The Steady-State Behaviors of Reactive Tray and Reactive Packed Distillation Acetalization Processes for Methylal Syntheses

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ABSTRACT

The behaviors of the reactive tray and the reactive packed distillation processesused for the productions of methylal from the acetalization reaction between methanol and formaldehyde at steady state have been investigated in this work. The investigations were carried out by modeling and simulating the columns with the aid of Aspen Plus. In the modeling of the columns, tray and packed RadFrac columnswere used and Van Laar/Redlich-Kwong equation of state with Henry's law was employed as the property method. Each of the columns, apart from the condenser and the reboiler, was divided into three sections and the middle section was made the reaction section. The acetalization reaction occurring in the reaction section of each of the columns was modeled as an equilibrium type with molarity as the basis of equilibrium constant computed from Gibbs energy. The simulations of the process occurring in the columns were accomplished using a reflux ratio of 3 and a reboiler duty of 0.35 kJ/s. The results obtained from the simulations showed that the behaviors of the temperature profiles, the liquid component mole fraction profiles and the vapor mole fraction profiles of the components involved in the reactive distillation processes of the tray and the packed columns were the same at steady state.

Keywords: Reactive distillation, modeling, simulation, acetalization, methylal.

1. INTRODUCTION

Methylal, also called dimethoxymethane, is a colorless, highly volatile solvent with a low boiling point, low viscosity and an excellent dissolving power. It has a good toxicological profile and it is biodegradable. Owing to its exceptional solvent power, its amphiphilic character (it is both hydrophilic and lipophilic), an extremely low viscosity, a low surface tension, a particularly high evaporation rate, it is useful in several fields, such as in aerosols for cosmetic and technical applications, paints and varnishes, paint strippers, cleaning and degreasing solvents, pharmaceuticals, synthesis, polymers, adhesives, extraction, fuel additive, insecticides, etc. (Carretier et al., 2003).It is also finding an increasing application in the production of acetal resin, which is widely used in automotive parts, machine construction, toys, etc. because of its outstanding features such as: hardness, toughness, rigidity, spring elasticity and resistance to fuels (Zhang et al., 2011).

Methylal is produced from methanolic formaldehyde solutions which typically also contain water from the formaldehyde-production process. The common process of methylal synthesis consists of a serial arrangement of a reactor in which the feed is converted using a heterogeneous acidic catalyst and a downstream separation sequence which is needed to separate the product from the unreacted educts and eventually from byproducts. One major disadvantage of that configuration results from the chemical equilibrium which limits the conversion of formaldehydein the reactor. Realizing chemical reaction and separation within one apparatus using a phenomenon known as "reactive distillation" can actually overcome this limitation. Therefore, the production of methylal by reactive distillation has been the focus of the research of different groups over the last years (Kolah et al., 1996; Masamoto and Matsuzaki, 1994; Zhang et al., 2011; Drunsel et al., 2012).

Reactive distillation is a process that combines both separation and chemical reaction in a single unit. It is sometimes an excellent alternative to conventional flow sheets with separate reaction and separation sections (Al-Arfaj and Luyben, 2002; Giwa and Karacan, 2012e; Giwa, 2013; Giwa et al., 2013). It combines the benefits of equilibrium reaction with distillation to enhance conversion provided that the product of interest has the highest or the lowest boiling point (Giwa, 2013; Giwa and

Karacan, 2012b; Giwa et al., 2013). It has a lot of advantages, especially for those reactions occurring at temperatures and pressures suitable for the distillation of the resulting components (Giwa, 2013; Giwa and Karacan, 2012c; Giwa et al., 2013), which include: (a) shift of chemical equilibrium and an increase of reaction conversion by simultaneous reaction and separation of products, (b) suppression of side reactions, and (c) utilization of heat of reaction for mass transfer operation, especially if the reaction is exothermic. In addition, another important advantage of reactive distillation is its ability to avoid azeotropes (Giwa and Karacan, 2012a). These good benefits of this process (reactive distillation) normally result in significant economic advantages of reactive distillation compared to a conventional design. These economic benefits include: (a) lower capital investment, (b) lower energy cost and, (c) higher product yields (Moritz and Hasse, 1999; Giwa and Karacan, 2012d; Giwa et al., 2013).

From the literature survey that was carried out about this topic, no work was discovered that has applied Aspen Plus to this process for methylal synthesis using acetalization reactive distillation process. However, it was discovered that Zhang et al. (2011) experimentally studied the synthesis of methylal by the acetalization of formaldehyde with methanol in a pilot scale catalytic distillation column packed with the structured catalytic packing Katapak-SP 12 in the reactive zone by investigating the effects of different operating parameters, such as reflux ratio, feed rate, molar ratio of methanol to formaldehyde, catalyst weight, formaldehyde concentration and effect of extractive agent.

Therefore, this work has been carried out to model and simulate the synthesis of methylal from the acetalization reaction occurring between methanol and formaldehyde using reactive tray distillation and reactive packed distillation columns.

2. PROCEDURES

The modeling and simulations of the acetalization processoccurring between methanol and formaldehyde in the reactive distillation columnsused for the production of methylal in this study were carried out with the aid of a process simulator known as “Aspen Plus” (Aspen, 2012).The columns including the acetalization processoccurring in them were first modeled using the process simulator (Aspen Plus) before they were simulated. In this work, two different reactive distillation processes were used for the investigations carried out. The first one was reactive tray distillation acetalization process occurring in a tray distillation column (Figure 1) while the second one was reactive packed distillationacetalizationprocess occurring in a packed distillation column (Figure 2).

