# Property Modelsand Reactive Distillation Processes

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**ABSTRACT**

This work has been carried out to study the effects of property models on the qualities of the desired products obtained from reactive distillation processes with the aid of Aspen PLUS. Esterification and transesterification processes with top ethyl acetate and bottom n-butyl acetate as the desired products respectively were used as the case studies. The reactive distillation column used for the simulations was a packed type with 25 segments including the condenser and the reboiler. Fourteen (14) different property models were investigated. The results obtained revealed that the highest mole fractions of ethyl acetate obtained from the top segment and n-butyl acetate obtained from the bottom segment of the column during the simulations of the reactive distillation esterification and transesterification processes were 0.9362 and 0.9821 when Wilson model and Peng-Robinson equation of state model were employed,respectively. Also, the relationships between the mole fractions of the desired products and their K-values were found to be of similar trends.

**Key words:**Property model, Aspen PLUS, Reactive distillation, Esterification, Transesterification, Ethyl acetate, n-Butyl acetate.

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## INTRODUCTION

In recent years, integrated reactive separation processes have attracted considerable attentions in both academic research and industrial applications (Völker et al., 2007). One of these processes which is known as reactive distillation is potentially attractive whenever conversion is limited by reaction equilibrium(Balasubramhanya and Doyle III, 2000; Giwa and Karacan, 2012a) Reactive distillation is a process that combines both separation and chemical reaction in a single unit (Giwa and Giwa, 2012).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, 2012c) 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 shift of chemical equilibrium and 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 Giwa, 2013) However, due to the integration of reaction and separation, reactive distillation exhibits complex behaviors (Khaledi and Young, 2005), such as steady state multiplicity, process gain sign changes (bidirectionality) and strong interactions between the process variables (Jana and Adari, 2009). These complexities have made the modeling of reactive distillation process extremely difficult(Giwa and Karacan, 2012c).

Among the factors influencing the modeling of reactive distillation is the type of a property method used to develop the model. A property method is a collection of methods and models that are used to compute thermodynamic and transport properties. The thermodynamic properties that are estimated with the property method are fugacity coefficient (K-value), enthalpy, entropy, Gibbs free energy and volume. Also, the transport properties that can be estimated using the property methodare viscosity, thermal conductivity, diffusion coefficient and surface tension. Property methods are of different categories which include the Ideal Property Methods (e.g., Ideal Gas/Raoult's law/Henry's law), Equation of State Property Methods (e.g., BWR Lee-Starling, Lee-Kesler-Plöcker, Peng-Robinson, Peng-Robinson with Boston-Mathias alpha function, Peng-Robinson with Wong-Sandler mixing rules, Peng-Robinson with modified Huron-Vidal mixing rules, Predictive Redlich-Kwong-Soave, Redlich-Kwong-Soave with Wong-Sandler mixing rules, Redlich-Kwong-Soave with modified Huron-Vidal mixing rules, Redlich-Kwong-Soave, Redlich-Kwong-Soave with Boston-Mathias alpha function and Schwartzentruber-Renon), Activity Coefficient Property Methods (e.g., for liquid phase: Bromley-Pitzer, Electrolyte NRTL, NRTL, Pitzer, UNIFAC, Dortmund-modified UNIFAC, Lyngby-modified UNIFAC, UNIFAC for liquid-liquid Systems, UNIQUAC, Van Laar, Wilson and Wilson with volume term; for vapor phase: Redlich-Kwong, Ideal gas, Hayden-O'Connell, Nothnagel, Redlich-Kwong, Redlich-Kwong-Soave and HF Hexamerization Model) and Property Methods for Special Systems (e.g., Kent-Eisenberg amines Model, API sour water model, Braun K-10, Ideal Gas/Raoult's law/Henry's law/solid activity coefficients, Chao-Seader corresponding states model, Grayson-Streed corresponding states model, ASME steam table correlations and NBS/NRC steam table equation of state) (Aspen, 2001).

From the literature, Giwa and Karacan (2012b) successfully used General NRTL property model to simulate and optimize ethyl acetate reactive packed distillation process with the aid of Aspen HYSYS. Giwa and Giwa (2012) applied UNIQUAC model to simulate a reaction integrated distillation columnfor the production of methanol and n-butyl acetate and they were able to achieve good results.

In the modeling of a reactive distillation process (being a complex process), choosing the appropriate property method is one of the key decisions in determining the accuracy of the outputs of the model. Based on this, care has to be taken in determining the property method to be employed when carrying out modeling and simulation of any reactive distillation process.

