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ESTIMATING THE OPTIMUM OPERATING PARAMETERS OF OLEFIN METATHESIS REACTIVE DISTILLATION PROCESS

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ABSTRACT

This work has been carried out to apply Fletcher Reeves, Quasi-Newton, BOX, SQP, and Mixed optimization algorithms to estimate the optimum operating parameters required for the achievement of high purities of trans-2-butene and trans-2-hexene respectively as the top and the bottom products using olefin metathesis process occurring in a reactive packed distillation column. The process was modeled and optimized with the aid of Aspen HYSYS. The model had a trans-2-pentene feed stream containing 1 ppm each of trans-2-butene and trans-2-hexene flowing at the rate of 35 mL/min into the column at a temperature of 298.15 K and a pressure of 1.125 bar. The results obtained from the optimizations of the process revealed that the constrained optimization was better than the unconstrained one for this process because, in the single objective optimizations carried out, the top and the bottom products were desired. It was discovered from the constrained optimizations carried out that Mixed algorithm was the best among the algorithms considered because it was able to give the optimum reflux ratio of 2.50, the optimum feed flow rate of 43.75 mL/min and the optimum reboiler duty of 0.28 kW that yielded trans-2-butene of mole fraction value of 1.0000 and trans-2-hexene of mole fraction of 0.9422 as the top and the bottom products, respectively.

Keywords: olefin metathesis, reactive distillation, Aspen HYSYS, optimization.

1. INTRODUCTION

Reactive distillation is a process that combines both separation and chemical reaction in a single unit. It is very attractive whenever conversion is limited by reaction equilibrium (Balasubramhanya and Doyle III, 2000; Giwa and Karacan, 2012a) because it combines the benefits of equilibrium reaction with distillation to enhance conversion provided that the product of interest has the largest or the lowest boiling point (Taylor and Krishna, 2000; Giwa and Karacan, 2012a). It has a lot of advantages which include reduced investment and operating costs due to increased yield of a reversible reaction by separating the product of interest from the reaction mixture (Pérez-Correa *et al.*, 2008; Giwa and Karacan, 2012a), higher conversion, improved selectivity, lower energy consumption, scope for difficult separations and avoidance of azeotropes (Jana and Adari, 2009; Giwa and Karacan, 2012a). However, due to the integration of reaction and separation, reactive distillation exhibits complex behaviors (Khaledi and Young, 2005; Giwa and Karacan, 2012a), such as steady state multiplicity, process gain sign changes (bidirectionality) and strong interactions between process variables (Jana and Adari, 2009; Giwa and Karacan, 2012a) involved.

Owing to the conditions required for the accomplishment of this reactive distillation process, it can only be applied to some specific processes. The reactions that have been investigated (either on a commercial scale or on a laboratory scale) as candidates or suggested to be investigated for reactive distillation process (Sharma and Mahajani, 2002) include etherification, esterification with alcohols/olefins, synthesis of vinyl acetate, transesterification, hydrolysis, acetalization, aldol condensation followed by dehydration, hydration, dehydration, alkylation, trans-alkylation, dealkylation, isomerization, chlorination, hydrogenation, hydrodesulfurization, dehydrogenation, olefin metathesis, disproportionation, condensation of aldehydes, dimerization, oligomerization, production of diethanol amine, carbonylation, addition of amines to aldehydes/ketones, amination, alcoholysis, neutralization (protonation of organic bases), amidation, nitration, separation of close boiling compounds, cracking, and impurity removal. The chemical process of concern to this work, among those listed, is olefin metathesis.

Olefin metathesis is a process of converting an olefin into lower and higher molecular weight olefins. It is a class of reactions that are ideally suited for reactive distillation applications because many of the reactions 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. Moreover, the relative order of olefin boiling points can be determined based on their molecular weights. Thus, for metathesis reactions, the boiling points of the products straddle the boiling point of the reactant (in such cases, reactive azeotropes do not form). This allows easy removal of the products, thereby minimizing side reactions or additional metathesis of products and overcoming reaction equilibrium limitations. A commercial process for conducting 1-butene metathesis within a distillation column was patented by Dow Chemical Co. (Jung *et al.*, 1987). They claimed that conducting reaction and separation simultaneously was able to reduce byproduct formation and overcome equilibrium limitations and thus resulted in increased selectivity and higher yield over conventional series processing (Okasinski and Doherty, 1998).

Owing to the complex nature of this process (reactive distillation), the selection of its operating conditions is always a challenge. It is always good to use a parameter estimation technique to determine the operating conditions that produce the desired product in high purity from the appropriate segment of the column. Optimization techniques are normally employed in process industries to accomplish this. The optimization techniques used in process industries include: Fletcher Reeves, Quasi-Newton, BOX, Sequential Quadratic Programming (SQP), and Mixed.

