# Sensitivity Analysis of ETBE Production Process Using Aspen PLUS

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**ABSTRACT**

The responsesof liquid ETBE mole fraction towards ethanol volumetric flow rate, butene volumetric flow rate, reflux ratio and reboiler duty have been investigated in this work using sensitivityanalysisof an etherification process carried out in a reactive packed distillation column. The process was modeled as an equilibrium type taking place in liquid phase with the aid of Aspen PLUS. The column used had 19 segments including the condenser and the reboiler. The results obtained from the analysis showed that the responses of liquid ETBE mole fraction towards ethanol flow rate were obtained without any "status error", but those towards the other parameters were with "status errors". Simulating the process with the optimum parameters obtainedfrom the analyses, the values of butene flow rate, reflux ratio and reboiler duty could not reproduce the maximum liquid ETBE mole fractions given by the sensitivity analyses, but that of ethanol volumetric flow rate could approximately reproduce the result. Therefore, the importance of volumetric flow rate of ethanol in influencing the purity of liquid ETBE obtained from the etherification process carried out in the reactive packed distillation column as well as the necessities of sensitivity analyses to chemical processes has been demonstrated.

**Key words:**Sensitivity analysis, Etherification, ETBE, Aspen PLUS, Reactive Distillation.

## INTRODUCTION

Air pollution has become one of the major environmental problems of the century. The emission of carbon monoxide and unburned hydrocarbons from consumption of gasoline in vehicles is a main source of the air pollution. Pollutant emission can be reduced by increasing the octane number of fuels by addition of oxygenate additives such as methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE) to fuels. These ether additives are produced by etherification of $C_4$ isoolefins with methanol for MTBE or ethanol for ETBE. MTBE and ETBE may be used as replacement for lead-based octane enhancers such as tetramethyl lead (TML) and tetraethyl lead (TEL). Recently, more attention has been given to ETBE production because of its higher octane enhancing properties and lower volatility. The low vapor pressure of ETBE reduces emission of volatile organic compounds of fuels. Therefore, it is considered as an environmentally friendly fuel additive (Khaledi and Young, 2005). So, the development of processes for the synthesis of ETBE is becoming popular these days.

It has been widely speculated that reactive distillation is equally applicable to ETBE synthesis and that significant advantages, similar to those achieved with MTBE synthesis, can be realized by upgrading a conventional process in the same way (CDTECH, 1995; Hüls, 1995; Sneesby et al., 1999).

Reactive distillation is a process that combines both separation and chemical reaction in a single unit. It is sometimes an excellent alternative to conventional flowsheets with separate reaction and separation sections (Al-Arfaj and Luyben, 2002; Giwa and Karacan, 2012d). 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 and Karacan, 2012a). It has a lot of advantages, especially for those reactions occurring at temperatures and pressures suitable for the distillation of the resulting components (Giwa and Karacan, 2012b), 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. These synergistic effects normally result in significant economic benefits 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, 2012c) Reactive distillation is a very advantageous process but, due to its complexity as a result of combined reaction and separation, it should be applied with care by given good considerations to its input and operating parameters.

According to Khaledi and Young (2005), the ETBE reaction system also includes an equilibrium limited side reaction (that is, the dimerization of isobutylene to produce diisobutylene) and that, in practice, this side reaction can be prevented by using some excess ethanol. This aspect of this process is pointing to the fact that the flow rate of ethanol passed into the reaction medium of this etherification process should be selected in such a way that the side reaction will become negligible. In order to determine how this process is influenced by the flow rate of ethanol as well as other input and operating parameters, the performance of the sensitivity analysis of the process is very necessary.

Sensitivity analysis is a means of determining the strength of the relation between a given input and an output (Saltelli et al., 2000; Saltelli et al., 2005). This is normally carried out in line with a process simulation. In fact, one of the benefits of process simulation is that it allows the study of the sensitivity of process performance to changes in operating variables. Using Aspen Plus as the process simulator, inputs can be allowed to vary and their effects on a set of results (responses) of a particular choice can thus be tabulated (Aspen, 2010). Sensitivity analysis (the study of the effect of changes in input variables on process outputs) has several benefits among which are studying the effect of changes in input variables on process (model) outputs, graphically representing the effects of input variables, verifying that a solution to a design specification is feasible, rudimentary optimization, and studying time varying variables using a quasi-steady state approach (Aspen, 2003).

Therefore, the aim of this work is to carry out the sensitivity analysis of the reactive distillation process used for the production of ethyl *tert*-butyl ether (ETBE) with the aid of Aspen PLUS by considering the volumetric flow rates of ethanol and butene, the reflux ratio and the reboiler duty manipulated variables and the mole fraction of ETBE obtained at the bottom section of the column as the output variable.