Therefore, this work has investigated the effects of some property models on the performances of reactive distillation esterification and transesterification processes with the aid of Aspen PLUSby taking the mole fraction of ethyl acetate present at the top segment and the mole fraction of n-butyl acetate obtained at the bottom segment of the reactive packed distillation column used in this study as the points of interests.

## MODELING

The modeling of the two reactive distillation processes (esterification and transesterification) studied in this work were carried out with the aid of Aspen PLUS (Aspen, 2011).
The developed model for the reactive distillation esterification process is shown in Figure 1 below. A RadFrac Packed column having 25 segments was used. The condenser type of the

column was 'total' while the reboiler type was 'kettle'. In the modeling of the process, both acetic acid and ethanol feeds were passed into the column on segments 9 and 17 respectively at room temperature, but the pressure of acetic feed was 1.2 bar while that of ethanol feed was 1.3 bar. The pressure of the condenser was taken to be 1.15 bar. The reaction occurring in the column was modeled as an equilibrium type using temperature approach as the source of equilibrium constant and the basis as the molarity. The reaction was allowed to take place in liquid phase. The detailed parameters used for the modeling of the reactive distillation esterification process are given in Table 1. Furthermore, the locations of the stages for the feeds were determined based on the basic properties of the components (see Table 2).

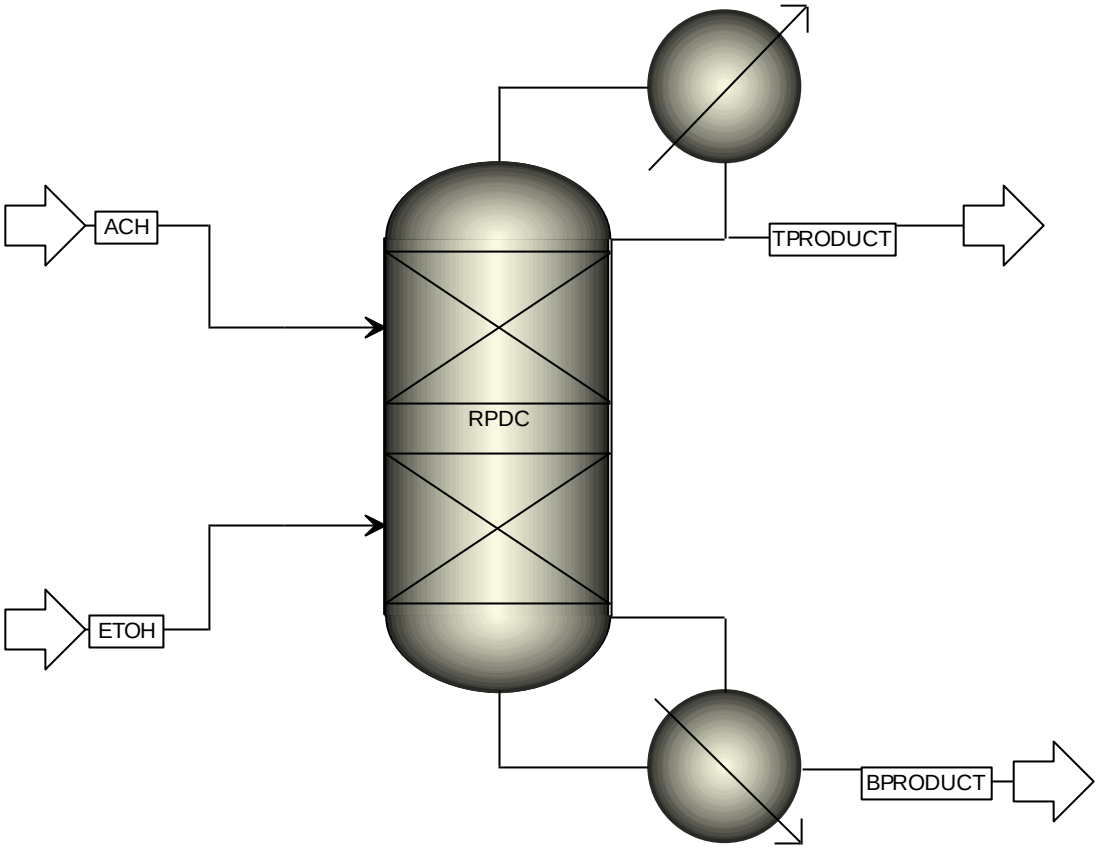


Figure 1. Reactive packed distillation column for ethyl acetate esterification process