In Fletcher Reeves Optimization Method, the procedure implemented is the Polak-Ribiere modification of the Fletcher-Reeves conjugate gradient scheme. The approach closely follows that of Press *et al*. (1988), with modifications to allow for lower and upper variable bounds. This method is efficient for general minimization with no constraints. The method used for the one-dimensional search can be found in Press *et al*. (1988). The Quasi-Newton method of Broyden-Fletcher-Goldfarb-Shanno (BFGS), according to Press *et al*. (1988), has been implemented. In terms of applicability and limitations, this method is similar to that of Fletcher-Reeves method. It calculates the new search directions from approximations of the inverse of the Hessian Matrix. BOX Method is loosely based on the “Complex” method of BOX (1965); the Downhill Simplex algorithm of Press *et al*. (1988) and the BOX algorithm of Kuester and Mize (1973). The BOX method is a sequential search technique which solves problems with non-linear objective functions, subject to non-linear inequality constraints. No derivatives are required. It handles inequality constraints but not equality constraints. The BOX method is not very efficient in terms of the required number of function evaluations. It generally requires a large number of iterations to converge on the solution. However, if applicable, this method can be very robust. The Sequential Quadratic Programming (SQP) method handles inequality and equality constraints. SQP is considered by many to be the most efficient method for minimization with general linear and non-linear constraints, provided a reasonable initial point is used and the number of primary variables is small. The implemented procedure is based entirely on the Harwell subroutines VF13 and VE17 (Harwell, 1990). The program follows closely the algorithm of Powell (1978). It minimizes a quadratic approximation of the Lagrangian function subjected to linear approximations of the constraints. The second derivative matrix of the Lagrangian function is estimated automatically. A line search procedure utilizing the “watchdog” technique (Chamberlain and Powell, 1982) is used to force convergence. The Mixed method attempts to take advantage of the global convergence characteristics of the BOX method and the efficiency of the SQP Method. It starts the minimization with the BOX method using a very loose convergence tolerance (50 times the desired tolerance). After convergence, the SQP method is then used to locate the final solution using the desired tolerance.

According to the information obtained from the literature, Giwa and Karacan (2012b) carried out the optimization of ethyl acetate reactive packed distillation process with the aid of Aspen HYSYS using Fletcher-Reeves, Quasi-Newton, and SQP algorithms. They used the optimum parameters of SQP to run an experimental setup for validation and were able to obtain a good agreement between the optimum top segment temperature and the experimental one.

Therefore, it is aimed in this work to apply the optimization techniques (Fletcher Reeves, Quasi-Newton, BOX, SQP, and Mixed) available in Aspen HYSYS to the reactive distillation process used for the production of trans-2-hexene and trans-2-butene from the metathesis reaction of trans-2-pentene.

2. PROCEDURES

The setup of the olefin metathesis process developed with the aid of Aspen HYSYS (Aspen, 2012) is as shown in Figure-1 below. It comprised a feed stream containing mostly trans-2-pentene with 1 ppm of trans-2-hexene and 1 ppm of trans-2-butene passed into the column at a temperature of 298.15 K and a pressure of 1.125 bar and flowing at a rate of 35 mL/min. UNIQUAC was employed as the Fluid Package of the simulation. The reactive distillation column was a packed type having 21 segments excluding the condenser and the reboiler. The column was divided into three sections of 7 segments each - rectifying section, reaction section and stripping section.

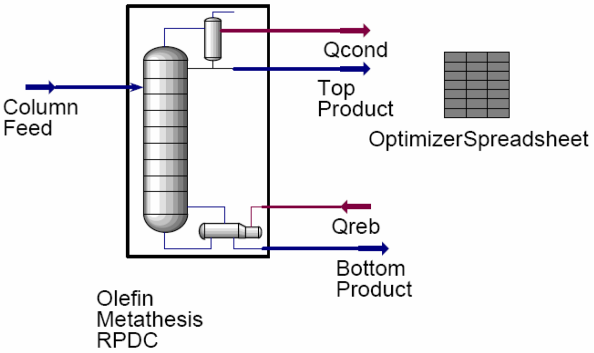

Figure-1. Olefin metathesis reactive packed distillation HYSYS model.

The olefin metathesis reaction occurring in the reaction section of the column was an equilibrium type given as shown in Equation (1).

$$2C_5H_{10} \xleftrightarrow{K_{eq}} C_4H_8 + C_6H_{12} \tag{1}$$

The reaction, which was occurring in liquid phase, was found to be exothermic with its heat of reaction estimated at 25 ^{o}C to be -774.45 kJ/kmol and its equilibrium constant was estimated using Gibbs free energy taking molar concentration as the basis.

After the Aspen HYSYS model of the process was set up, its steady-state simulation was first carried out using a reflux ration of 2, a feed flow rate of 35 mL/min and a reboiler duty of 0.3 kW. Thereafter, it was optimized using Fletcher Reeves, Quasi-Newton, BOX, SQP, and Mixed optimization algorithms with the aid of Aspen HYSYS.

To carry out the optimization, the Aspen HYSYS optimizer was incorporated into the developed Aspen HYSYS model of the olefin metathesis process. The manipulated variables of the optimization were the reflux ratio, the feed flow rate and the reboiler duty while the objective function was the maximization of the mole fraction of trans-2-butene in the top product of the column. The lower and the upper bounds chosen for the manipulated variables are as given in Table-1 below.

Table-1. Lower and upper bounds of the manipulated variables.

Parameters	Low bound	High bound
Reflux ratio	1	4
Feed flow rate (mL/min)	17.5	70
Reboiler duty (kW)	0.15	0.6

Both unconstrained and constrained optimizations were carried out on the process using the five different (Fletcher-Reeves, Quasi-Newton, BOX, SQP, and Mixed) optimization algorithms. In the constrained optimization, the constraint function was taken to be the mole fraction of trans-2-hexene present in the bottom product of the column. The constraint was formulated by making the lowest mole fraction of trans-2-hexene present in the bottom segment of the column to be 0.9 while the mole fraction of trans-2-butene present in the top segment of the column was being maximized

3. RESULTS AND DISCUSSIONS

The results obtained from the steady-state simulation of the olefin metathesis process carried out in a reactive distillation column used for the production trans-2-butene and trans-2-hexene from trans-2-pentene are as shown in Figures 2 and 3 below. Shown in Figure-2 is the steady-state temperature profile of the reactive distillation column. As can be seen from the Figure, taking the start point of the profile as the condenser, the temperature of the column was found to increase from the condenser segment towards the reboiler segment. At segment 11 where the feed was passed into the column, there was a sharp increase in the temperature profile of the column. This sharp increase in the temperature was as a result of the exothermic nature of the metathesis reaction occurring in the segments around the feed segment. All in all, for the temperature profile, as expected, the maximum temperature of the column was found to occur in the reboiler segment.