## ASPEN PLUS MODELING

The Aspen PLUS (a market-leading process modeling environment for conceptual design, optimization, and performance monitoring for the chemical, polymer, specialty chemical, metals and minerals, and coal power industries (Aspen, 2012, Giwa, 2012)) model used for the accomplishment of the etherification process of this work is as shown in Figure 1 below.
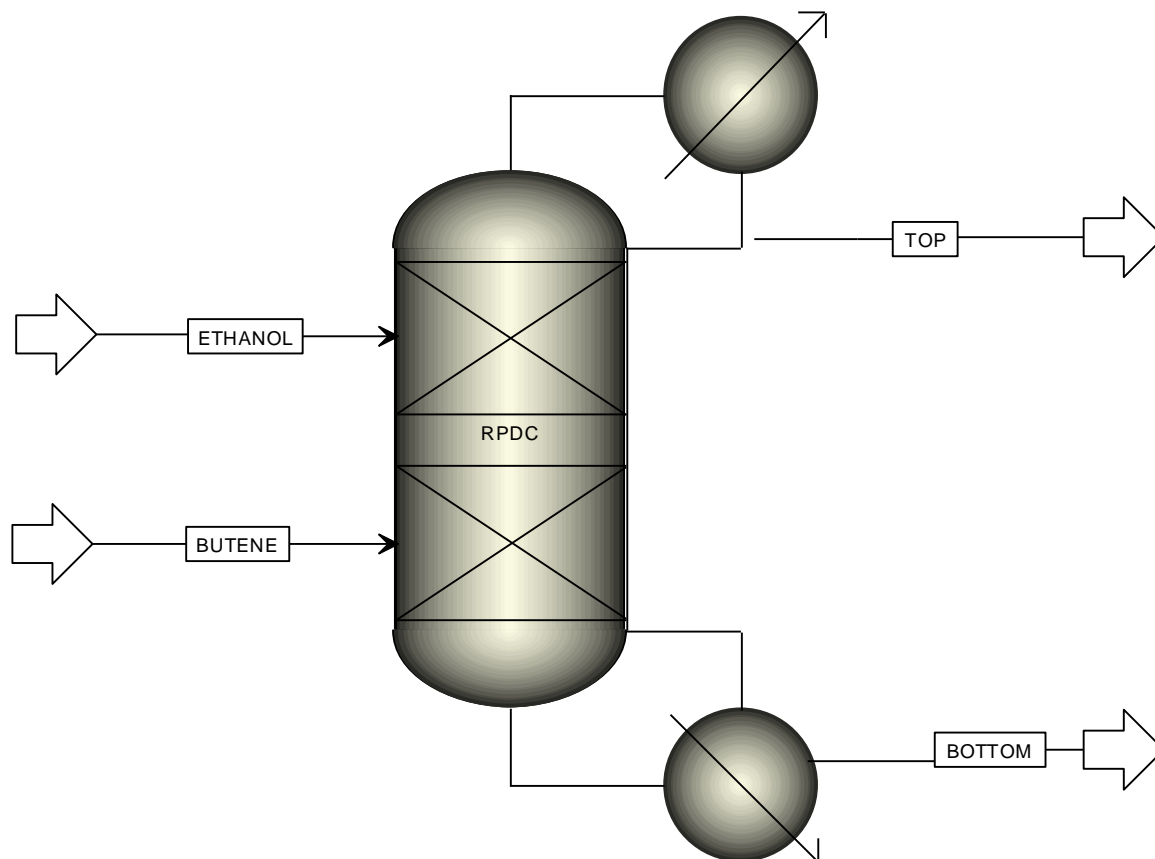
Figure 1. Reactive packed distillation column for the production of ETBE using etherification process

The development of the model was carried out by picking the RadFrac packed column from the column tab of the model library and pasting it unto the Aspen PLUS run page. Thereafter, the material streams were picked and attached appropriately to the column. Then, the components (ethanol, i-butene, n-butene and ETBE) were selected, the feed specifications entered, the reaction set specified and attached unto the reaction section of the column and the property method was set. The details of the data used for the model development can be found in Table 1.

Table1. Aspen PLUS ETBE production process model development parameters

| Parameter | Value |
|---|---|
| **Ethanol feed** | |
| Flow rate (L/min) | 0.005 |
| Temperature (K) | 298 |
| Pressure (atm) | 1.2 |
| | |
| **Butene feed** | |
| Feed composition | |
| i-butene | 0.4 |
| 1-butene | 0.6 |
| Flow rate (L/min) | 0.035 |

| Temperature (K) | 273 |
|---|---|
| Pressure (atm) | 1.3 |
| | |
| **Property method** | Dortmund modified UNIFAC |
| | |
| **Reaction** | |
| Type | Equilibrium |
| $K_{eq}$ source | Temperature approach |
| $K_{eq}$ basis | Molarity |
| Reacting phase | Liquid |
| | |
| **Distillation column** | |
| Type | RadFrac Packed |
| No of segment[*] | 19 |
| Ethanol feed segment[*] | 6 |
| Butene feed segment[*] | 12 |
| Reflux ratio | 3 |
| Reboiler duty (kJ/s) | 0.35 |
| Condenser type | Total |
| Reboiler type | Kettle |
| Condenser pressure (atm) | 1.1 |
| Pressure drop (atm) | 0 |

[*]Segment numbers includingcondenser and reboiler

The feed stages were located by considering some of the basic properties (especially the boiling points) of the components as given in Table 2.