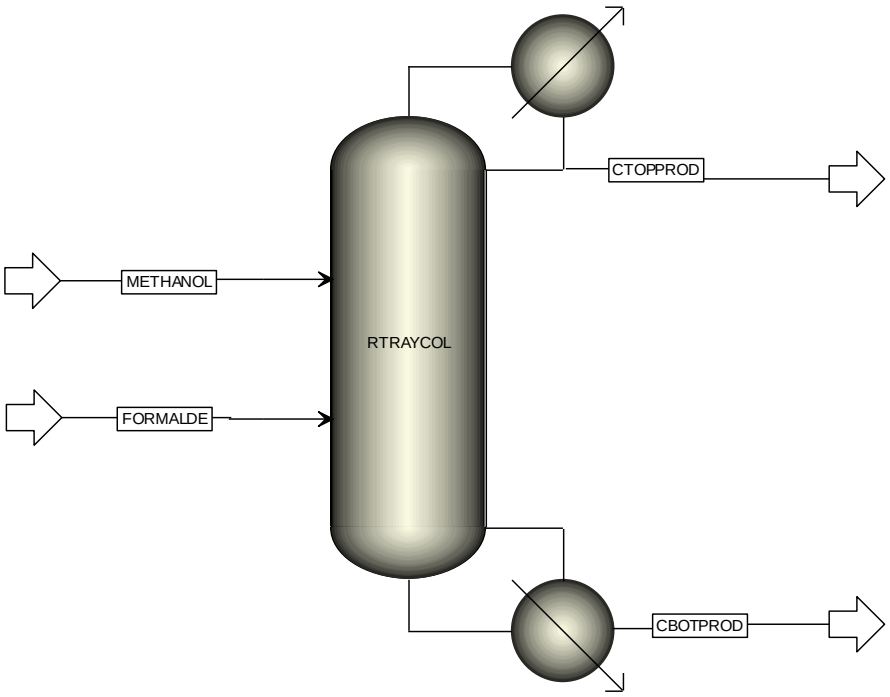

Figure 1. Reactive tray distillation column for the production of methylal

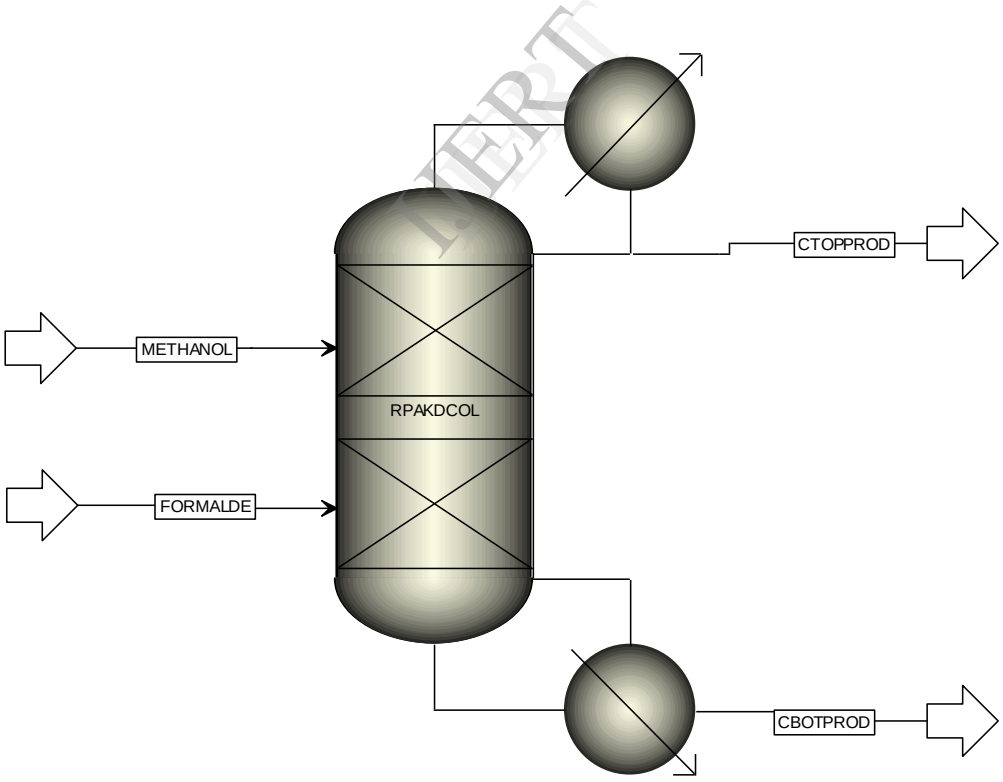

Figure 2. Reactive packed distillation column for the production of methylal

The two reactive distillation columns developed had two feed streams – methanol and formaldehyde. The flow rate of each of the feeds was 0.05 L/min. The temperature of methanol feed was 298K while its pressure was 1atm. Also, the temperature and the pressure of formaldehyde feed

were 277K and 1 atm, respectively. The main parts of the two columns were divided into three sections; that is, upper (rectifying) section, middle (reaction) section and lower (stripping) section.

