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RESEARCH ARTICLE

Effects of Feed Stage on the Product Composition of a Reactive Distillation Process: A Case Study of *trans*-2-Pentene Metathesis

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Abstract

Investigating the effects of feed stage on the purity of the top and bottom products obtained from a reactive distillation process used to produce *trans*-2-butene and *trans*-2-hexene by employing a metathesis reaction has been carried out in this work. The investigation was done by developing a model of the process with the aid of Aspen Plus of the reactive distillation process using RadFrac column that had 21 stages including the condenser and the reboiler. The developed Aspen Plus model of the process was simulated with Wilson model as the property package, and the feed of the process was passed into the column at a temperature and a pressure of 25 ^{o}C and 1 atm respectively at the rate of 0.035 L/min. The metathesis reaction occurring in the reaction (middle) of the column was an equilibrium type, and its equilibrium constant was calculated from Gibbs energy. After developing the olefin metathesis reactive distillation process model using the Aspen Plus, it was simulated by varying the feed stage from stage 2 (the stage below the condenser) to 21 (the reboiler). The results of the simulations showed that the highest mole fraction of the products (*trans*-2-butene and *trans*-2-hexene) were obtainable from the reactive distillation process when the feed (*trans*-2-pentene) was fed at the reaction section of the column. Therefore, it has been discovered that the feed stage of *trans*-2-pentene was affecting the purities of the *trans*-2-butene and *trans*-2-hexene obtained as the main products of the metathesis process considered because as the feed stage was varied, their mole fractions were also discovered to vary.

INTRODUCTION

The process of converting an olefin into lower and higher molecular weight olefins is known as olefin metathesis. This process belongs to a class of reactions that are ideally suited for reactive distillation applications as many of the reactions involved in it are in liquid phase at ambient to moderate conditions, and the reactants and products are similar chemicals; so, they exhibit very little deviation from Raoult's law. Also, in this process, the relative order of olefin boiling points are determined based on their molecular weights. As such, the boiling points of the products for metathesis reactions straddle the boiling point of the reactant so that reactive azeotropes do not form, and this allows easy removal of the products, thereby minimizing side reactions or additional metathesis of products and overcoming reaction equilibrium limitations (Okasinski and Doherty, 1998; Giwa and Giwa, 2013a; Giwa and Giwa, 2015).

Dow Chemical Company patented a commercial process for conducting 1-butene metathesis using a distillation column (Jung *et al.*, 1987), and they claimed that conducting reaction and separation simultaneously was able to reduce by-product formation and overcome equilibrium limitations. This resulted in increased selectivity and higher yield of the product from the process involving simultaneous reaction and separation over conventional method of separation following reaction in series (Okasinski and Doherty, 1998; Giwa and Giwa, 2013a; Giwa and Giwa, 2015). This process of accomplishing reaction and separation simultaneously, in a single unit, is what is referred to as “reactive distillation”.

Reactive distillation can be defined as a process that has the capability of combining both separation and chemical reaction in a single unit. It is a very attractive process whenever reaction equilibrium is the factor limiting conversion (Balasubramhanya and Doyle III, 2000; Lai *et al.*, 2007; Giwa and Karacan, 2012e; Giwa and Giwa, 2012; Giwa, 2013; Giwa *et al.*, 2014). It is an excellent alternative to conventional flowsheets with different reaction and separation sections (Al-Arfaj and Luyben, 2002; Giwa and Karacan, 2012d) because it combines the benefits of equilibrium reaction with distillation to enhance conversion (Giwa and Karacan, 2012a; Giwa and Karacan, 2012c). There are several advantages associated with combining reaction and distillation; among them is shift of chemical equilibrium and an increase of reaction conversion by simultaneous reaction and separation of products, suppression of side reactions and utilization of heat of reaction for mass transfer operation (Giwa and Karacan, 2012b; Giwa *et al.*, 2015). Utilizing heat of reaction for mass transfer operation results into low external energy consumption of the process, and this gives rise to reduced investment and operating costs (Giwa, 2012; Giwa and Giwa, 2015) of the process.