Table 2. Some basic properties of the components

| **Components** | **Molecular weight (kg/kmol)** | **Boiling point (K)** |
|---|---|---|
| Ethanol | 46.07 | 351.44 |
| i-Butene | 56.11 | 266.25 |
| n-Butene | 56.11 | 266.9 |
| ETBE | 102.18 | 365.35 |

The equilibrium reaction of the etherification process for the production of ETBE occurring in the reactive packed distillation column is as given in Equation 1. The side reaction involved in the process was neglected in this work.

$$(CH_3)_2 C = CH_2 + C_2H_5OH \longleftrightarrow (CH_3)_3 COC_2H_5 \tag{1}$$

After all the required data were entered into the developed Aspen PLUS model, it was simulated by clicking start and the steady-state results were obtained before performing the sensitivity analysis of the process.

## RESULTS AND DISCUSSIONS

The results obtained from the steady-state simulations of the reactive packed distillation column modeled with the etherification process used for the production of ethyl *tert*-butyl ether (ETBE) are as shown in Figures 2 and 3 respectively for the temperature profile and the composition profiles.
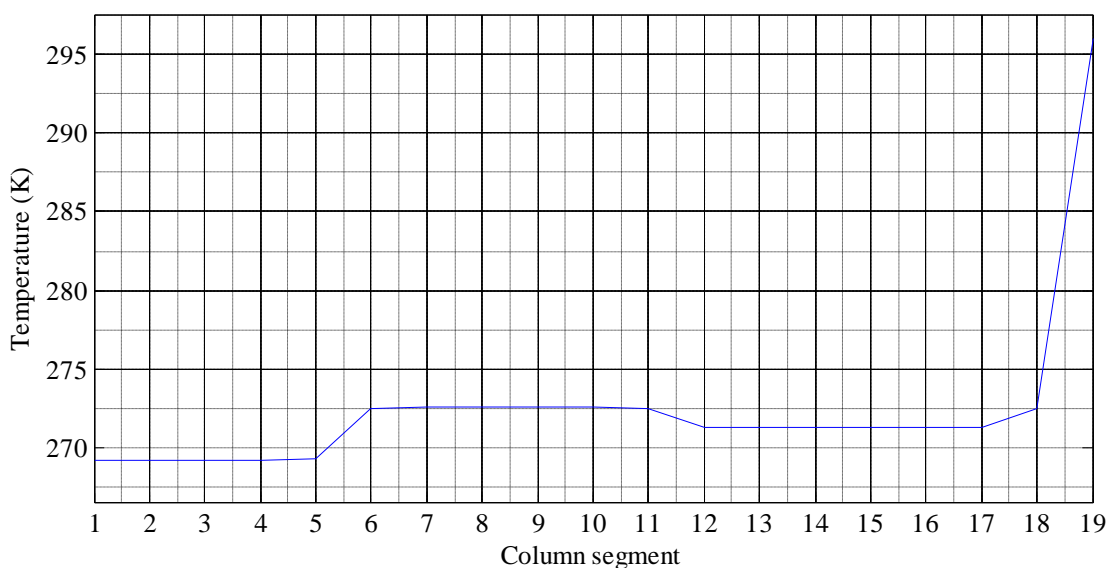


Figure 2. Steady-state simulation temperature profile of the column ($\upsilon_{ethanol}$ = 0.005 L/min, $\upsilon_{butene}$ = 0.035 L/min, R = 3, $Q_{reb}$ = 0.35 kJ/s)