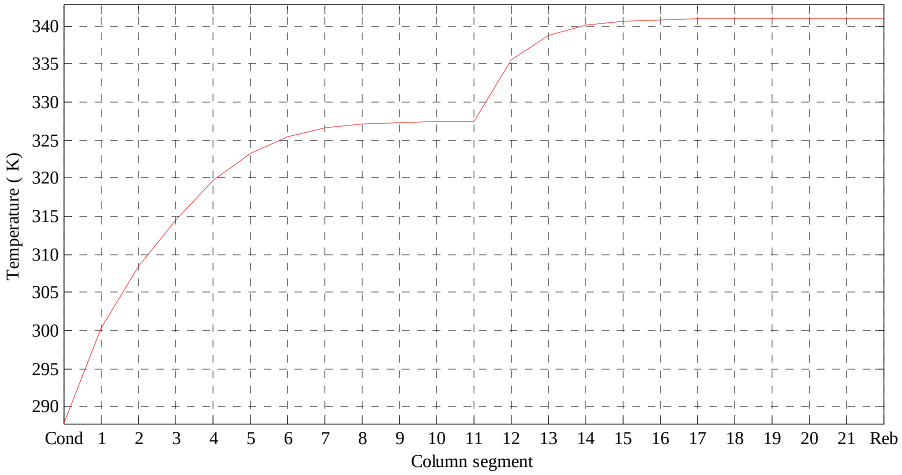

Figure-2. Steady-state temperature profile of olefin metathesis reactive distillation process for the production of trans-2-butene and trans-2-hexene.

Looking at the composition profile shown in Figure-3, it was discovered that the component with the highest mole fraction in the top product was trans-2-pentene (the main reactant) followed by trans-2-butene. This was an indication that the conversion obtained in the column with the operating conditions used was low; thus, the need to obtain the optimum parameters to increase the conversion of trans-2-pentene. In the bottom product, trans-2-hexene was found to have the highest mole fraction while the mole fractions of the other two components were approximately zero there. At the 11th segment where the reactive distillation column was fed and where a sharp increase in the temperature profile of the column was observed, there was also a sharp increase in the mole fraction of trans-2-hexene as well as slight decreases in the mole fractions of both trans-2-pentene and trans-2-butene.

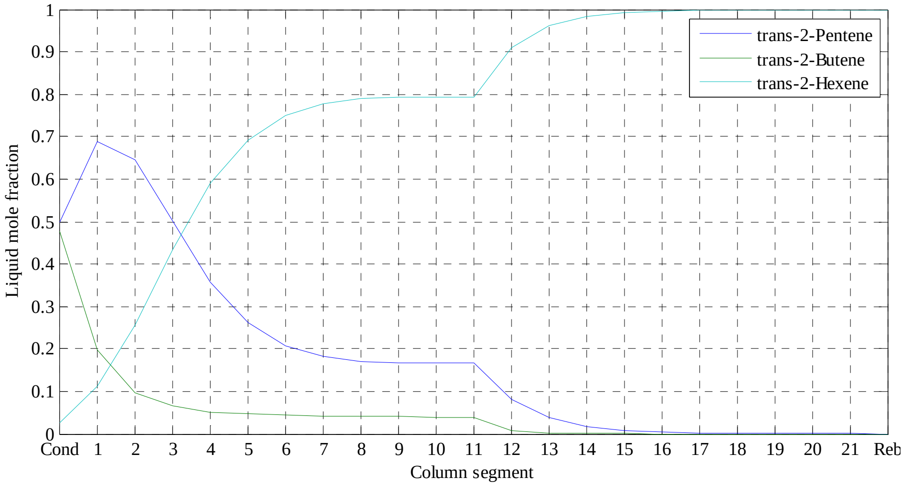

Figure-3. Steady-state composition profile of olefin metathesis reactive distillation process for the production of trans-2-butene and trans-2-hexene.

As can be noticed from the results of the steady-state simulation, trans-2-hexene, the heavy product, was found to have very high purity at the reboiler segment of the column, but the purity of the other product (trans-2-butene), the light one, was not pure in the condenser segment of the column. According to the results obtained, the steady-state mole fraction of trans-2-butene found in the top product was 0.4761 while that of trans-2-hexene obtained in the bottom product was 1.0000. The need to achieve very high purity of trans-2-butene in the condenser segment of the column was another reason that necessitated the need to optimize the process in order to obtain the optimum parameters that will give very high purities of trans-2-butene and trans-2-hexene at the condenser and the reboiler segments of the column, respectively.

Given in Table-2 below are the results obtained from the unconstrained optimizations carried out on the olefin metathesis reactive distillation process using the five optimization algorithms (Fletcher-Reeves, Quasi-Newton, BOX, SQP, and Mixed) considered in this work.

Table-2. Results of steady-state and unconstrained optimization simulations.

