Multicomponent Distillation Modeling of An Essential Oil by the SRK and PSRK State Equations

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ABSTRACT: *The equation of state Soave-Redlich-Kwong (SRK) and its modification (predictive SRK or PSRK) are applied to simulate multicomponet distillation, which separate main component of spearmint essential oil. The simulation model is based on bubble point method, and the Wang-Henke algorithm. Spearmint essential oil is considered in the study and the original experimental data were obtained from pilot plant. The models were validated by continuous distillation column with trays of one to five numbers. The work allows concluding on the advantages, disadvantages and expected accuracy of SRK and PSRK equations of state for multicomponent distillation data in the system as those studied.*

KEY WORDS: *Spearmint essential oil, Simulation, Multicomponent distillation, PSRK, SRK.*

INTRODUCTION

A large number of plant species contain volatile chemical compounds which can be extracted as an essential oil. Main component of essential oils are used in many industries such as the pharmaceutical and cosmetics industries. Carvone is one of the most important components of spearmint essential oil [1]. One of the most important Carvone separation methods is the use of multicomponent distillation.

Labarta et al. [2] published a description of a systematic and analytical tray by tray method for the optimal and rigorous design of multicomponent distillation columns where, for a given feasible separation, convergence is almost always guaranteed in calculation times comparable to those used by commercial simulation packages. *Loperena & Scheffer* [3] developed a simple, reliable and fast algorithm for the simulation of multicomponent distillation columns, where any equilibrium stage can accept a feed-stream and/or a vapor-side-stream and/or liquid-side-stream. *Komissarov & Sang* [4] studied Broyden's method that is applied to systems of nonlinear equations involved in multicomponent distillation calculations, with the convergence of the algorithm ensured.

A literature survey carried out by the author indicated lack of essential oil distillation simulation with PSRK equation of states. In this study, a novel simulation with PSRK equation of states is proposed to Carvone separation. Then the results of the two PSRK and SRK equations are compared.

The Soave-Redlich-Kwong (SRK) equation of state is probably the most widely employed model to correlate and predict fluid properties and phase equilibria in the oil and petrochemical industries. This equation has been many times extended and modified in different ways.

One of this modification is *Holderbaun & Gmehling* [5], known as the Predictive SRK (PSRK) equation. The original SRK equation and its modification are applied in this study to simulate multicomponent distillation of spearmint essential oil.

The main objective of this article is to obtain a better understanding of multicomponent distillation simulation with SRK and PSRK equations and has been subdivided into two specific purposes:

The separation of main component of spearmint essential oil and determination of recovery yield under pilot plant conditions.

The development of a numerical model with SRK and PSRK equation of states that able to prediction of the main component enrichment from process variables.

The numerical model is validated by qualitatively and quantitatively comparing with the pilot plant results. This model and its state equations will be used in a future work to optimize process conditions and product quality.

EXPERIMENTAL SECTION

The experimental pilot plant is shown in Fig. 1. It was designed and constructed at the Khorasan Research Institute for Food Science and Technology. The unit was mainly composed of 316A stainless steel column (diameter = 20 cm and height = 207 cm) that contained one to five perforated plates. The distillate flow rate and the reboiler heat duty were set. Once the system reached steady state both temperature and pressure remained constant. A stable steady state was typically observed after 35 minutes. Measurements were made after at least 25 minutes of steady state operation. Pressure gauges were placed at the top and bottom of the column to measure pressure and three thermocouples were used to measure the temperature inside the column. The external reflux ratios were two and three. The feed flow rate was 25 L/h and containing 31% carvone.

Main components of essential oil were measured on a Pye-Unicam Philips (PU4500) gas chromatograph with equipped with Packed SE-30 (1.52m × 4mm) column. The relative error for each of the experiments is typically below 2%.