Table 1. Aspen PLUS reactive distillation esterification process model parameters

| **Parameter** | **Value** |
|---|---|
| **Acetic acid feed** | |
| Flow rate (L/min) | 0.02 |
| Temperature (K) | 298 |
| Pressure (bar) | 1.2 |
| | |
| **Ethanol feed** | |
| Flow rate (L/min) | 0.02 |
| Temperature (K) | 298 |
| Pressure (bar) | 1.3 |
| | |
| **Reaction** | |

| | |
|---|---|
| Type | Equilibrium |
| $K_{eq}$ source | Temperature approach |
| $K_{eq}$ basis | Molarity |
| Reacting phase | Liquid |
| | |
| **Reactive distillation column** | |
| Type | RadFrac Packed |
| Total no of column segment | 25 |
| Acetic acid feed segment | 9 |
| Ethanol feed segment | 17 |
| Reflux ratio | 3 |
| Reboiler duty (kJ/s) | 0.35 |
| Condenser type | Total |
| Reboiler type | Kettle |
| Condenser pressure (bar) | 1.15 |
| Packing type | |
| Rectification section | Raschig |
| Reaction section | Wire-pack |
| Stripping section | Raschig |
| Section packed height (m) | 0.5 |

As can be noticed from Table 1, the reflux ratio used for the reactive distillation esterification process simulation was 3 while the reboiler duty was 0.35 kJ/s.

Table 2. Some basic properties of the components involved in the esterification process

| **Component** | **Molecular weight (kg/kmol)** | **Boiling point (K)** |
|---|---|---|
| Acetic acid | 60.05 | 391.05 |
| Ethanol | 46.07 | 351.44 |
| Ethyl acetate | 88.11 | 350.21 |
| Water | 18.02 | 373.15 |

The equilibrium esterification reaction occurring in the column is as given in Equation (1).

$$CH_3COOH + C_2H_5OH \xleftrightarrow{K_{eq}} CH_3COOC_2H_5 + H_2O \quad (1)$$

Shown in Figure 2 is the developed model for the reactive distillation transesterification process. The column used for the reactive distillation transesterification process had the same parameters as that used for the esterification process except that, in this case, the feeds were n-butanol and ethyl acetate, and the reboiler duty was taken to be 0.7 kJ/s. The difference between the reboiler duties of the esterification and that of the transesterification processes was as a result of the differences in the boiling points of the components involved in the processes. The components involved in the transesterification processes required more heat to boil up and, as such, more heat duty was supplied to the reboiler of the column. The detailed parameters used for the modeling of the transesterification process carried out in the reactive packed distillation column of this work are given in Table 3. Considering the basic properties of the components involved in this process, as given in Table 4, for this modeling, n-butanol

was passed into the column at the upper feed segment while ethyl acetate was fed from the lower feed segment.