From Figure 2 in which the steady-state temperature profile of the simulation is shown, it was observed that the temperature of the column did not change significantly from the condenser segment downwards, because the steady-state temperatures of the condenser and segment 5 were found to be 269.16 and 269.28°C respectively, until it got very close to the reaction section where a significant increase (from 269.28 °C in segment 5 to 272.51°C in segment 11) in the temperature was observed.
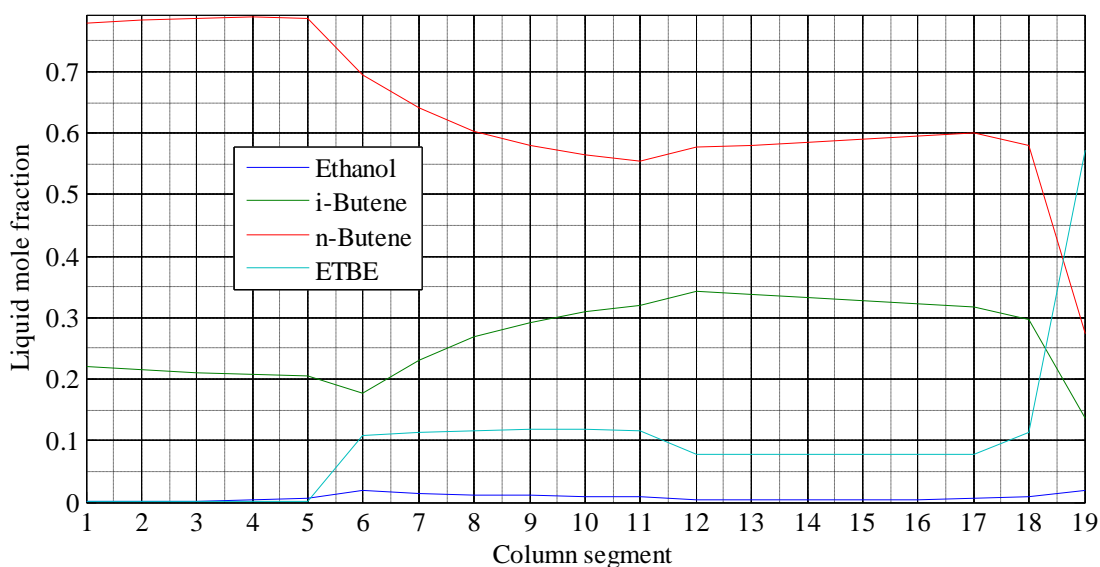


Figure 3. Steady-state simulation composition profiles of the components in the column ($\upsilon_{ethanol}$ = 0.005 L/min, $\upsilon_{butene}$ = 0.035 L/min, R = 3, $Q_{reb}$ = 0.35 kJ/s)

This increase in the temperature at this section was due to the exothermic nature of the etherification reaction occurring there. Thereafter, there was a decrease in the temperature up to 271.26 $^{o}$C (at the lower feed segment). This temperature did not change significantly until after segment 17 where there existed a sharp increase in the temperature towards the reboiler section. The temperature of the reboiler was found to be 295.97 $^{o}$C.

From the composition profiles of the components (ethanol, i-butene, n-butene and ETBE) shown in Figure 3, it was discovered that the steady-state mole fraction of the desired product (ETBE) was the highest at the reboiler section from where the ETBE was expected to be obtained because it was the heaviest one among the components (see Table 2). Of course, as expected, the mole fraction of this component (ETBE) was found to be very negligible at the condenser section. As can be seen from the figure, the mole fraction of i-butene was found to be higher than that of ethanol at the reaction section. This is an implication that balances have to be made between the amounts of the feeds passed into the reaction medium so as to accomplish better reaction conversion. In other words, the outputs of the desired product towards the inputs and the operating parameters of the process have to be investigated using sensitivity analysis approach and the results of the analysis are as discussed thus.

The results of the sensitivity analyses of this process are as shown in Figures 4 – 7. Figure 4 shows the response of ETBE mole fraction to the changes in the volumetric flow rate of ethanol feed. As can be seen from the figure (Figure 4), the maximum mole fraction of liquid ETBE was obtained to be 0.8541 when the volumetric flow rate of ethanol was 0.009 L/min. Also noticed from the figure was that the point at which 0.8541 was obtained as the maximum mole fraction of liquid ETBE was the only maximum point obtained from the sensitivity analysis of liquid ETBE mole fraction with respect to the volumetric flow rate of ethanol. That is to say, this sensitivity analysis gave a single maximum point.
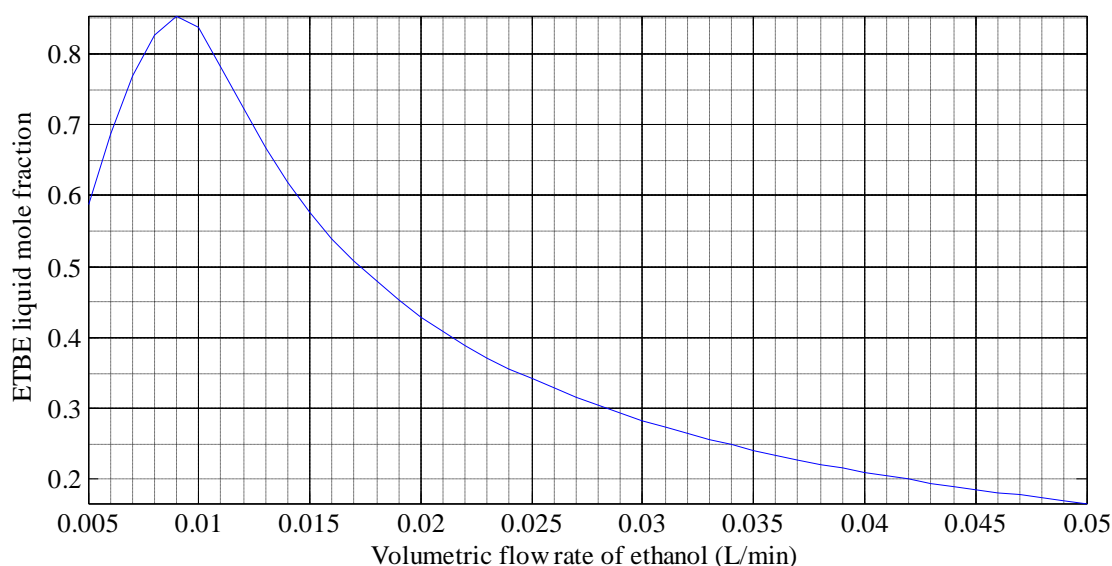