Reactive distillation exhibits complex behaviours as a result of the integration of reaction and separation (Khaledi and Young 2005; Giwa and Karacan, 2012a; Giwa and Giwa, 2013b), such as steady state multiplicity, process gain sign changes (bidirectionality) and strong interactions between process variables (Jana and Adari 2009; Giwa and Karacan, 2012a). These complexities have made the operation of reactive distillation process a little bit tasking. Thus, there is a need to understand the factors affecting the operation of the process as much as possible so that it can be easily handled and made to give desired product(s).

Several researches have been carried out on reactive distillation process, and those concerning olefin metathesis process include that of Giwa and Giwa (2013a) in which the optimum parameters required for the operation of a reactive distillation column used for the production of *trans*-2-butene and *trans*-2-hexene were estimated with the aid of Aspen HYSYS model of the process they developed. Also, Giwa and Giwa (2013b) used layer-recurrent neural network to model a reactive distillation column in which olefin metathesis was taking place, even though the model they developed was not explored towards estimating the parameters required for the operation of the column. Furthermore, Giwa and Giwa (2015) developed AutoRegressive with eXogenous Inputs (ARX) and AutoRegressive Moving Average with eXogenous Inputs (ARMAX) models for olefin metathesis process accomplished using a reactive distillation column. Just as in the case of the work of Giwa and Giwa (2013b), the model they too developed was not utilized to carry out investigations on the operation of the process.

Based on the information obtained from the literature, among the researches carried out on the metathesis of olefin of the production of other olefin, no one has considered finding out what could happen when the stage of the feed is changed. As a result of that, this work has been carried out to study the effects that changing the feed stage of the olefin metathesis reactive distillation process has on the purities of the products obtained from the column used.

Material and Methods

The program used to develop the model of the olefin metathesis reactive distillation process producing *trans*-2-butene and *trans*-2-hexene from the metathesis reaction of *trans*-2-pentene in this work was Aspen Plus (Aspen, 2001), and the developed model was as shown in Figure 1.

The feed was pure *trans*-2-pentene that was passed at a temperature of 25 ^{o}C and a pressure of 1 atm at the rate of 0.035 L/min into the column having 21 stages including its total condenser and kettle reboiler. The condenser pressure was also 1 atm and the pressure drop along the column was neglected.

The metathesis reaction occurring in the reaction section (stages 7 -15) of the column was an equilibrium type given as shown in Equation (1); the phase of the reaction was liquid and the basis of the equilibrium constant computed from Gibbs energy was mole fraction.

$$2C_5H_{10} \xleftrightarrow{K_{eq}} C_4H_8 + C_6H_{12} \qquad (1)$$

To simulate the developed model of the process, Wilson property method was employed, and the molar reflux ratio and the reboiler duty were 2 and 0.15 kW respectively.

In investigating the effects of the feed stage on the composition (purity) of the products, the feed was passed into the column at different stage ranging from 2 (the stage below the condenser) to 21 (reboiler), and the variation of the mole fractions of the components present in the top and the bottom products with the change in the feed stage were obtained.