The reactive tray distillation column had 7 trays each for the rectifying, the reaction and the stripping sections. Also the condenser and the reboiler typesof the column were total and kettle, respectively. The rectifying and the stripping sections of the reactive tray distillation column were sized using sieve trays with a column tray spacing of 0.1 m for each of the sections.

In the reactive packed distillation column, the rectifying, the reaction and the stripping sections each also had 7 packed segments. As in the reactive tray distillation column, the condenser type was total and the reboiler was kettle type. Raschig ring was employed for the sizing of the packings involved in the rectifying and the stripping sections of the column each having a section packed height of 0.7 m.

For the two reactive distillation columns, RadFrac type was used and Van Laar/Redlich-Kwong equation of state with Henry's law was employed as the property method.

The acetalization reaction occurring in the reaction sections of the columns, modeled as an equilibrium type with molarity as the basis of equilibrium constant computed from Gibbs energy, is as given in Equation (1) below:

$$2CH_3OH + HCHO \leftrightarrow CH_3OCH_2OCH_3 + H_2O$$

After the completion of the modeling of the two reactive distillation columns, their steady-state simulations were achieved also in the same Aspen Plus environment using a reflux ratio and a reboiler duty of 3 and 0.35 kJ/sec, respectively.

3. RESULTS AND DISCUSSIONS

This work has been carried out to simulate the reactive distillation process using tray and packed distillation columns for the production of methylal. The process was modeled and simulated using Aspen Plus. The results obtained from the simulation of the reactive traydistillation column were compared with those of the reactive packed distillation columnas shown in the figures that follow.