Figure 4. Sensitivity analysis results of ETBE mole fraction with respect to ethanol feed ($\upsilon_{butene}$ = 0.035 L/min, R = 3, $Q_{reb}$ = 0.35 kJ/s)

Also shown in Figure 5 is the effect of the change in the volumetric flow rate of butene feed that comprised i-butene and n-butene on ETBE liquid mole fraction. It was noticed from the figure that there were many maximum values of liquid ETBE mole fraction with respect to the volumetric flow rate of butene. In contrast to what was noticed in the case of the

sensitivity analysis of the volumetric flow rate of ethanol and liquid ETBE mole fraction in which there was only one maximum value, in this case, multiplemaximum points (many local maximum and one global maximum mole fraction values of liquid ETBE) were given. The global maximum liquid ETBE mole fraction was obtained when the volumetric flow rate of butene feed was also 0.009 L/min to be 1.0000. However, the status of this global maximum point of liquid ETBE mole fraction was found to be "error" during the sensitivity analysis.
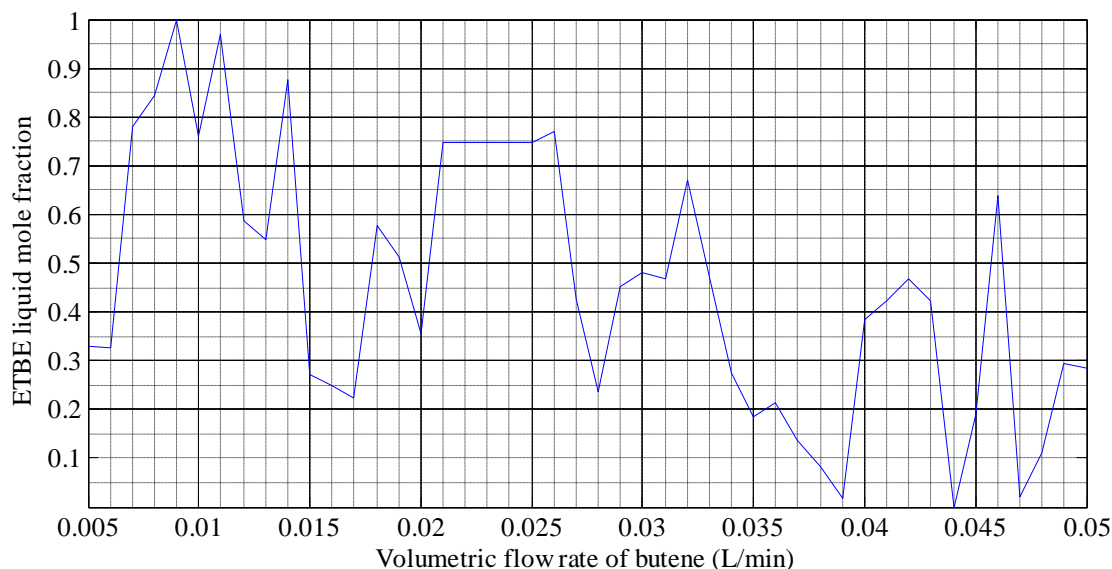


Figure 5. Sensitivity analysis results of ETBE mole fraction with respect to butene feed ($\upsilon_{ethanol}$ = 0.005 L/min, R = 3, $Q_{reb}$ = 0.35 kJ/s)