COMPUTER SIMULATION

spearmint essential oil has a narrow boiling point range (160 °C to 240 °C) thus we use the bubblepoint (BP)
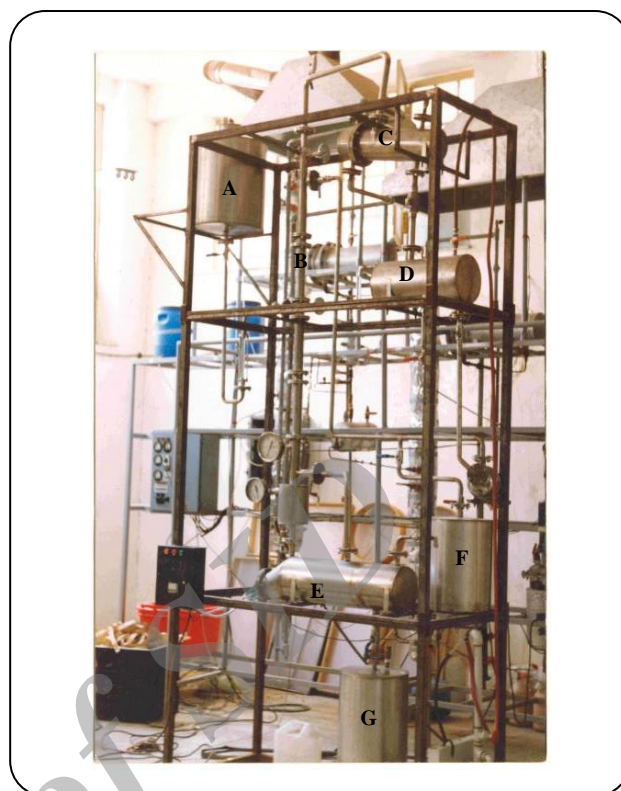

Fig. 1: Picture of the distillation pilot plant A. feed vessel B. distillation column C. condenser D. decanter E. reboiler F. vessel for product from top of column G. vessel for product from bottom of column.

method [6,7]. In the Bubble Point (BP) method, all equations are partitioned and solved sequentially except for the modified M equations, which are solved separately for each component by the tridiagonal matrix technique [7].

Governing Equations

For a system with N stages and NC components, the equations that describe the counter-current, multistage separation processes are derived by making material and heat balances around the *jth* tray of the model [7]. The equations are often referred to as the MESH equations after *Wang & Henke* [8]. These equations are M equations-Material balance for each component (C equations for each stage), E equations-phase-Equilibrium relation for each component (C equations for each stage), S equations-mole-fraction Summations (one for each stage), H equation-energy balance (one for each stage). In the BP methods, the MESH equations are grouped by types. With this approach, stage temperatures and flow

rates are guessed. The M equations, are combined with the E equations, to form the first subset of equations. These equations are linearized by holding the values of the flow rates and separation factors invariant and are then solved componentwise for stage composition, using the Thomas algorithm (see, for instance, work by *Chapra & Canale* [9]). Using the calculated composition, the S equations and the H equations are then solved separately for the new values of tray temperatures and flow rates. The entire procedure is repeated until all equations are satisfied [6,7]. The pure-component physical properties required in the calculation were taken from work by *Chemstations* [10], *Daubert, et al.* [11], *Poling, et al.,* [12] and *Valderrama & Silva* [13].

The SRK equation of state

All the equation of states used obeys the following general expression [14]:

$$P = \frac{RT}{V-b} - \frac{a_c \alpha(T_r)}{V(V+b)} \tag{1}$$

For the SRK equation:

$$a_c = 0.42748 \frac{R^2 T_c^2}{P_c} \tag{2}$$

$$b = 0.08664 \frac{R\ T_c}{P_c} \tag{3}$$

$$\alpha(T_r) = [1 + m(1 - T_r^{0.5})]^2 \tag{4}$$

$$m = 0.48 + 1.574\omega - 0.176\omega^2$$

That T_r is reduction temperature.

The PSRK equation of state

The PSRK equation is in the following form [14]:

$$P = \frac{RT}{V-b} - \frac{a_c \alpha(T_r)}{V(V+b)} \tag{5}$$

$$a_c = 0.42748 \frac{R^2 T_c^2}{P_c} \tag{6}$$

$$b = 0.08664 \frac{R\ T_c}{P_c} \tag{7}$$

$$T_r < 1: \ \alpha(T_r) = \tag{8}$$

$$[1 + c_1(1 - T_r^{0.5}) + c_2(1 - T_r^{0.5})^2 + c_3(1 - T_r^{0.5})^3]^2$$

$$T_r > 1: \ \alpha(T_r) = [1 + c_1(1 - T_r^{0.5})]^2$$

c_1, c_2 and c_3 are empirical constants given in the literature [10].

K-values and Activity Coefficient

To solve equations by the Thomas method, $K_{i,j}$ values are required. The K-values are updated between iterations in a process from Chao - Seader K-value:

$$K_i = \frac{\gamma_{iL} \Phi_{iL}^o}{\hat{\Phi}_{iV}^o} \tag{9}$$

The values of Φ_{iL}^o and $\hat{\Phi}_{iV}^o$ are obtained from SRK or PSRK equations [7,13] and γ_{iL} is computed from Flory-Huggins equation [7]. The following convergence criterion based on successive sets of the stage temperatures was considered [6,7]:

$$\tau = \sum_{j=1}^{N} \left[T_j^{(k)} - T_j^{(k-1)} \right]^2 \leq 0.01N \tag{10}$$

where τ and N are the convergence criterion and number of stages. The original code is written in FORTRAN and numerical computations were performed on a Pentium 4 computer. Typical CPU times ranged from 8 to 10 minutes.