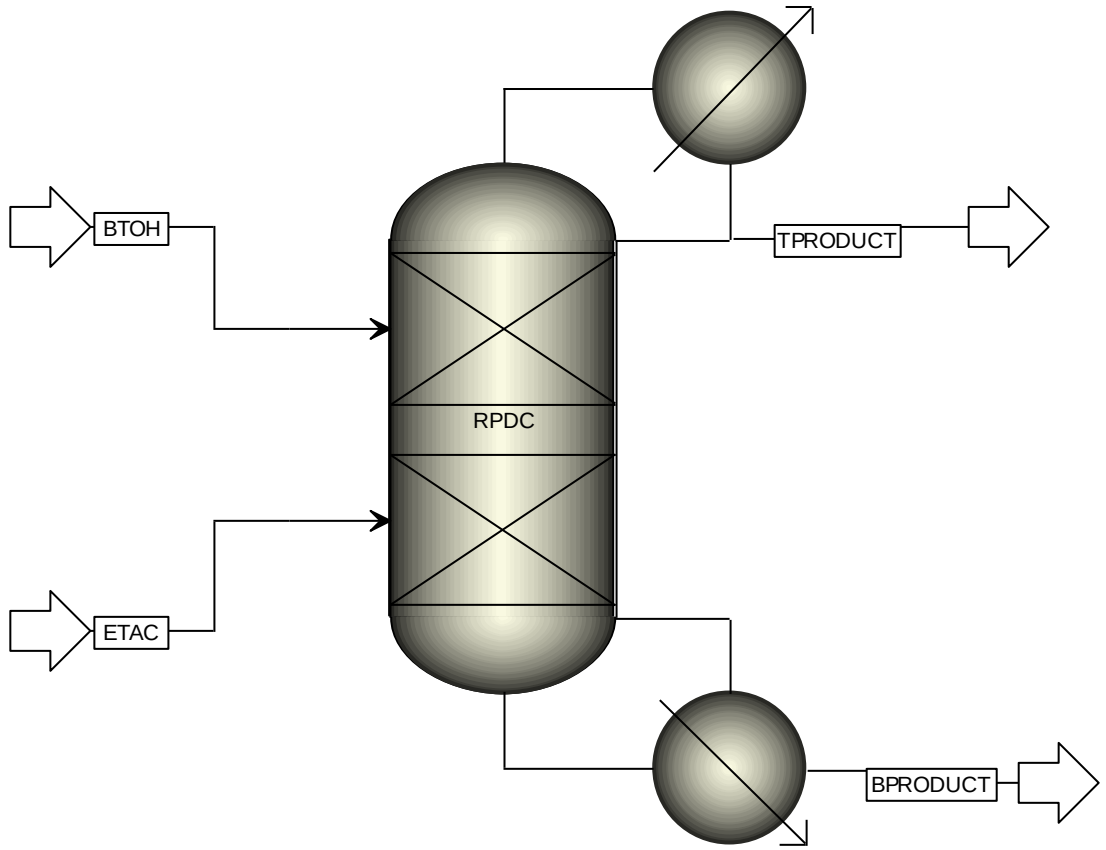


Figure 2. Reactive packed distillation column for n-butyl acetate transesterification process

Table 3. Aspen PLUS reactive distillation transesterification process model parameters

| Parameter | Value |
|---|---|
| **n-Butanol feed** | |
| Flow rate (L/min) | 0.02 |
| Temperature (K) | 298 |
| Pressure (bar) | 1.2 |
| | |
| **Ethyl acetate feed** | |
| Flow rate (L/min) | 0.02 |
| Temperature (K) | 298 |
| Pressure (bar) | 1.3 |
| | |
| **Reaction** | |
| Type | Equilibrium |
| $K_{eq}$ source | Temperature approach |
| $K_{eq}$ basis | Molarity |
| Reacting phase | Liquid |
| | |
| **Reactive distillation column** | |

| | |
|---|---|
| Type | RadFrac Packed |
| Total no of column segment | 25 |
| Acetic acid feed segment | 9 |
| Ethanol feed segment | 17 |
| Reflux ratio | 3 |
| Reboiler duty (kJ/s) | 0.7 |
| Condenser type | Total |
| Reboiler type | Kettle |
| Condenser pressure (bar) | 1.15 |
| Packing type | |
| Rectification section | Raschig |
| Reaction section | Wire-pack |
| Stripping section | Raschig |
| Section packed height (m) | 0.5 |

Table 4. Some basic properties of the components involved in the transesterification process

| **Component** | **Molecular weight (kg/kmol)** | **Boiling point (K)** |
|---|---|---|
| n-Butanol | 74.12 | 391.9 |
| Ethyl acetate | 88.11 | 350.21 |
| n-Butyl acetate | 116.16 | 399.26 |
| Ethanol | 46.07 | 351.44 |

The equilibrium reaction of the transesterification process used for the production of n-butyl acetate from the bottom segment of the reactive packed distillation column is given as shown in Equation (2).

$$C_4H_9OH + CH_3COOC_2H_5 \xleftrightarrow{K_{eq}} CH_3COOC_4H_9 + C_2H_5OH \quad (2)$$

## RESULTS AND DISCUSSIONS

The results obtained from the simulations of reactive packed distillation esterification process with 14 different property models are as given in Table5.In the table, the mole fractions of the desired product (ethyl acetate obtained at the top segment of the column) and its K-values (fugacity coefficients- measures of non-idealities) are given. It was observed from Table 5 that, in the simulations of the reactive distillation esterification process, 4 out of the 14 simulations carried out did not converge normally (that is, converged with errors).