Apart from investigating the responses of liquid ETBE mole fraction toward the feeds, the sensitivity analyses were also carried considering the operating parameters of the reactive packed distillation column. The operating parameters considered in this work were the reflux ratio and the reboiler duty of the column.
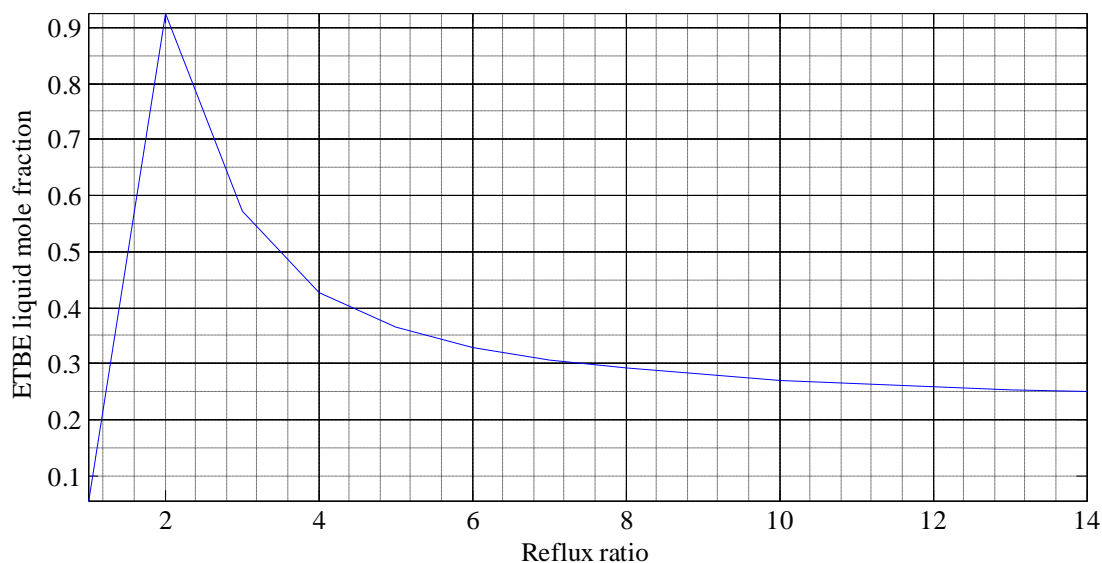


Figure 6. Sensitivity analysis results of ETBE mole fraction with respect to reflux ratio ($\upsilon_{ethanol}$ = 0.005 L/min, $\upsilon_{butene}$ = 0.035 L/min, $Q_{reb}$ = 0.35 kJ/s)

Shown in Figure 6 is the plot of the results obtained from the sensitivity analysis of liquid ETBE and the reflux ratio. As can be seen from the figure, single maximum liquid ETBE mole fraction value was found to exist in this case too (similar to the results of the sensitivity analysis of ethanol volumetric flow rate and liquid ETBE mole fraction). The maximum liquid ETBE mole fraction was obtained, also with "error" status, to be 0.9260 when the value of reflux ratio was 2.

The results of the sensitivity analysis of liquid ETBE mole fraction with the respect to the reboiler duty of the column are shown in Figure 7. The multiple maximum liquid ETBE mole fraction values observed in the case of the volumetric flow rate of butene was also discovered in this case. However, there was a global maximum liquid ETBE mole fraction value of 0.9078 when the reboiler duty was 1.00 kJ/s, but it was also obtained with "error" status during the sensitivity analysis.
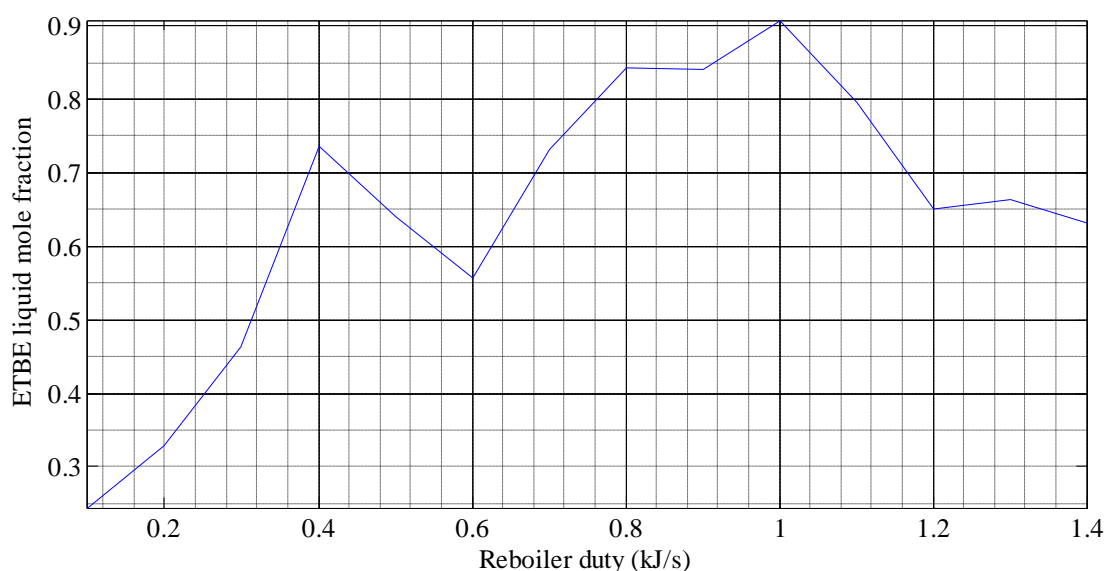