RESULTS AND DISCUSSION

Only some typical results from the experimental study are presented here together with their prediction by the multicomponent distillation model described above. In the simulations, the feed flow rate and the column pressure as well as the reflux and distillate flow rate were specified according to the experimental numbers.

Comparison Model - Experiment

a) Carvone enriching

The enriched carvone exits from a reboiler connected to the bottom of the column. Results are presented in Figs. 2 and 3 for the SRK and PSRK equations respectively.

The predicted profiles of simulation are in qualitative agreement with the experimental data. Quantitative agreement is fair at a first glance. Deviations, however, occur in the predictions of the carvone concentration for the greater number of trays. The relative error is shown in the Fig. 6 and is about 27% for the model with the SRK equation but the relative error is about 20 % for the model with the PSRK equation that shown in this figure.
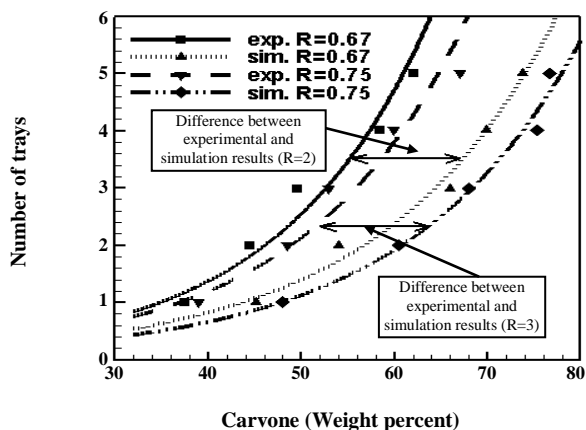
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Fig. 2: A comparison between experimental and numerical results (SRK eq.) for the evolution of carvone separation (separation percent vs. number of trays) A. experimental results (R=2) B. numerical results (R=2). C. experimental results (R=3) D. numerical results (R=3).
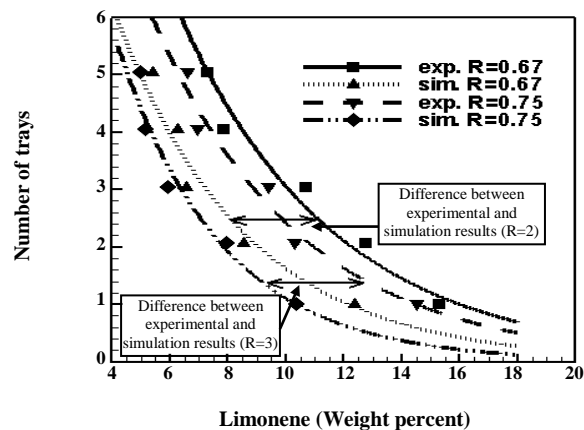

Fig. 4: A comparison between experimental and numerical results (SRK eq.) for the evolution of limonene separation (separation percent vs. number of trays) A. experimental results (R=2) B. numerical results (R=2). C. experimental results (R=3) D. numerical results (R=3).
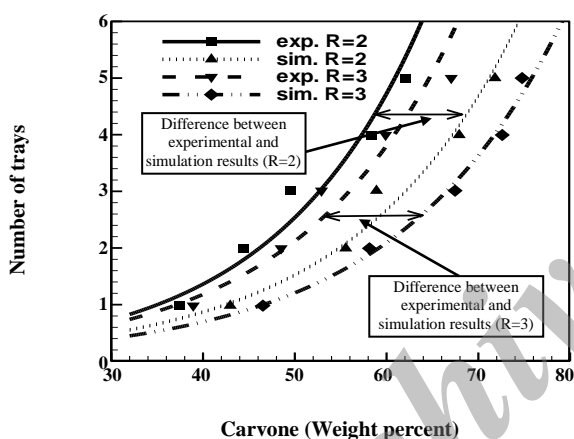

Fig. 3: A comparison between experimental and numerical results (PSRK eq.) for the evolution of carvone separation (separation percent vs. number of trays) A. experimental results (R=2) B. numerical results (R=2). C. experimental results (R=3) D. numerical results (R=3).
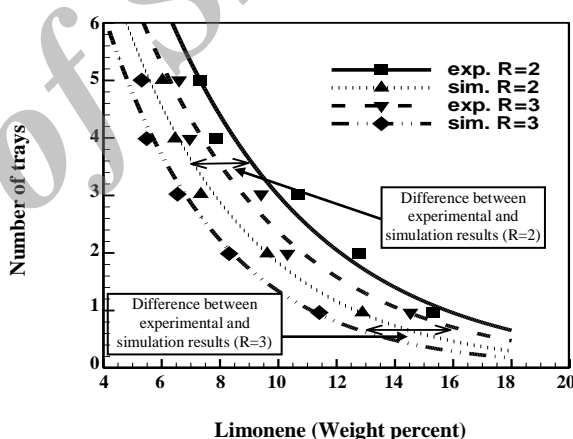

Fig. 5: A comparison between experimental and numerical results (PSRK eq.) for the evolution of limonene separation (separation percent vs. number of trays) A. experimental results (R=2) B. numerical results (R=2). C. experimental results (R=3) D. numerical results (R=3).