Result and Discussion

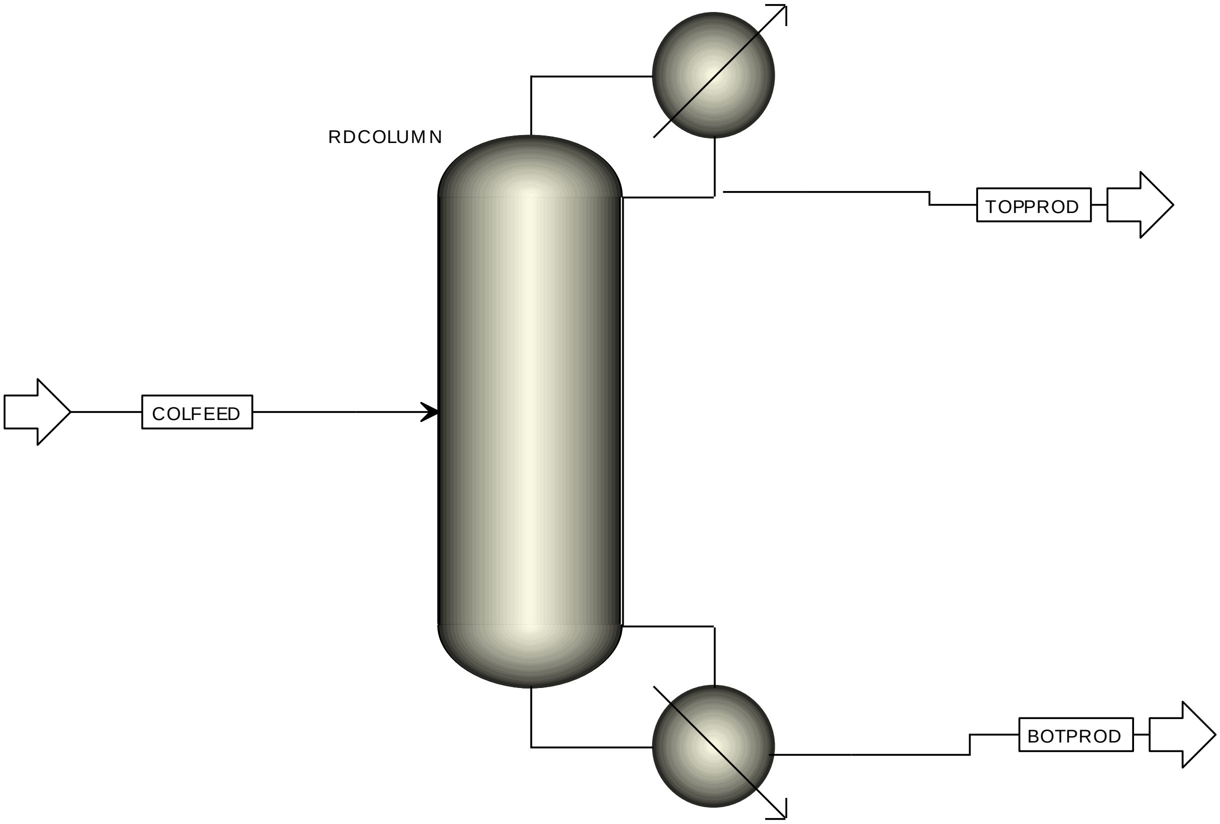

Figure 1. Aspen PLUS model of olefin metathesis reactive distillation process

The mole fraction obtained for the components present in the top product of the olefin metathesis reactive distillation process are given in Figures 2 – 5. In Figure 2, the variation of the mole fraction of *trans*-2-pentene as the stage through which the feed was introduced into the column was also varied is shown. According to the figure, the reactant (*trans*-2-pentene) had its highest mole fraction at the top of the column when the feed was introduced through the bottom (reboiler) section of the column. Also, the mole fraction of *trans*-2-pentene obtained from the simulation carried out when it was fed at the 2nd stage, counted from the top, of the column was high, but not as high as that of when it was fed at the bottom section. From the results given in Figure 2, it was clear that introducing the feed at any part of the reaction section of the column was able to favour the conversion of the reactant because the mole fraction of *trans*-2-pentene leaving the top section of the column, in that case, was found to be negligible.