Table 5. Simulation results of reactive distillation esterification process with the models

| **S/N** | **Property model** | **Top ETAC mole fraction** | **K-value** | **Comment** |
|---|---|---|---|---|
| 1 | WILSON | 0.9362 | 1.0249 | Converged normally |
| 2 | NRTL | 0.7726 | 0.8666 | Converged normally |
| 3 | UNIQUAC | 0.5335 | 1.1063 | Converged with errors |
| 4 | WILS-HOC | 0.8678 | 1.0666 | Converged normally |
| 5 | NRTL-HOC | 0.7704 | 0.8651 | Converged normally |
| 6 | UNIQ-HOC | 0.8058 | 0.8659 | Converged normally |
| 7 | WILS-RK | 0.9187 | 1.0379 | Converged normally |

| | | | | |
|---|---|---|---|---|
| 8 | NRTL-RK | 0.7691 | 0.8681 | Converged normally |
| 9 | UNIQ-RK | 0.5257 | 1.1241 | Converged with errors |
| 10 | PENG-ROB | 0.4659 | 0.1491 | Converged with errors |
| 11 | RK-SOAVE | 0.7707 | 0.5796 | Converged with errors |
| 12 | UNIFAC | 0.7319 | 0.8874 | Converged normally |
| 13 | UNIF-DMD | 0.6147 | 0.9926 | Converged normally |
| 14 | UNIF-LBY | 0.7301 | 0.8976 | Converged normally |

As seen in Table 5, among the property models investigated in this work, the one that gave the highest mole fraction value of 0.9362 of ethyl acetate at the top segment of the column was found to be WILSON. In addition, the K-value of this desired product at that segment was found to be 1.0249. Actually, under normally circumstances, K-values (that is, fugacity coefficients) are less than one, but under some certain conditions (e.g., at very high pressures), it can be greater than one. The high K-value obtained for the desired product at the top segment of the column has shown that the component was non-ideal at that segment. This observation was found to be true because ethyl acetate is not an ideal component; rather, it is a real component.

Furthermore, in order to know the relationships between the qualities (mole fractions) of the desired product obtained at the top segment of the column and its fugacity coefficients (K-values), the two values were plotted against the property models used, as shown in Figure 3. From the figure, it was discovered that the two parameters (mole fraction and K-value) had almost the same trend for the reactive distillation esterification process except that few abnormal situations were observed from the models that converged with errors.

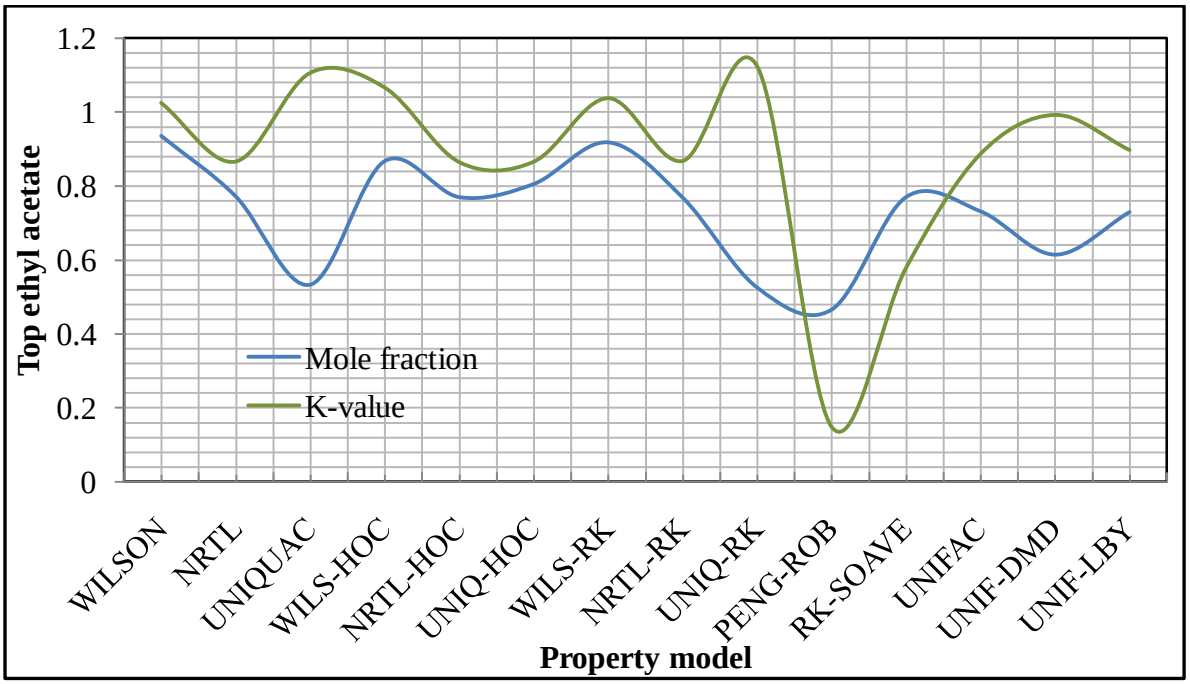


Figure 3. Mole fractions and K-values of ethyl acetate reactive distillation process versus property models