Parameters	**Steady-State**	**Optimization**				
		Fletcher-Reeves	**Quasi-Newton**	**BOX**	**SQP**	**Mixed**
Reflux ratio	2.00	2.49	2.49	2.96	2.90	2.83
Feed flow rate (mL/min)	35.00	50.75	50.75	52.82	35.00	49.58
Reboiler duty (kW)	0.30	0.17	0.17	0.15	0.15	0.23
Top product mole fraction						
trans-2-Pentene	0.4981	0.0000	0.0000	0.0000	0.0000	0.0000
trans-2-Butene	0.4761	1.0000	1.0000	1.0000	1.0000	1.0000
trans-2-Hexene	0.0258	0.0000	0.0000	0.0000	0.0000	0.0000
Bottom product mole fraction						
trans-2-Pentene	0.0000	0.2865	0.2865	0.3004	0.2696	0.2582
trans-2-Butene	0.0000	0.1790	0.1790	0.2215	0.1436	0.1248
trans-2-Hexene	1.0000	0.5346	0.5346	0.4781	0.5868	0.6170
Top product temperature (K)	287.90	274.00	274.00	274.00	274.00	274.00
Bottom product temperature (K)	341.03	308.87	308.87	305.13	312.45	314.57
Comment	Converged	OMF	OMF	OF	OF	OF

From the results of the unconstrained optimization given in Table-2, all the five optimization algorithms used were able to give very high purity (mole fraction of 1.0000) of trans-2-butene as the top product of the column, but this resulted in the decrease in the mole fraction of trans-2-hexene present as the bottom product (from the reboiler) of the column from each of the optimization algorithms. For instance, for each of the optimization algorithms, a mole fraction of 1.0000 was obtained as the trans-2-butene present in the top product, as against 0.4761 obtained from the steady-state simulation, but 0.5346, 0.5346, 0.4781, 0.5868 and 0.6170 were the mole fractions of trans-2-hexene obtained respectively from Fletcher-Reeves, Quasi-Newton, BOX, SQP, and Mixed optimization algorithms. The values of the input parameters (reflux ratio, feed flow rate and reboiler duty) as well as the top and bottom temperatures given by each of the optimization algorithms are given in Table-2. It was noticed from the Table that the value of the input parameters (reflux ratio of 2.49, feed flow rate of 50.75 mL/min and reboiler duty of 0.17 kW) given by Fletcher-Reeves and Quasi-Newton optimization algorithms were the same. This was, of course, the reason why the values of their objective functions and their segment temperatures were also the same. The input parameters of the other three optimization algorithms (BOX, SQP and Mixed) were actually found to be different from one another and from those of the other two algorithms (Fletcher-Reeves and Quasi-Newton). Considering the mole fractions of the two products, the optimization algorithm that gave the input (operating) parameters that produce the highest mole fractions of the two products was Mixed algorithm and the input parameters given by it were found to be 2.83, 49.58 mL/min and 0.23 kW for the reflux ratio, the feed flow rate and the reboiler duty, respectively. Also from the unconstrained optimizations carried out, as mentioned before, the results (mole fractions and temperatures) given by Fletcher-Reeves and Quasi-Newton were found to be the same and different from those of the other ones which were also found to be different from one another. Moreover, from the results of the unconstrained optimization shown in Table-2, it was discovered that the steady-state simulation used as the starting point for the optimizations was able to converge successfully, but after the optimization, the convergence comment given by each of Fletcher-Reeves and Quasi-Newton was “optimizer method failed (OMF)” while BOX, SQP and Mixed optimization algorithms gave “optimum found (OF)” as their convergence comment. Thereby, it became clear that BOX, SQP and Mixed were more appropriate for this complex olefin metathesis reactive distillation process than Fletcher-Reeves and Quasi-Newton.

In addition to giving values of the manipulated variables and the parameters of the top and the bottom products, it was also deemed necessary to investigate what happened inside the column by plotting the temperature and the composition profiles for each of the optimization algorithms.

Shown in Figure-4 are the temperature profiles obtained from the unconstrained optimizations carried out with the five algorithms. As can be seen from the Figure, the trends of the temperature profiles obtained from the optimizations were found to be similar to one another but very different from that of the steady-state temperature profile. The differences in the temperature profiles of the steady-state simulation and those of the unconstrained optimizations were due to the different operating parameters (see Table-2) given by the optimizations that were used to simulate the Aspen HYSYS model of the process.

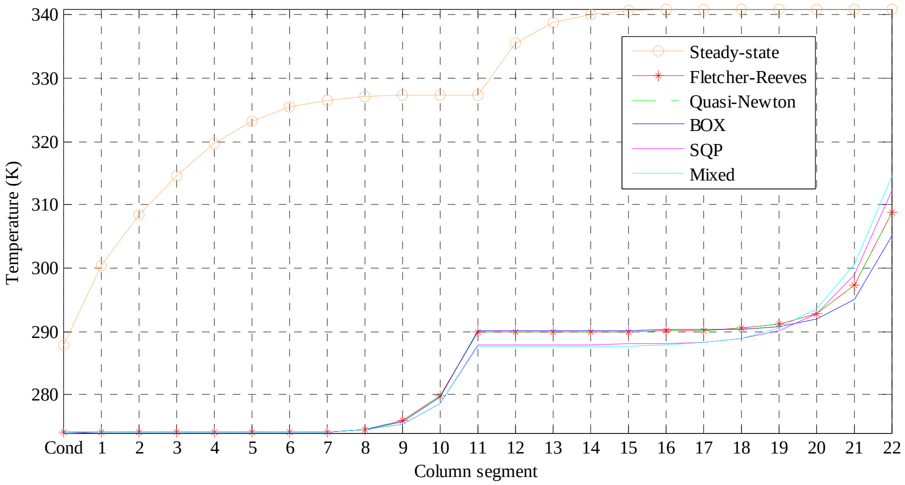

Figure-4. Temperature profiles of the unconstrained optimizations of olefin metathesis reactive distillation process for the production of trans-2-butene and trans-2-hexene.