Figure 7. Sensitivity analysis results of ETBE mole fraction with respect to reboiler duty ($v_{ethanol}$ = 0.005 L/min, $v_{butene}$ = 0.035 L/min, R = 3)

It can be noticed that among the sensitivity analyses carried out, it was only the one between liquid ETBE mole fraction (as the output variable) and ethanol volumetric flow rate (as the input variable) that converged without any "status error". So, the optimum input value (ethanol volumetric flow rate) value of 0.009 L/min was used to simulate the reactive packed distillation column, but the value of the liquid ETBE mole fraction obtained was discovered to be approximately 0.8503, which was less than to the value obtained during the sensitivity analysis. The difference in the simulation and the sensitivity analysis results was found to be as a result of an approximation error. As such, it was decided to use and manipulate the value of the volumetric flow rate of ethanol obtained at the optimum state to obtain the real maximum value of liquid ETBE mole fraction. Based on this, starting from the value of ethanol volumetric flow rate (0.009 L/min) obtained from the sensitivity analysis, and using a step of 0.0001 L/min for the volumetric flow rate of ethanol, the maximum value of liquid ETBE mole fraction was found to be 0.8547 when the ethanol volumetric flow rate was 0.0094 L/min. In addition, the temperature and composition profiles of the reactive packed distillation column at this optimum condition were also investigated and they are as shown in Figures 8 and 9 respectively.
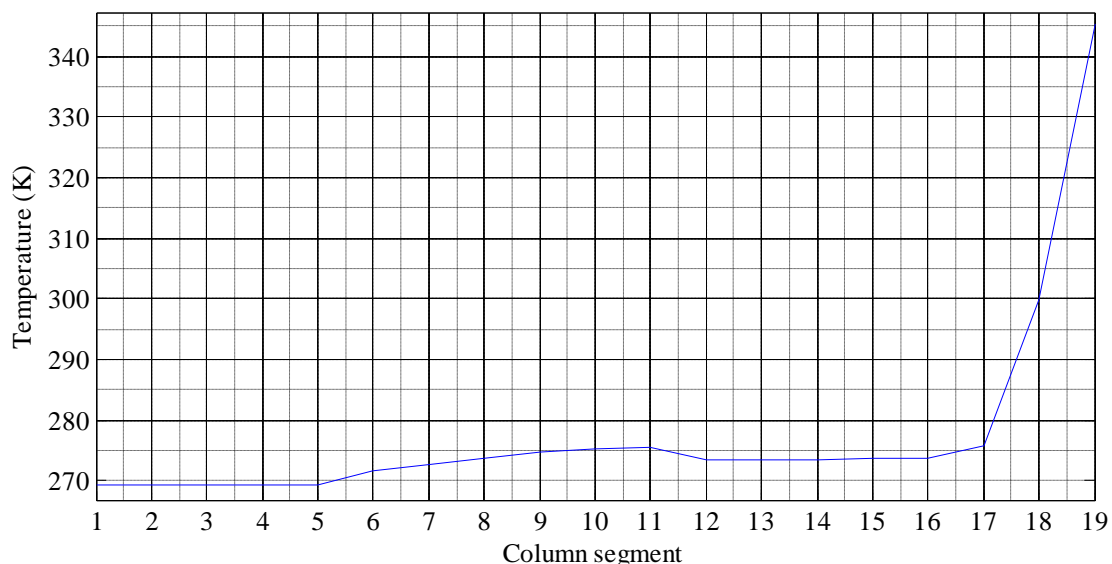
Figure 8. Optimum ethanol volumetric flow rate simulation temperature profile of the column ($\upsilon_{ethanol}$ = 0.0094 L/min, $\upsilon_{butene}$ = 0.035 L/min, R = 3, $Q_{reb}$ = 0.35 kJ/s)

Figure 8 shows the temperature profile of the column when the real optimum ethanol volumetric flow rate was used to simulate the reactive packed distillation column. It can be observed from the figure (Figure 8) that there was a rise in the temperature profile at the reaction section of the column as compared to the temperature profile observed at the rectification section of the column. The rise in the profile was as a result of the heat liberated from the reaction taking place at that (the reaction) section because, according to Khaledi and Young (2005), etherification reaction is an exothermic equilibrium limited reaction that takes place in liquid phase. This observation (temperature rise at the reaction section) was found to be the same as that obtained in the case of the steady-state simulation temperature profile of the process.