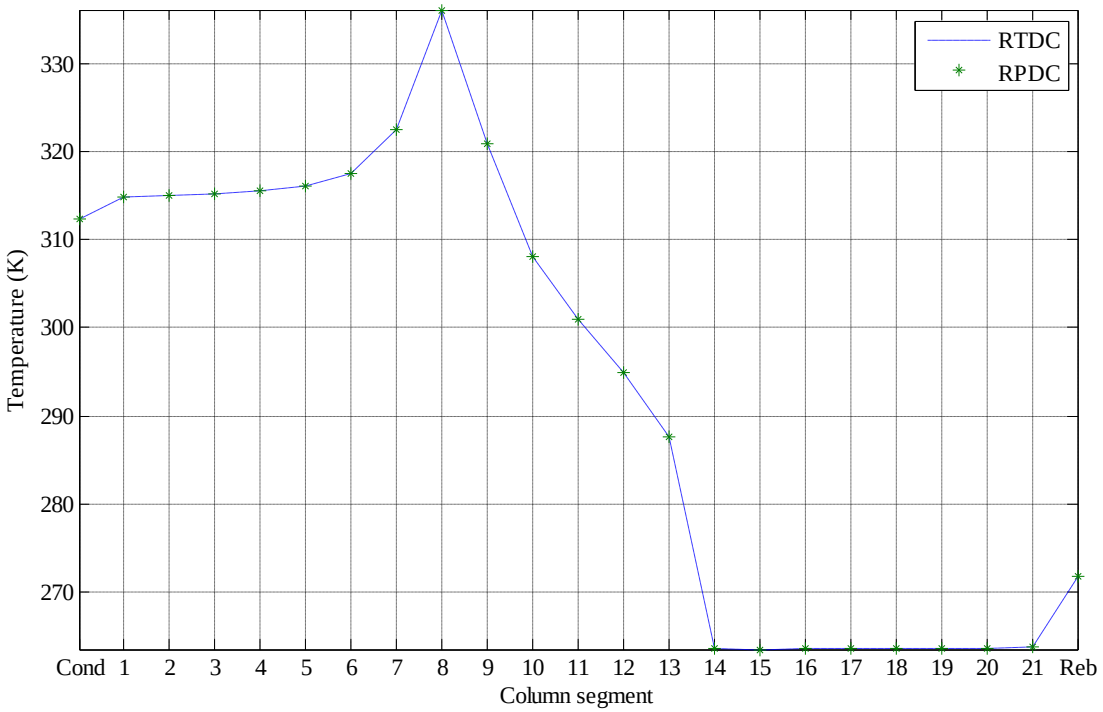

Figure 3. Temperature profiles of reactive tray and packed distillation columns

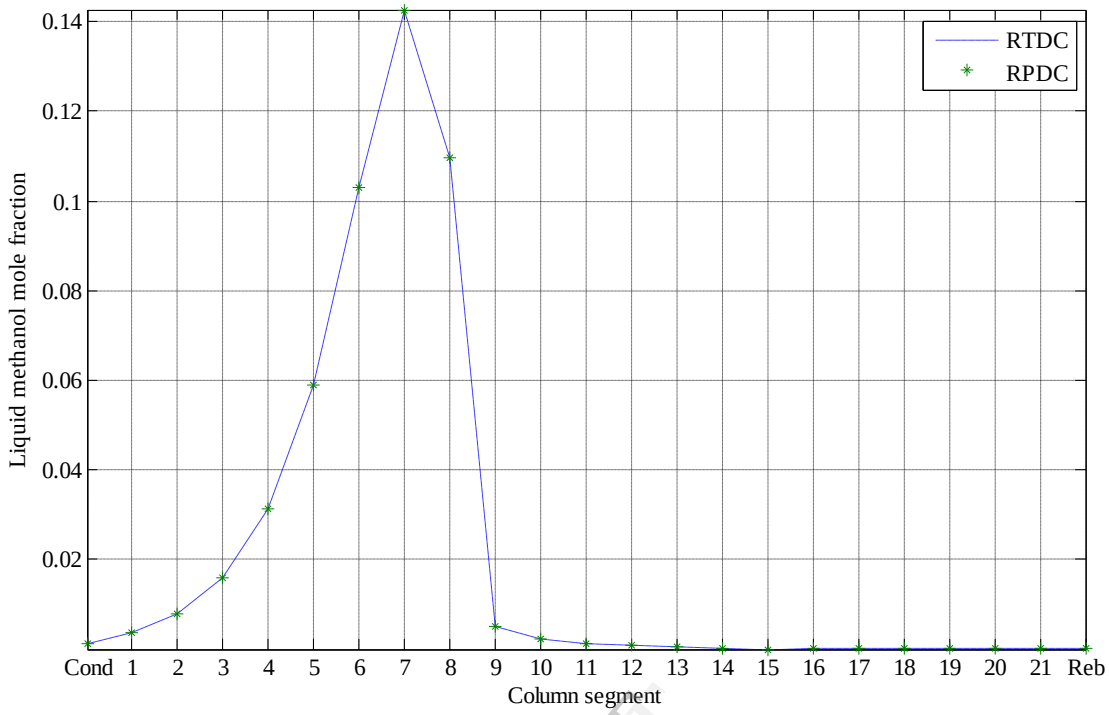

Figure 4. Liquid methanol mole fraction profiles of reactive tray and packed distillation columns

Shown in Figure 3 are the temperature profiles of the reactive tray and the reactive packed distillation columns studied in this work. As can be seen from the figure, the profiles of the two reactive distillation columns were found to be in good agreement with each other because they were able to follow the same trends. According to the figure, the maximum temperatures of the columns were found to occur at the beginning of the reaction sections of the columns; that is, at the points where methanol feeds werepassed into the columns. One interesting thing noticed in the temperature profile of each of the columns was that the temperature of the reboiler was lower than that of the condenser. This situation was actually found contrary to what was being expected because, normally, the temperature of a condenser is expected to be less than that of a reboiler. Nevertheless, it has been discovered from this study that the reverse is also possible, depending on the process being considered. This observation was found to be a very new finding in the course of reactive distillation process studied so far, and it needs further thorough investigation.

Also shown in Figure 4 are the composition profiles of liquid methanol obtained from the simulations of the reactive tray and the reactive packed distillation processes. From the figure, it was observed that the trends of the mole fractions of liquid methanol obtained from the two columns were the same. In addition, the maximum liquid methanol mole fractions for the two columns were found to be present in tray 7 and segment 7 for the reactive tray distillation column and the reactive packed distillation column, respectively. As from that point (tray/segment 7), the liquid methanol mole fractions contained in the reaction sections of the columns were discovered to decrease downwards towards the formaldehyde feeding tray/segment. The decreasing phenomenon of liquid methanol mole fractions in the reaction sections down the column was found to be normal because it was certain that liquid methanol, being one of the reactants of the acetalization process, was being consumed in the reaction sections of the columns.

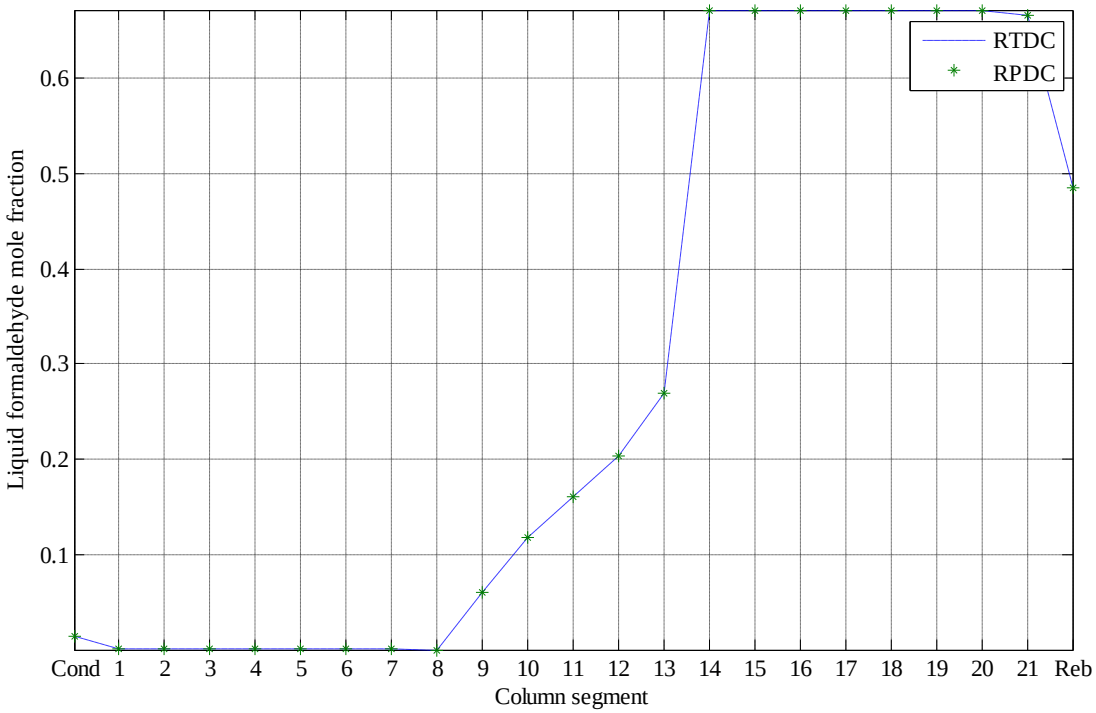

Figure 5. Liquid formaldehyde mole fraction profiles of reactive tray and packed distillation columns