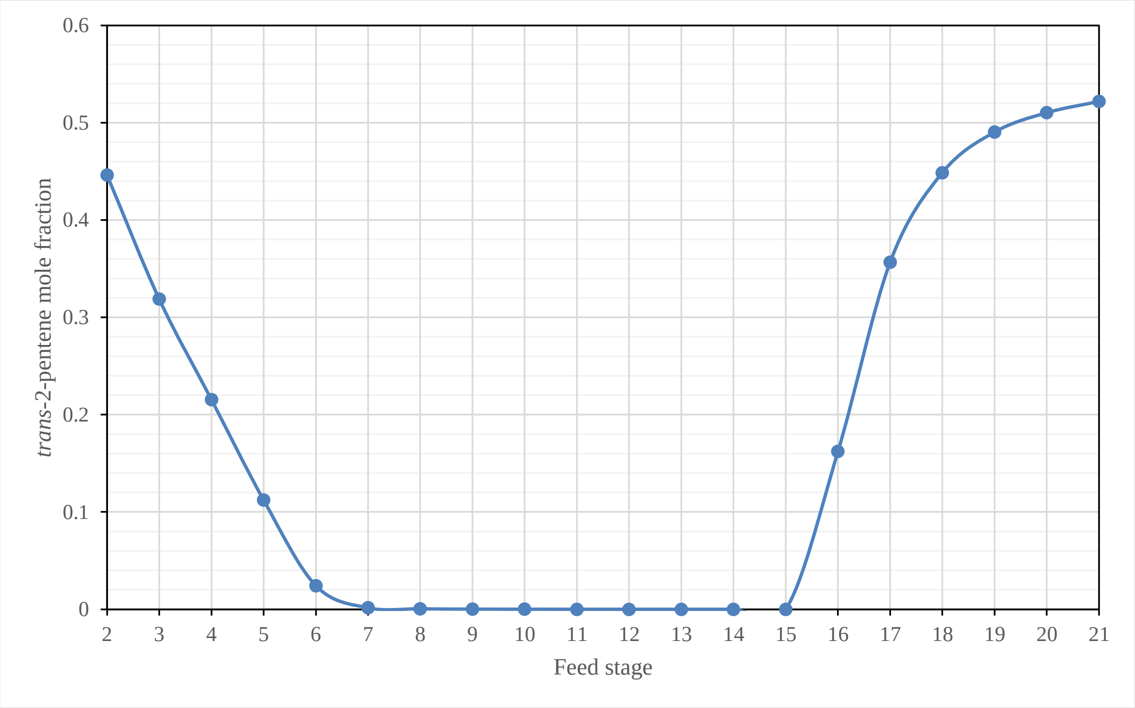

Figure 2. Variation of mole fraction of *trans*-2-pentene obtained from the top product with feed stage

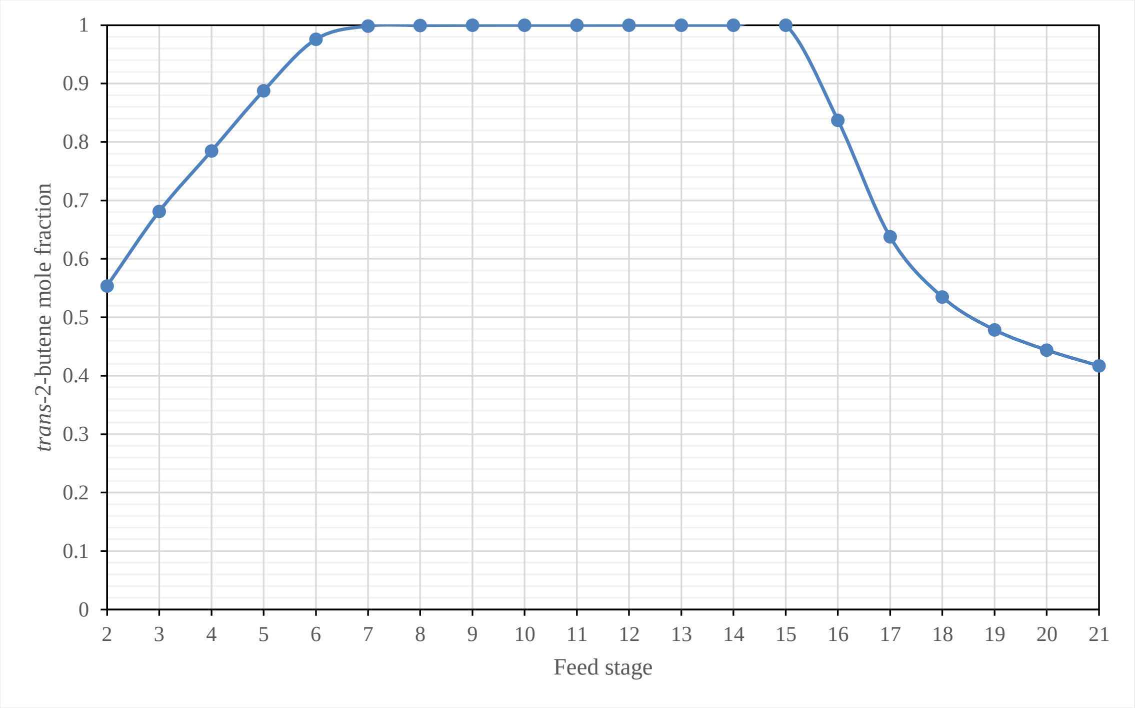

Figure 3. Variation of mole fraction of *trans*-2-butene obtained from the top product with feed stage

Shown in Figure 3 is the variation of the mole fraction of *trans*-2-butene (one of the products of the process) with the feed stage. From the figure, it was observed that the product had its highest mole fraction at the top (condenser) section of the column when the feed was introduced at the reaction section. It should be recalled that it was when the feed was introduced at the reaction section that the reactant (*trans*-2-pentene) had its own lowest mole fraction at the top section of the column. It has, thus, been discovered that the behaviour of the mole fractions of *trans*-2-pentene and *trans*-2-butene were in opposite relationship to each other.