In Figure-5, the steady-state and the unconstrained optimization mole fraction profiles of trans-2-pentene are shown. From the Figure, it was also discovered that the steady-state composition profile of trans-2-pentene was very different from those of the optimizations, just as it was found in the case of the temperature profiles shown in Figure-4. As was seen from the optimization mole fraction profiles, even though the mole fraction of trans-2-pentene was found to be approximately zero at the top segment of the column, especially in the top product obtained from the condenser segment, its mole fractions obtained at the feed segment of the column were found to be higher than that of the steady-state value.

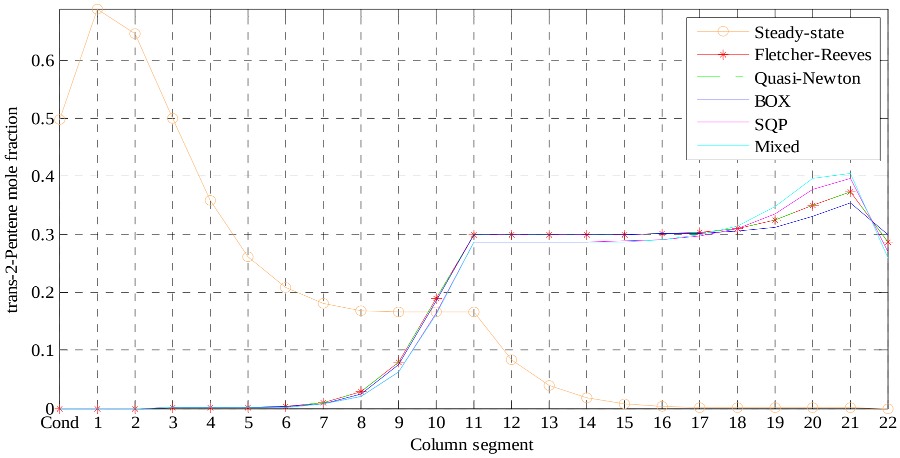

Figure-5. trans-2-Pentene mole fraction profiles of the unconstrained optimizations of olefin metathesis reactive distillation process for the production of trans-2-butene and trans-2-hexene.

The mole fraction profile of trans-2-butene (one of the products of the process) is given in Figure-6. According to the Figure, the mole fractions of trans-2-butene obtained from the optimizations were higher than that of the steady-state simulations not only at the top segment of the column but also throughout the entire column, even at the bottom segment. The achievements of very high purities of trans-2-butene at the top segment of the column from the unconstrained optimizations were indications that the optimization algorithms were very effective in giving the optimum parameters that could produce trans-2-butene in high purity as the product of the column.

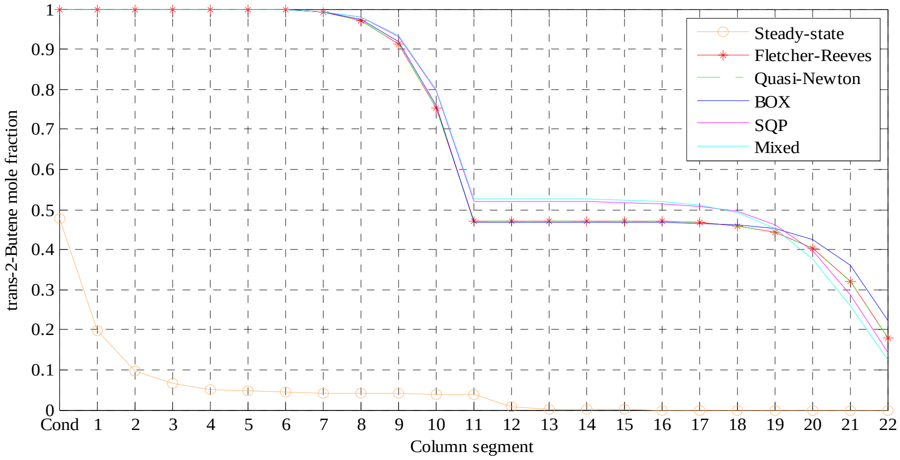

Figure-6. trans-2-Butene mole fraction profiles of the unconstrained optimizations of olefin metathesis reactive distillation process for the production of trans-2-butene and trans-2-hexene.

Considering the mole fraction profile of trans-2-hexene (the other product of the process) given in Figure-7, it was observed that its (trans-2-hexene's) purities obtained from the unconstrained optimizations were less than that given by the steady-state simulation along the column. This situation was actually found favorable at the top segment of the column where the component with the highest mole fraction was, actually, expected to be trans-2-butene (owing to the fact it was the lightest component of the process) and not trans-2-hexene; however, trans-2-hexene was desired at very high purity at the bottom segment of the column. Unfortunately, this situation was not found to be so from the results obtained from the unconstrained optimizations carried out for the olefin metathesis reactive distillation process, as shown in Figure-7.