In Figure 5, the composition profiles of the liquid formaldehyde mole fractions given by the simulations of the columns are shown. As was observed in the case of the liquid methanol mole fractions in which the trends of the profiles were the same for the reactive tray and the reactive packed distillation columns, the same thing was also discovered to occur in this case of the liquid formaldehyde mole fraction profiles. However, in this case, the mole fractions of formaldehyde was found to decrease upwards in the reaction sections towards the liquid methanol feed tray/segment of the columns.

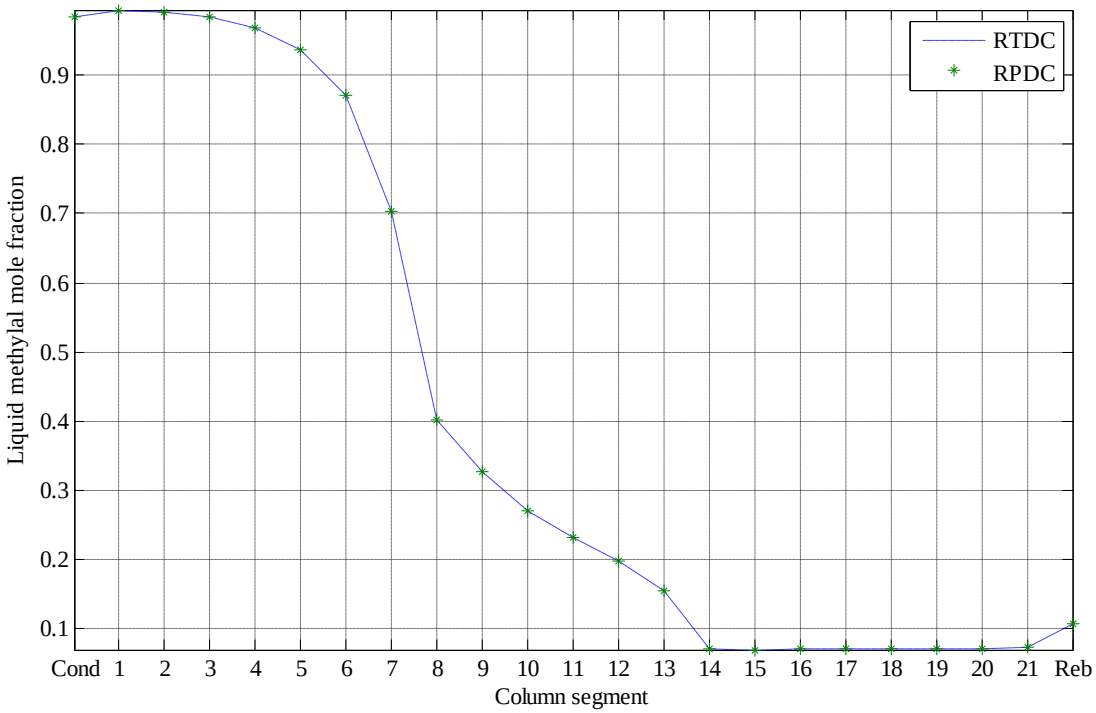

Figure 6. Liquid methylal mole fraction profiles of reactive tray and packed distillation columns

