, feed stage, catalyst loading, reflux ratio, and distillate rate to feed ratio was conducted using Aspen Plus simulation software.

2. Methodology

The glycerol esterification with acetic acid in reactive distillation (RD) was simulated using ASPEN Plus software. The followings are the main reactions as illustrated in Eqs.(1)-(3).

$$\text{Glycerol (G)} + \text{Acetic acid (AA)} \leftrightarrow \text{Mono-acetin} + H_2O \quad (1)$$

$$\text{Mono-acetin} + \text{Acetic acid (AA)} \leftrightarrow \text{Di-acetin} + H_2O \quad (2)$$

$$\text{Di-acetin} + \text{Acetic acid (AA)} \leftrightarrow \text{Tri-acetin} + H_2O \quad (3)$$

The RADFRAC model was used to model a RD column with the NRTL model for predicting the thermodynamic properties of the non-ideal reaction mixture. The kinetic parameters of the Purolite C160 catalyzed esterification of glycerol and acetic acid was used in the simulations [5]. The kinetics was validated with their experimental results with the maximum discrepancy of less than 5%.

3. Results and discussion

Figure 1 shows the schematic diagram of the RD column consisting of 1 rectifying stage, 13 reactive stages of Purolite C160 and 1 stripping stage. The simulations were based on 1,000 kg/h of glycerol feed. In order to design a suitable RD and its operating condition, various parameters such as acetic acid to glycerol ratio, feed stage, catalyst loading, reflux ratio, and distillate rate to feed ratio were investigated. The simulations found that the AA/G and feed location have influence on the product distribution. For selective production of mono-acetin, an AA/G ratio of 1:1 with top feed location for both glycerol and acetic acid was suggested. While increasing the ratio of AA/G to 5:1 was required for production of tri-acetin using RD based on the same feed location. However, for the selective production of di-acetin, different feed location of the RD– top-glycerol and bottom-acetic acid feed location, was appropriate, and the suitable AA/G ratio was 4:1. Moreover, the simulations showed that increasing residence time in RD column is favorable for tri-acetin production.

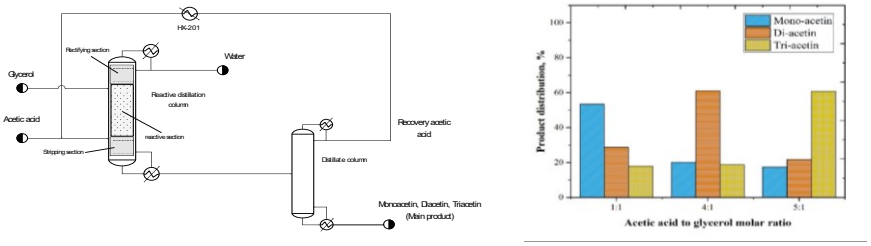

Figure 1. Reactive distillation column for glycerol esterification and product distribution of mono-, di-, tri-acetin production at different acetic acid to glycerol molar ratios (AA/G)

4. Conclusions

RD can overcome the equilibrium conversion of the glycerol esterification with acetic acid. It is possible to achieve selective mono-, di- or tri-acetin in RD to meet different demands of various industrial applications. The AA/G ratio and the feed location show significant effect on the product distribution. For selective production of mono-, di- and tri-acetin, the AA/G ratios of 1:1, 4:1 and 5:1, respectively are required. Moreover, increasing residence time in the column provides the complete reaction to produce the final product of tri-acetin.

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Keywords
Reactive distillation; Glycerol esterification; Mono-acetin; Di-acetin; Tri-acetin