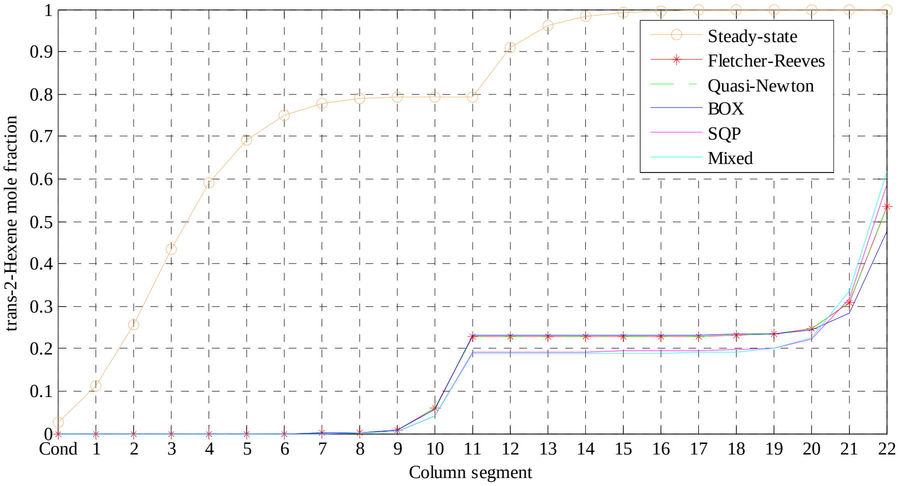

Figure-7. trans-2-Hexene mole fraction profiles of the unconstrained optimizations of olefin metathesis reactive distillation process for the production of trans-2-butene and trans-2-hexene.

In order obtain higher purities of trans-2-butene and trans-2-hexene respectively from the condenser and the reboiler segments of the column, a constraint function was written for the mole fraction of trans-2-hexene present in the reboiler segment. The minimum mole fraction of trans-2-hexene in the reboiler segment was set to 0.9, and then the optimizations were carried out again for the process with the incorporated constraint function. The results obtained from the constrained optimizations carried out using the five optimization algorithms are as given in Table-3.

Table-3. Results of steady-state and constrained optimization simulations.

Parameters	**Steady-State**	**Optimization**				
		Fletcher-Reeves	**Quasi-Newton**	**BOX**	**SQP**	**Mixed**
Reflux ratio	2.00	2.49	2.49	2.35	2.20	2.50
Feed flow rate (mL/min)	35.00	50.75	50.75	45.38	35.00	43.75
Reboiler duty (kW)	0.30	0.17	0.17	0.27	0.15	0.28
Top product mole fraction						
trans-2-Pentene	0.4981	0.0000	0.0000	0.0000	0.0000	0.0000
trans-2-Butene	0.4761	1.0000	1.0000	1.0000	1.0000	1.0000
trans-2-Hexene	0.0258	0.0000	0.0000	0.0000	0.0000	0.0000
Bottom product mole fraction						
trans-2-Pentene	0.0000	0.2865	0.2865	0.0719	0.2325	0.0543
trans-2-Butene	0.0000	0.1790	0.1790	0.0063	0.0918	0.0035
trans-2-Hexene	1.0000	0.5346	0.5346	0.9218	0.6757	0.9422
Top product temperature (K)	287.90	274.00	274.00	274.00	274.00	274.00
Bottom product temperature (K)	341.03	308.87	308.87	336.41	318.77	337.71
Comment	Converged	OMF	OMF	OF	OF	OF

From the results given in Table-3, it was discovered that while the mole fraction of the top trans-2-butene obtained from each of the optimization algorithms was 1.0000, that of the bottom trans-2-hexene obtained from each of Fletcher-Reeves and Quasi-Newton optimization algorithms was the same with that of the unconstrained optimization value of 0.5346. For the BOX, SQP and Mixed optimization algorithm, the bottom trans-

2-hexene mole fraction obtained were found to be different from those of their unconstrained optimizations with the values of 0.9218, 0.6757 and 0.9422, respectively. The values of the input parameters (reflux ratio, feed flow rate and reboiler duty) given by Fletcher-Reeves and Quasi-Newton optimization algorithms were found to be the same, but those of the other three optimization algorithms were obtained to be different from one another, just as it was discovered in the results of the unconstrained optimizations discussed before. Also from Table-3, from the results obtained from the constrained optimizations carried out, it was discovered that the input parameters that produced the best mole fraction of 1.0000 of trans-2-butene in the condenser segment of the column as well as a mole fraction of 0.9422 of trans-2-hexene in the reboiler segment of the column were reflux ratio of 2.50, feed flow rate of 43.75 mL/min and reboiler duty of 0.28 kW, and those input parameters were given by Mixed optimization algorithm. It should be recalled that the same Mixed algorithm gave the best mole fractions of both products from the results of the unconstrained optimizations (refer to Table-2). Furthermore, according to Table-3, the convergence comments given by the optimization algorithms in the constrained optimization were discovered to be the same as those given by the unconstrained optimizations for each corresponding optimization algorithm. This implied that the convergence behavior of the algorithms was the same in both the unconstrained and the constrained optimization of the olefin metathesis reactive distillation process investigated in this work.

Considering the constraint function incorporated into the Aspen HYSYS optimization model of the process, BOX and Mixed algorithms were found to have performed very well because each of them was able to give a mole fraction of bottom trans-2-hexene greater than its constraint value of 0.9. Also looking at the results very well, the best optimization algorithm for the process considered in this work can be said to be Mixed algorithm because it was able to produce top trans-2-butene of a mole fraction value of 1.0000 as well as the highest bottom trans-2-hexene mole fraction of 0.9422, obtainable among all the optimization algorithms studied.

Just as the profiles of the optimizations were investigated and compared to the steady-state ones for the unconstrained optimizations, the profiles of the constrained optimizations were also plotted and compared to the steady-state ones. These comparisons were found necessary so as to investigate the inside-column behavior of the constrained optimizations also.