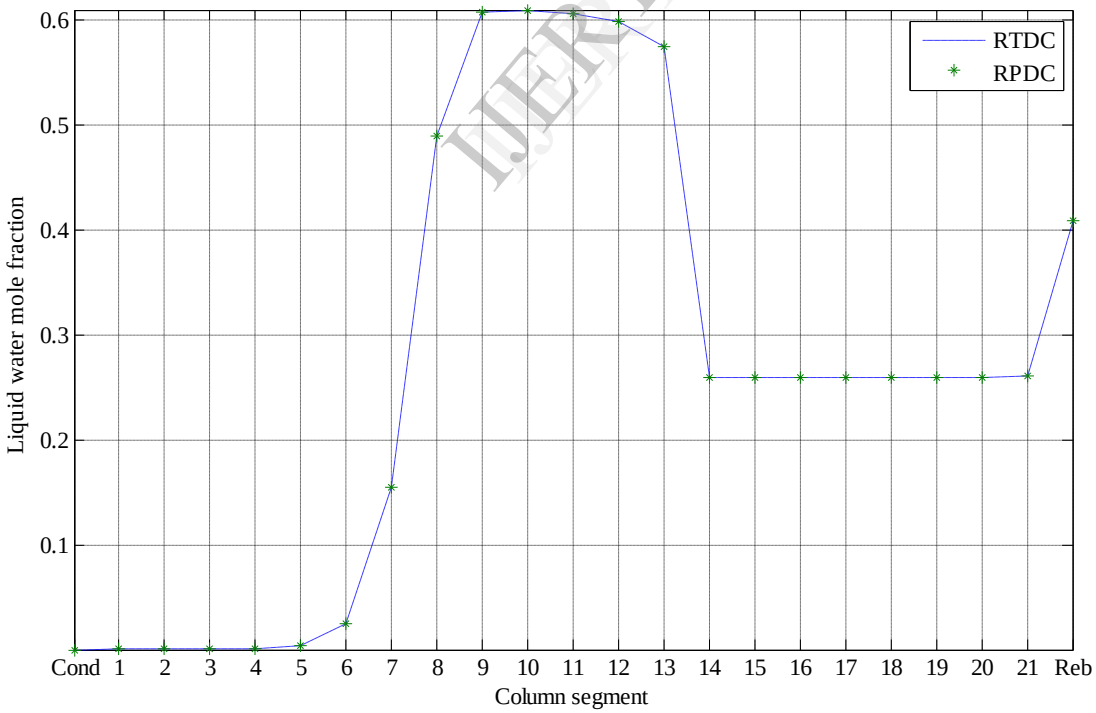

Figure 7. Liquid water mole fraction profiles of reactive tray and packed distillation columns

The liquid mole fraction profiles of the desired product (methylal) are as shown in Figure 6. As can be observed from the figure, the trends of the liquid methylal were also found to be the same for the two columns considered in this work. Furthermore, very high mole fractions of methylal were

able to be obtained at the top sections of the columns. Specifically, methylal product as pure as having 0.9841 as the mole fraction was obtained from each of the columns.

Shown in Figure 7 are the composition profiles of water obtained as one of the products from the simulations of the columns. According to the profiles shown in Figure 7, the trends of the two composition profiles of the two reactive distillation columns were found to be the same as well. Also, the maximum mole fractions of water given by the processes were found to be present within the reaction sections of the columns. As can be seen from the figure, the mole fractions of water present in the condensers of the columns were very negligible. It was also noticed that there were no significant changes in the mole fractions of water present in the stripping sections of the columns.

Considering the temperature and the liquid composition profiles, it has been discovered that the behaviors of the two reactive distillation columns (reactive tray distillation column and reactive packed distillation column) studied in this work were the same under steady-state simulations. It was deemed necessary to also investigate the relationships between the vapor mole fractions of the components of the two reactive distillation columns under steady state. Based on this, the vapor mole fraction profiles of the components obtained from the steady-statesimulations of the reactive tray and the reactive packed distillation columns were plotted and discussed as outlined thus.

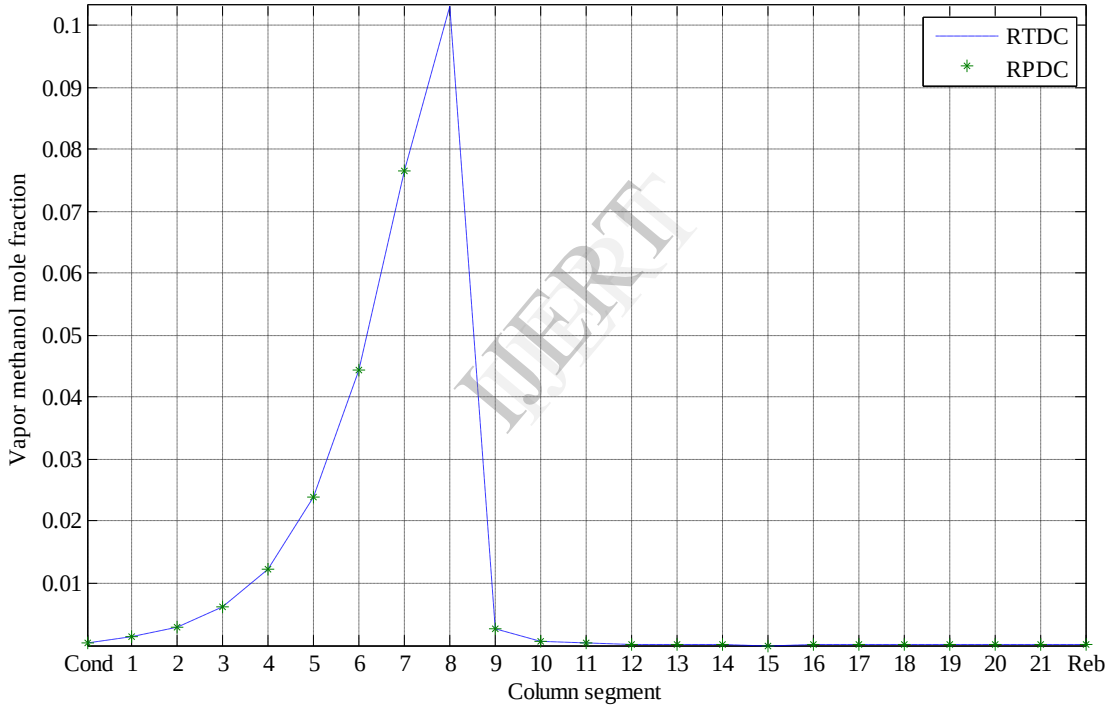

Figure 8. Vapor methanol mole fraction profiles of reactive tray and packed distillation columns

Shown in Figure 8 are the composition profiles of the vapor methanol obtained from the simulations of the columns. From the figure, it was noticed that the trends of the profiles of the vapor methanol present in the two columns were the same. Besides, the highest mole fraction of vapor methanol was found to exist in tray/segment 8 of the columns, in contrary to the case of the liquid methanol (Figure 4) in which the highest liquid methanol mole fractions occurred in tray/segment 7 of the columns.In addition, close similarities were found to exist between the profiles of the liquid methanol and that of the vapor methanol obtained from the two columns.