The compositions profiles of the simulation carried out with the real optimum ethanol volumetric flow rate are as shown in Figure 9.
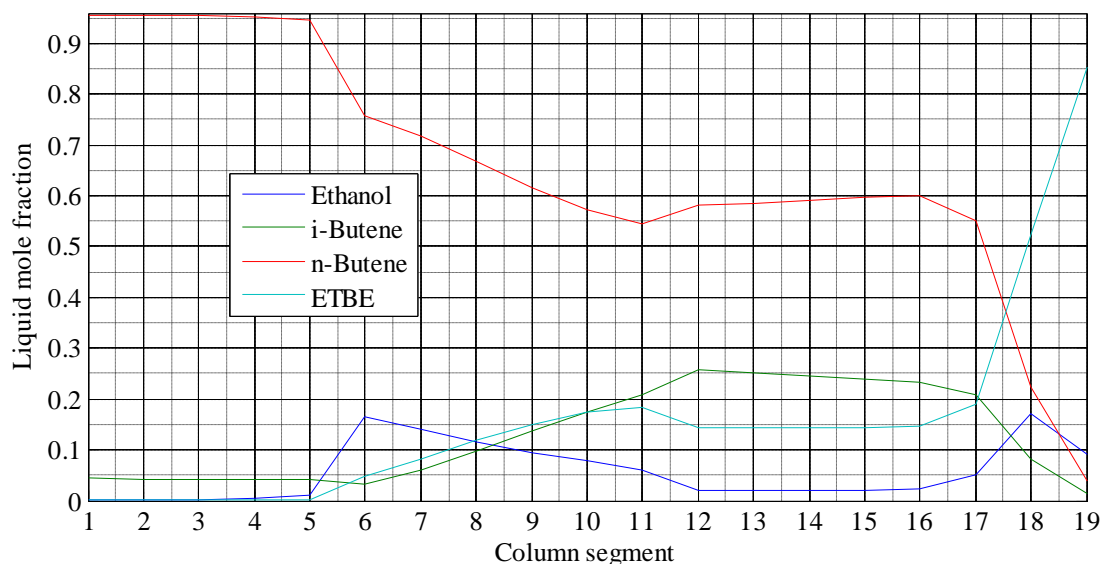


Figure 9. Optimum ethanol volumetric flow rate simulation composition profile of the column ($\upsilon_{ethanol}$ = 0.0094 L/min, $\upsilon_{butene}$ = 0.035 L/min, R = 3, $Q_{reb}$ = 0.35 kJ/s)

Comparing this figure (Figure 9) to the composition profile obtained, before, from the steady-state simulation (Figure 3), and especially considering the mole fraction of one of the main reactant component (i-butene) present at the reaction section, it was discovered that there was an improvement in the reaction conversion obtained when the real optimum ethanol volumetric flow rate was used to simulate the process because the mole fraction of i-butene present at the reaction section was found to be lower in this case. This is an indication that the real optimum value of ethanol volumetric flow rate used to simulate the process has actually improved the efficiency of the process to the extent of even improving the conversion of the reaction.

Also noticed from Figure 9 was that while the mole fraction of ethanol decreased downward towards the stripping section of the column, but that of i-butene increased. This was found to be due to fact that ethanol was fed into the column at the upper feed section while butene was fed at the lower feed section of the column;as the ethanol entered the column, it was flowing downward and being consumed at the reaction section while i-butene contained in the butene feed was vaporizing and finding its way upwards towards the reaction section where the two main reactants were meeting for the reaction to occur.

## CONCLUSIONS

The results of the sensitivity analysis carried out in this work has revealed that liquid ETBE mole fraction was able to respond to ethanol volumetric flow rate without any "status error" while the responses towards butene volumetric flow rate, reflux ratio and reboiler ratio only converged with "status errors". When the input and operating parameter values obtainedfrom the sensitivity analyses, at the optimum state, were used to simulate the process, the values of butene volumetric flow rate, reflux ratio and reboiler duty could not reproduce the maximum liquid ETBE mole fraction values given by the sensitivity analyses, but that of ethanol volumetric flow rate could approximately reproduce the result. Theresults of this work have, therefore, demonstrated the importance of volumetric flow rate of ethanol in influencing the purity of ETBE obtained from the etherification process carried out in the reactive packed distillation column as well as showing the benefits of sensitivity analyses to chemical processes.

## NOMENCLATURES

| | |
|---|---|
| BOTTOM | Bottom product |
| BUTENE | Butene feed |
| ETBE | Ethyl *tert*-butyl ether |
| ETHANOL | Ethanol feed |
| MTBE | Methyl *tert*-butyl ether |
| $Q_{reb}$ | Reboiler duty (kJ/s) |
| R | Reflux ratio |
| RPDC | Reactive packed distillation column |
| TEL | Tetraethyl lead |
| TML | Tetramethyllead |
| TOP | Top product |
| υ | Volumetric flow rate(L/min) |
| $υ_{butene}$ | Volumetric flow rate of butene feed (L/min) |

$\upsilon_{ethanol}$             Volumetric flow rate of ethanol feed (L/min)

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