In Figure 4, the mole fraction profile of the second product of the process (*trans*-2-hexene) obtained from the top section of the column when the feed stage was varied from 2 to 21 is shown, and it was observed that, regardless of the stage at which the feed was introduced, the *trans*-2-hexene component obtained from the top section of the column was negligible at that section of the column because its highest mole fraction given at the top section, as indicated on the figure, was found to be approximately 0.061. Looking at the results very well, the mole fraction of *trans*-2-hexene present at the top section when *trans*-2-pentene was fed between stages 2 and 15 was approximately equal to zero.

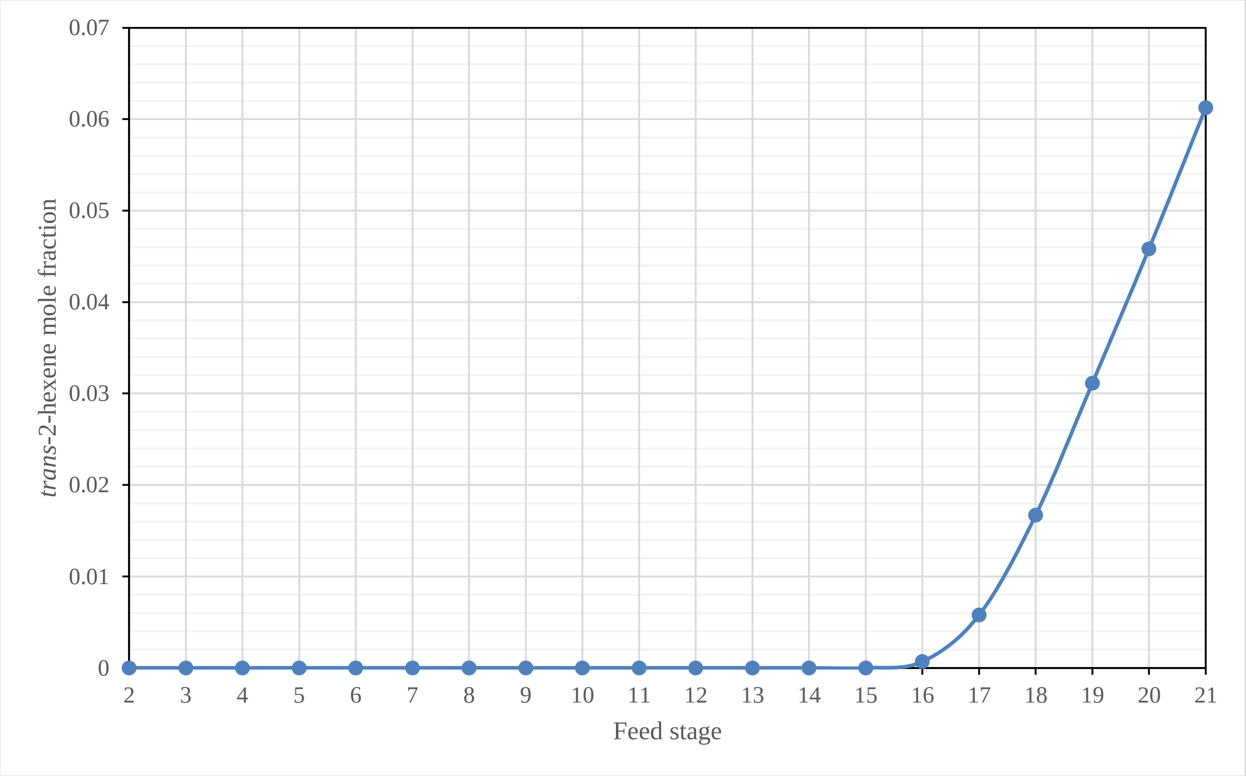

Figure 4. Variation of mole fraction of *trans*-2-hexene obtained from the top product with feed stage

Since there are two points from which products were being withdrawn from the column – top (condenser) section and bottom (reboiler) section, the mole fractions of the components obtained from the reboiler section of the column as the feed stage was varied were also considered, and shown in Figures 5 – 7 are the results obtained for *trans*-2-pentene, *trans*-2-butene and *trans*-2-hexene, respectively.