The results obtained from the simulation of the reactive packed distillation esterification process when NRTL was used, in this work, could not be compared with the work of Giwa and Karacan (2012b) because the input parameters used were not the same, even though ethyl acetate was also produced in their work. Besides, Aspen HYSYS was used in the work of

Giwa and Karacan (2012b) while Aspen PLUS was used in this one. According to the results and the literature informationobtained, the two simulations (that of Giwa and Karacan (2012b) and this study) carried out using NRTL property model were found to converge normally.

The results obtained from the reactive distillation transesterification process are also given in Table 6. In the table, the mole fractions of the desired product (in this case, n-butyl acetate present at the bottom segment of the column) and its K-values are given. From the results obtained, all the simulations carried out with the 14 different property models converged normally (that is, without any error). In addition, Peng-Robinson equation of state model was found to give the highest mole fraction (0.9821) of n-butyl acetate at the bottom segment of the column and the K-value of the component (n-butyl acetate) at that segment was estimated to be 0.9910.

Table 6. Simulation results of reactive distillation transesterification process with the models

| S/N | Property model | Bottom BTAC mole fraction | K-value | Comment |
|---|---|---|---|---|
| 1 | WILSON | 0.9102 | 0.9340 | Converged normally |
| 2 | NRTL | 0.9104 | 0.9347 | Converged normally |
| 3 | UNIQUAC | 0.9089 | 0.9341 | Converged normally |
| 4 | WILS-HOC | 0.9142 | 0.9398 | Converged normally |
| 5 | NRTL-HOC | 0.9150 | 0.9408 | Converged normally |
| 6 | UNIQ-HOC | 0.9130 | 0.9401 | Converged normally |
| 7 | WILS-RK | 0.9125 | 0.9380 | Converged normally |
| 8 | NRTL-RK | 0.9130 | 0.9388 | Converged normally |
| 9 | UNIQ-RK | 0.9108 | 0.9380 | Converged normally |
| 10 | PENG-ROB | 0.9821 | 0.9910 | Converged normally |
| 11 | RK-SOAVE | 0.9666 | 0.9841 | Converged normally |
| 12 | UNIFAC | 0.8435 | 0.8554 | Converged normally |
| 13 | UNIF-DMD | 0.9184 | 0.9430 | Converged normally |
| 14 | UNIF-LBY | 0.9156 | 0.9425 | Converged normally |

As investigated in the case of the reactive distillation esterification process, the relationships between the mole fractions of n-butyl acetate and its K-values for the different property models studied were investigated by plotting the mole fractions and the K-values against the property models used for the simulations, as shown in Figure 4. As can be seen from the figure, the trend of the plot of mole fractions of n-butyl acetate obtained from the bottom segment of the column was exactly the same as that of its K-values.

It was found in the literature that Giwa and Giwa (2012) worked on reaction integrated distillation transesterification process using UNIQUAC property model. However, the reactive distillation transesterification process carried out in this work could not be compared with their work because, apart from other differences in the input parameters, n-butanol and methyl acetate were used as the feeds in their work while n-butanol and ethyl acetate were used as the feeds in this work. As observed from the two studies (that of Giwa and Giwa (2012) and this one), the simulations carried out with UNIQUAC property model were found to converge normally.