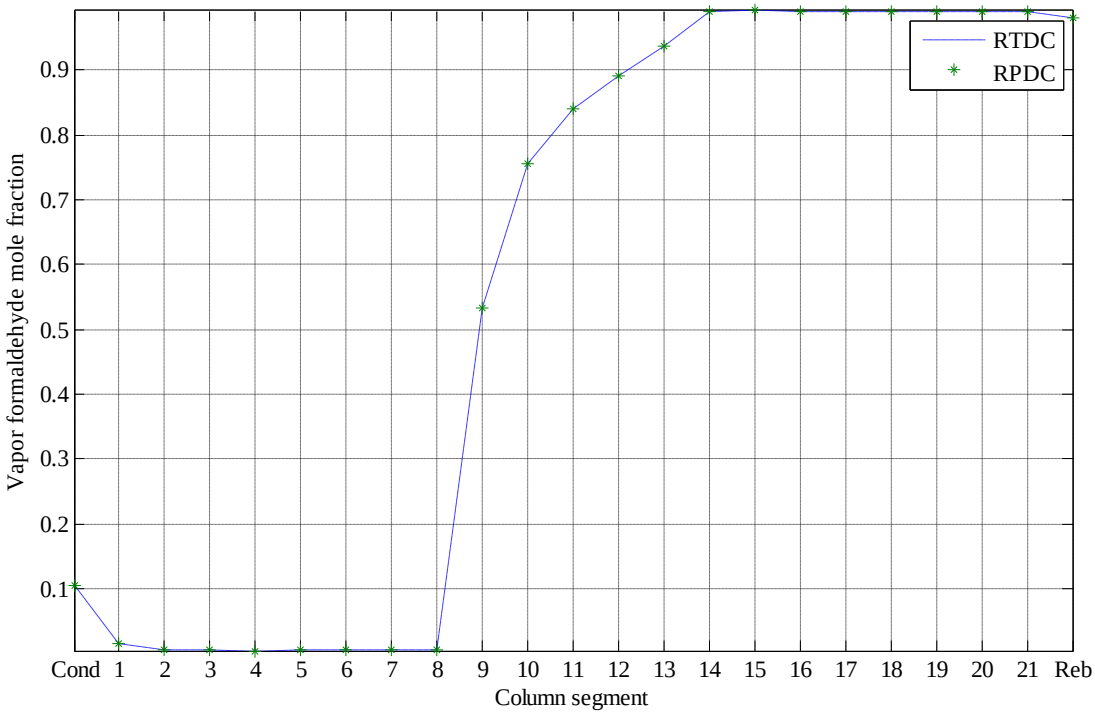

Figure 9. Vapor formaldehyde mole fraction profiles of reactive tray and packed distillation columns

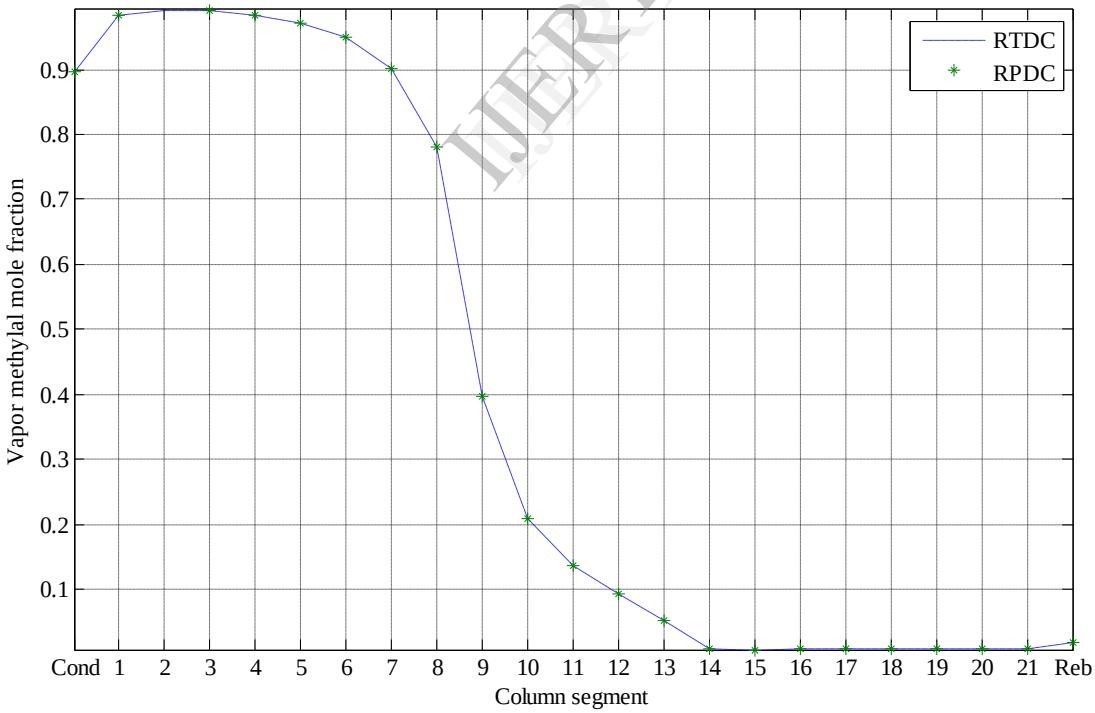

Figure 10. Vapor methylal mole fraction profiles of reactive tray and packed distillation columns