From the results given in Figure 5 that is showing the variation of the mole fraction of *trans*-2-pentene present in the bottom product of the process as the feed stage was varied from 2 to 21, it was discovered that the feed stage that favoured the conversion of the reactant (*trans*-2-pentene) for the bottom product also was at the reaction section of the column because that was where the mole fraction of the unconverted reactant of the process coming out from the reboiler section of the column was the lowest.

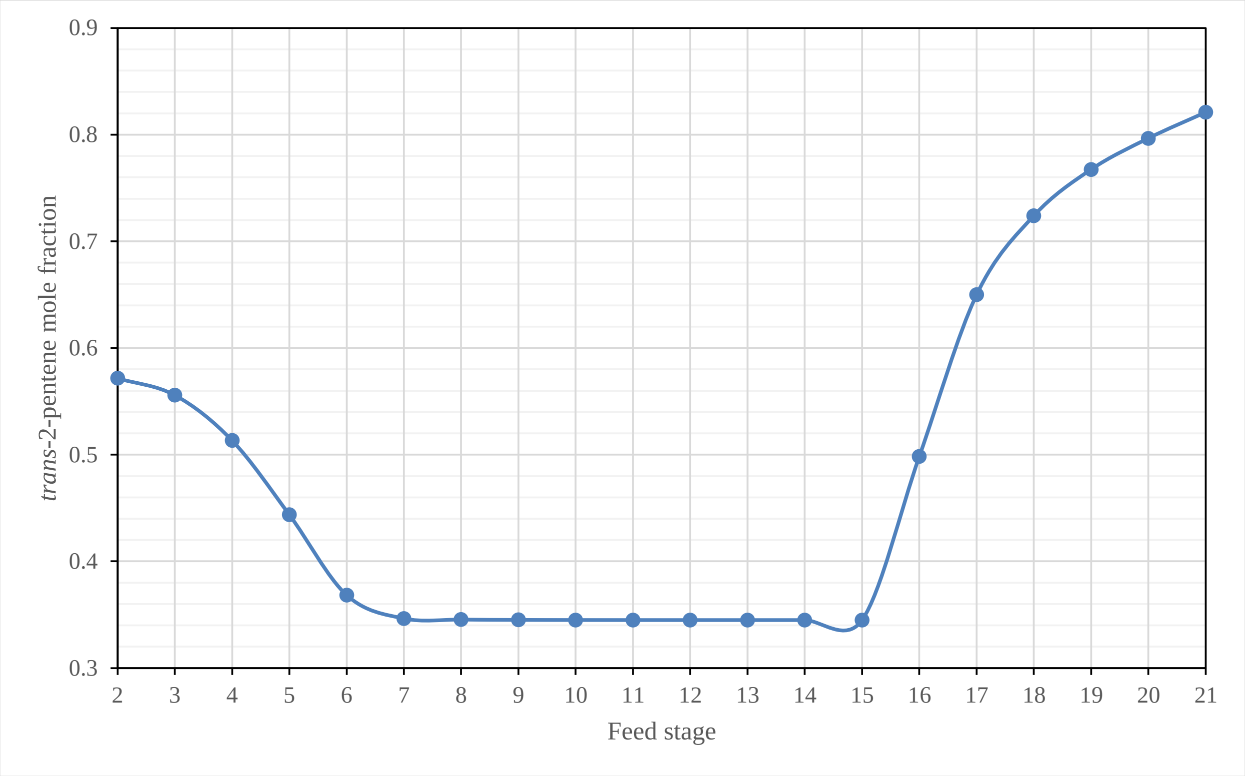

Figure 5. Variation of mole fraction of *trans*-2-pentene obtained from the bottom product with feed stage