Figure-8 shows the temperature profiles of the constrained optimizations together with that of the steady-state simulation of the process. As seen in the figure, the temperature profiles of Fletcher-Reeves, Quasi-Newton and SQP were found to be similar to one another while those of BOX and Mixed were also found to be similar to each other and all different from that of the steady-state simulation. It was discovered that the general observation made in this constrained optimization was different from that obtained from the unconstrained optimization where all the temperature profiles of all the optimization algorithms were found to be similar to one another. This has shown that the behaviors of the olefin metathesis reactive distillation process used for the production of trans-2-butene and trans-2-hexene from trans-2-pentene in this work are not always the same all the time. This inconsistency in the behavior of the process was discovered to be as a result of the different input parameters given by the constrained optimizations in contrast to the ones given by the unconstrained optimizations.

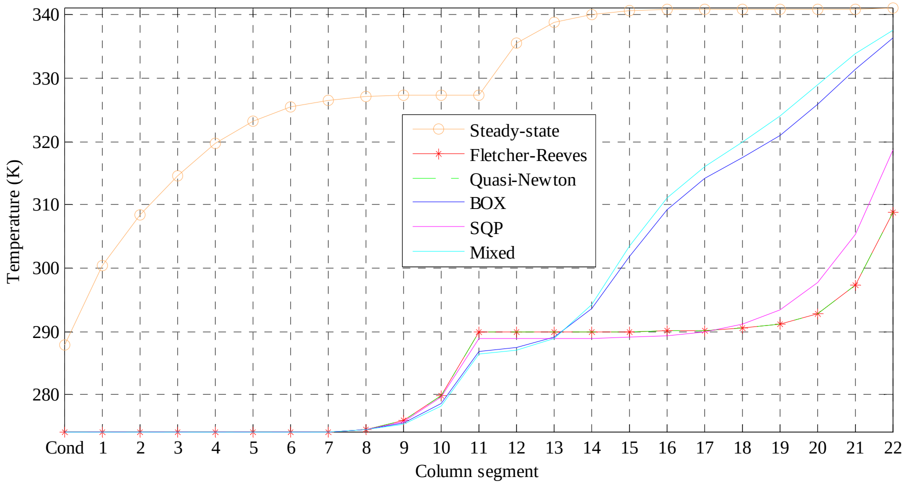

Figure-8. Temperature profiles of the constrained optimizations of olefin metathesis reactive distillation process for the production of trans-2-butene and trans-2-hexene.

In Figure-9, the mole fractions of trans-2-pentene obtained from the optimizations as well as that of the steady-state simulation are shown. It was observed from the figure that the mole fractions of trans-2-pentene obtained from the optimizations increased from the top segment of the column towards the stripping section, and later decreased a bit towards the reboiler while that of the steady-state simulation increased from the condenser segment towards the first segment of the main column and, then, decreased towards the reboiler. In addition, the trends of the mole fraction profiles of trans-2-pentene obtained from the constrained optimizations carried out using Fletcher-Reeves, Quasi-Newton and SQP algorithms were discovered to be similar but different from the trends obtained from BOX and Mixed algorithms that were also found to be similar to each other. These observations were found to be in support of what was noticed in the temperature profiles of the constrained optimization algorithms. In the steady-state simulation, the maximum mole fraction of trans-2-pentene was found at the first segment (segment 1) of the main column while in the constrained optimizations, its maximum mole fractions were found at different locations depending on the optimization algorithm but, all in all, after the feed segment, down the column.

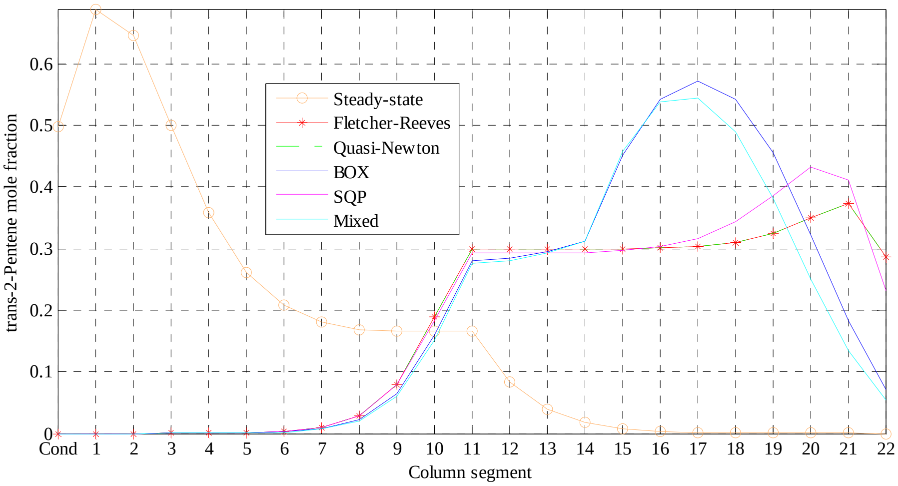

Figure-9. trans-2-Pentene mole fraction profiles of the constrained optimizations of olefin metathesis reactive distillation process for the production of trans-2-butene and trans-2-hexene.

As discovered from the mole fraction profiles of trans-2-butene shown in Figure-10, the mole fractions of trans-2-butene obtained along the column from the optimizations were found to be higher than that obtained from the steady-state simulation of the olefin metathesis reactive distillation process. Looking at the figure very well, and as mentioned before, the profiles of BOX and Mixed optimization algorithms were found to be very good because they were able to give the manipulated variables that could produce very high and very low purities of trans-2-butene at the condenser segment and the reboiler segment of the column, respectively.