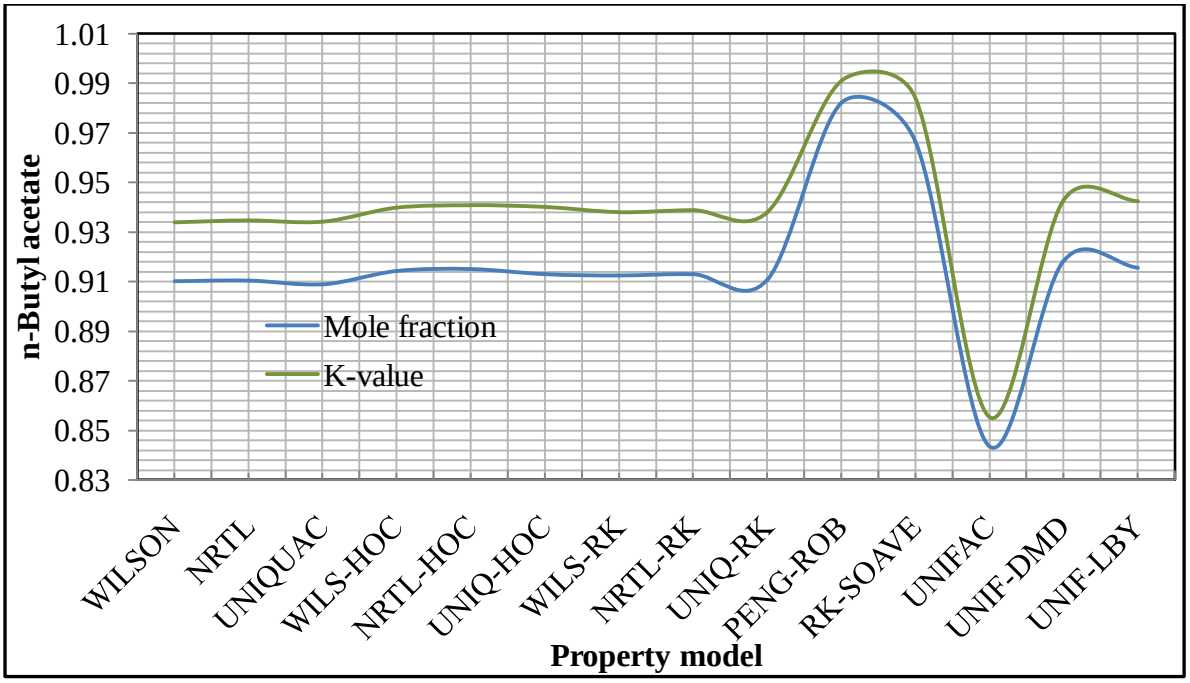


Figure 4. Mole fractions and K-values of n-butyl acetate reactive distillation process versus property models

Considering the two processes studied, it has been discovered that even when the same column was used to simulate them, different property models gave the highest mole fractions of the desired products. For instance, the highest mole fraction of ethyl acetate was obtained by simulating the esterification process using Wilson model while the highest mole fraction of n-butyl acetate was obtained when Peng-Robinson equation of state model was used to simulate the transesterification process. This is implying that the property models actually affected the processes that occurred inside the column and not the column in particular.

## CONCLUSIONS

The results obtained from the simulations of the reactive distillation esterification and transesterification processes studied in this work have revealed that the highest mole fractions of top ethyl acetate and bottom n-butyl acetate obtained from the esterification and the transesterification processes were 0.9362 and 0.9821 respectively. These results were obtained when Wilson model and Peng-Robinson equation of state model were respectively used to simulate the esterification and the transesterification processes. In addition, the trends of the relationships between the mole fractions of the desired products and their K-values were found to be very similar.

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## NOMENCLATURES

| | |
|---|---|
| ACH | Acetic acid feed |
| BPRODUCT | Bottom product |
| BTAC | n-Butyl acetate |
| BTOH | n-Butanol feed |
| ETAC | Ethyl acetate |
| ETAC | Ethyl acetate feed |
| ETOH | Ethanol feed |
| NRTL | Non-Random Two-Liquid model |
| NRTL-HOC | NRTL/Hayden-O'Connell model |
| NRTL-RK | NRTL/Redlich-Kwong model |
| PENG-ROB | Peng-Robinson model |
| RK-SOAVE | Redlich-Kwong-Soave model |
| RPDC | Reactive packed distillation column |
| TPRODUCT | Top product |
| UNIFAC | UNIQUAC Functional-group Activity Coefficients model |
| UNIF-DMD | Dortmund modified UNIFAC model |
| UNIF-LBY | Lyngby modified UNIFAC model |
| UNIQ-HOC | UNIQUAC/Hayden-O'Connell model |
| UNIQ-RK | UNIQUAC/Redlich-Kwong model |
| UNIQUAC | UNIversal QUAsiChemical model |
| WILS-HOC | WILSON/Hayden-O'Connell model |
| WILSON | Wilson model |
| WILS-RK | WILSON/Redlich-Kwong model |

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