In Figure 9, the mole fraction profiles of the vapor formaldehyde present in the columns are given. Similar to the trends obtained among the discussed profiles so far, the trends of the vapor formaldehyde profiles of the columns were also discovered to be the same with each other, as clearly shown in Figure 9. As was observed in the case of liquid formaldehyde mole fraction profiles (Figure

5), the highest mole fraction of vapor formaldehyde was found to also occur in the stripping sections of the columns. In addition, the highest mole fractions of vapor formaldehyde obtained in the stripping sections of the columns were found to be constant throughout thosesections of each columns.

Considering the vapor methylal mole fraction profiles obtained from the reactive distillation columns, shown in Figure 10, it was also discovered that the trends of the profiles of vapor methylal for both the reactive tray and the reactive packed distillation columns were the same, just as it was found in the case of the liquid methylal mole fraction profiles. Also, as methylal was the desired product that was found to be more volatile than the second product (water) and, which was expected to be collected from the condensers of the columns, methylal was found to have very high mole fraction at the top sections of the columns, especially at the condensers of the columns from where the top product was collected in liquid form after being condensed.

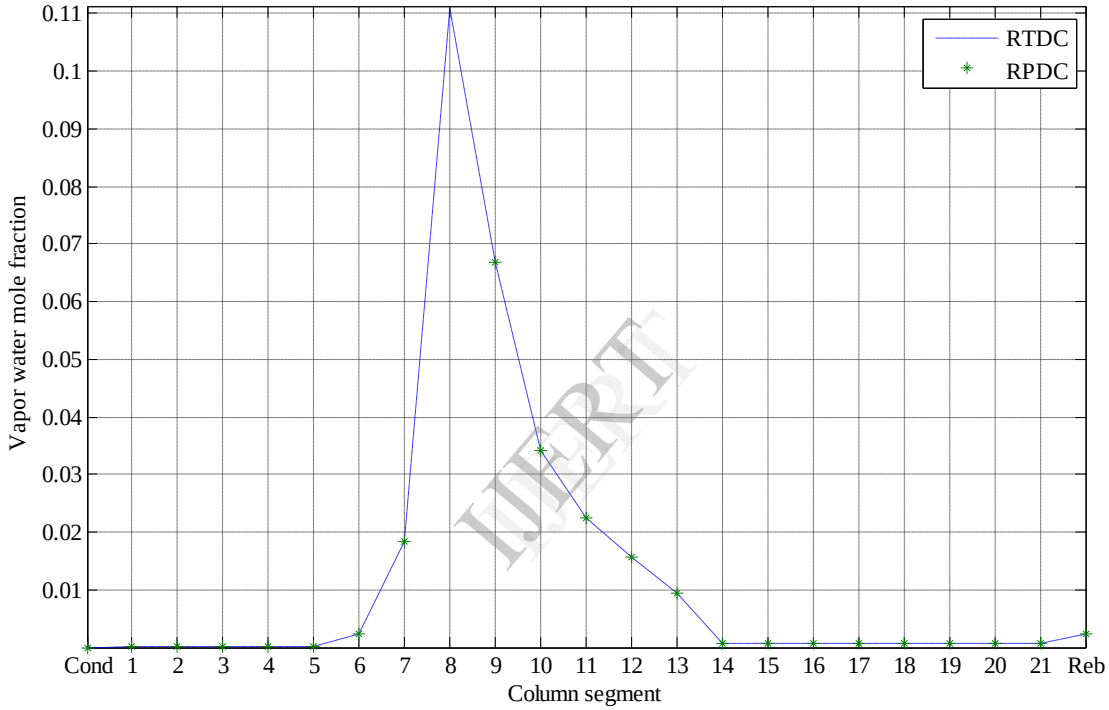

Figure 11. Vapor water mole fraction profiles of reactive tray and packed distillation columns

The last profiles considered in this work, and shown graphically in Figure 11, was that of the vapor mole fractions of the second product of the process (water). As can be seen from the figure, the mole fraction profiles of the vapor water obtained from the simulations of the reactive tray and the reactive packed distillation columns were found to be the same. Apart from that, the highest mole fractions of vapor water in the columns were found to occur in tray/segment 8 of the columns.

4. CONCLUSIONS

The results obtained from this work have shown that the behaviors of the temperature profiles of the reactive tray and the reactive packed distillation columns studied in this work were the same with each other. Apart from that, the liquid component mole fraction profiles of the two reactive distillation columns were also found to be the same. Not only that, the vapor mole fraction profiles of the components obtained from the simulations of the two reactive distillation columns considered were as well revealed to be the same. It has, therefore, been found that, at steady state, the behaviors of both the reactive tray distillation column and the reactive packed distillation column used for the

production of methylal from the acetalization reaction between methanol and formaldehyde were the same.

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NOMENCLATURES

CBOTPROD	Column bottom product
CTOPPROD	Column top product
FORMALDE	Formaldehyde feed
METHANOL	Methanol feed
RPAKDCOL	Reactive packed column
RPDC	Reactive packed distillation column
RTDC	Reactive tray distillation column
RTRAYCOL	Reactive tray column

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