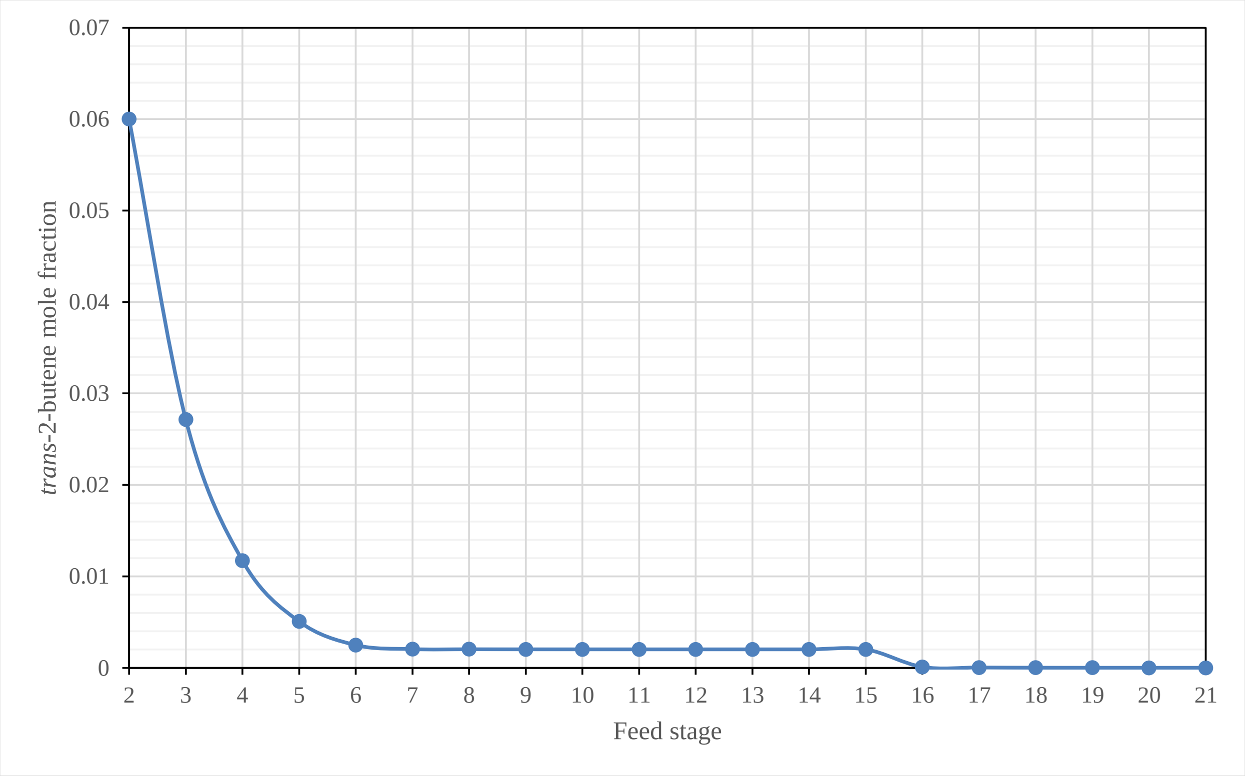

Figure 6. Variation of mole fraction of *trans*-2-butene obtained from the bottom product with feed stage

Owing to the fact that *trans*-2-butene was the lightest component of the process, its mole fraction obtained from the bottom section of the column was found to be negligible, as can be seen from the profile shown in Figure 6. Even when the feed was passed into the column from the reboiler section of the column, the mole fraction of *trans*-2-butene was still found to be very low, in fact, approximately zero.