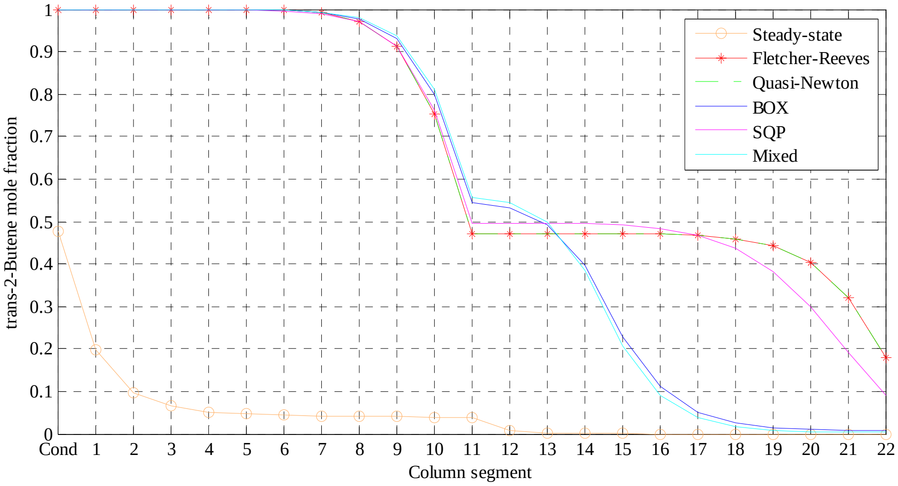

Figure-10. trans-2-Butene mole fraction profiles of the constrained optimizations of olefin metathesis reactive distillation process for the production of trans-2-butene and trans-2-hexene.

The composition profiles of trans-2-hexene are also shown in Figure-11 where the steady-state and the constrained optimization mole fractions of trans-2-hexene are plotted against the column segment, including the condenser and the reboiler. From the figure, it was discovered that the mole fraction of trans-2-hexene at the condenser segment of the column was approximately zero for each of the optimization algorithms, but the maximum mole fraction was obtained for this component (trans-2-hexene) at the reboiler segment of the column using Mixed optimization algorithm. The optimization algorithm that could give a mole fraction of trans-2-hexene close to that of Mixed algorithm at the reboiler segment of the column was discovered to be BOX algorithm.

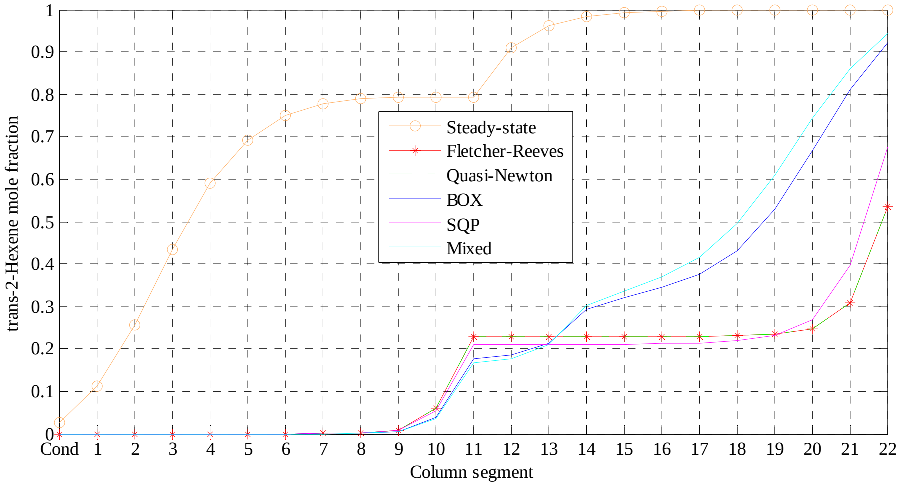

Figure-11. trans-2-Hexene mole fraction profiles of the constrained optimizations of olefin metathesis reactive distillation process for the production of trans-2-butene and trans-2-hexene.

It can be noticed from all the results given that the trends of the composition profiles were found to change as the trends of the temperature profiles changed. This is demonstrating the dependence of the compositions of the components involved in the olefin metathesis reactive distillation process considered in this work on the temperatures of the segments of the column of the process.

Apart from that, it was also discovered in this work that the process was able to give good responses as a result of the changes in the operating parameters. This was found to be an indication that the input parameters used as the manipulated parameters of the process were actually valid and appropriate for this process. If the responses of the mole fractions of the products had not changed, despite the changes in the values of the input parameters, it would have meant that the chosen input variables were not suitable for the olefin metathesis process studied.

4. CONCLUSIONS

The results obtained from the optimizations of the metathesis reactive distillation process used for the production of trans-2-butene and trans-2-hexene from trans-2-pentene using Fletcher-Reeves, Quasi-Newton, BOX, SQP, and Mixed algorithms with the aid of Aspen HYSYS revealed that constrained optimization was better than unconstrained one for this process because, in the single objective function optimizations carried out, not only the top but also the bottom product was desired. From the constrained optimizations carried out, it was discovered that, among the optimization algorithms considered, Mixed algorithm was the best because it was able to give optimum reflux ratio of 2.50, optimum feed flow rate of 43.75 mL/min and optimum reboiler duty of 0.28 kW that could produce trans-2-butene of mole fraction value of 1.0000 and trans-2-hexene of mole fraction of 0.9422 as the top and the bottom products, respectively.

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NOMENCLATURES

OF	Optimum found
OMF	Optimizer method failed
Qcond	Condenser heat duty (kW)
Qreb	Reboiler heat duty (kW)
RPDC	Reactive Packed Distillation Column
SQP	Sequential Quadratic Programming
UNIQUAC	UNIversal QUAsiChemical model

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