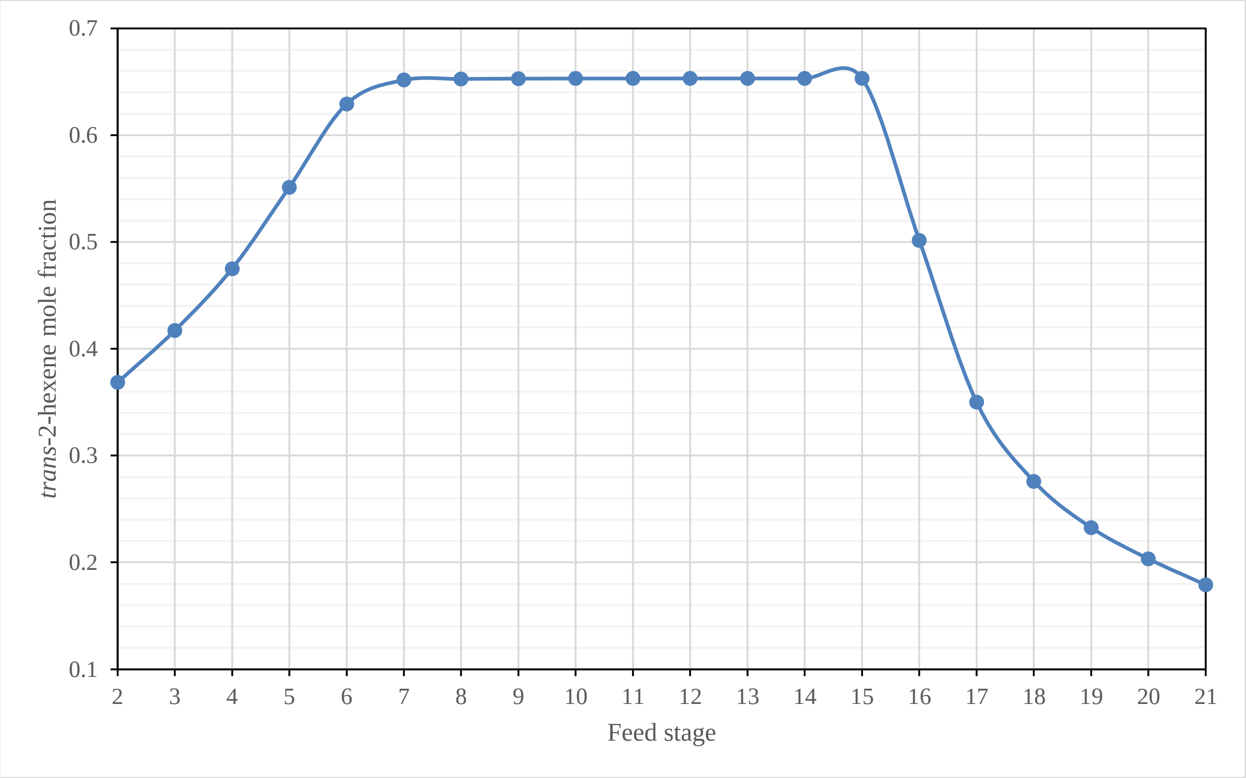

Figure 7. Variation of mole fraction of *trans*-2-hexene obtained from the bottom product with feed stage

Considering the mole fraction of the heavy product, given in Figure 7, it was noticed that feeding the reactant at the reaction section of the column was favourable to the production of *trans*-2-hexene because the mole fraction of the *trans*-2-hexene product was found to be high as a result of feeding *trans*-2-pentene at the reaction section of the column.

Considering all the results obtained from the simulations carried out using Aspen Plus to investigate the effects of feed stage on the purity of products obtained from the olefin metathesis reactive distillation process considered in this work, it was found that the highest mole fraction (0.999999) of *trans*-2-butene was obtained from the top product of the column when the feed was introduced into the column within the reaction section. Also, *trans*-2-hexene was obtained from the bottom product with its highest purity of 0.653033 obtained with the feed stage being in the reaction section of the column. As can be seen, the light product of the process (*trans*-2-butene) was obtained in the top product and the heavy product was obtained in the bottom product in their highest purities in the process when the feed was passed into the column at the reaction section.

Conclusion

The results obtained from the simulations of the olefin metathesis reactive distillation process model developed with the aid of Aspen Plus revealed that the highest mole fraction of the products (*trans*-2-butene and *trans*-2-hexene) were obtained from the reactive distillation process when the feed (*trans*-2-pentene) was fed at the reaction section of the column. Therefore, *trans*-2-pentene feed stage has been found to affect the purities of the products given by the olefin metathesis reactive distillation process because their mole fractions were discovered to vary as the stage from which *trans*-2-pentene was introduced into the column was also varied.

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Nomenclature

BOTPROD	Bottom product
COLFEED	Column feed
K_{eq}	Equilibrium constant
RDCOLUMN	Reactive distillation column
TOPPROD	Top product

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