As seen in the Fig. 6, the PSRK equation gives the lowest deviation. The lower deviation given by the PSRK model is probably due to the greater number of parameters included in the model.

Furthermore, as shown in the Figs. 2 and 3, the slop of the lines shows that the value of separation is reduced in the greater number of trays relative to the small number of trays, although the total rate of separation is increased. Separation theories show that these findings are typical for all distillation processes [7].

The variation of the reflux has an important influence on the column performance. By increasing the reflux ratio the internal flows in the column are increased, so that enriching in the column become better. Figs. 2 and 3 show results of the carvone separation which was carried out with two and three reflux ratios.

b) Limonene removal

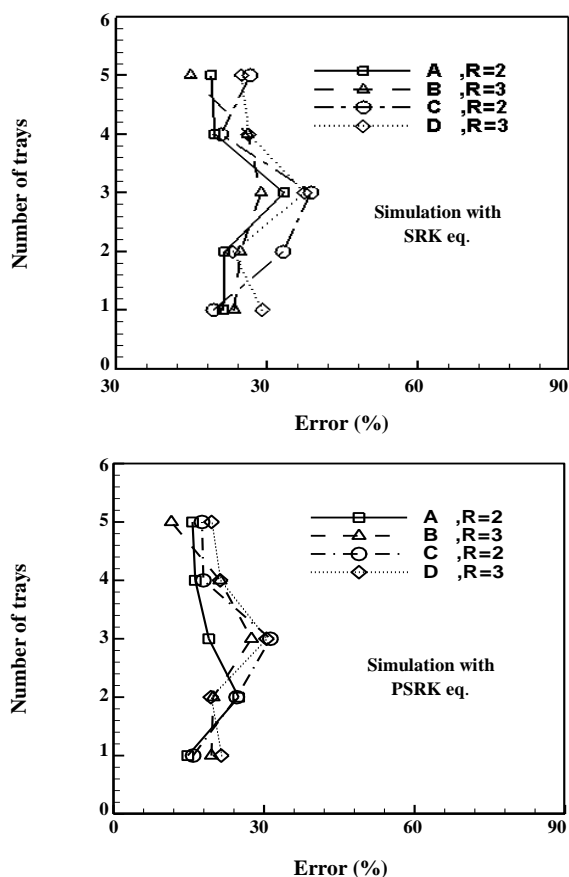Figs. 4 and 5 show the experiment and simulation results of the limonene exits from a reboiler connected

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Fig. 6: The percent error between the results of computer simulations (SRK and PSRK eqs.) with experimental results. A. Carvone enrichment with R=2 B. Carvone enrichment with R=3. C. Limonene removal with R=2 D. Limonene removal with R=3.

to the bottom of the column. It can be seen that the concentration profiles for limonene are correctly predicted. The concentrations of limonene observed in the experiments are higher than the model predictions. The relative error is shown in the Fig. 6 for the model with SRK equation and the model with PSRK equation. Also these deviations can be understood as a consequence of state equation effects. As seen in the Fig. 6, the PSRK equation gives the lowest deviation.

CONCLUSIONS

The separation of main component of spearmint essential oil was modeled with SRK and PSRK equations of state. Experimental runs were performed in the pilot plant. Pilot scale of multicomponent distillation of spearmint oil was carried out in a 270cm column equipped

with condenser, reboiler and decanter. The consistency between the experiments and simulations was good both qualitatively and quantitatively. The results shown that the PSRK equation gives the lowest deviation relative to the SRK equation. The distillation process was found to be sensitive to the number of trays and the amount of reflux ratio. Results show that increasing the number of trays has an impact on the carvone separation. Limitation of the simulation is its restriction to ideal trays modeling thus one area of future extension is the inclusion of the real trays study.

Nomenclature

Latin Capital and Lowercase Letters

a	Constant in equations of state
b	Constant in equations of state
E	Equations-phase-Equilibrium
K	Equilibrium ratio for vapor-liquid equilibria
N	Number of equilibrium (theoretical, perfect) stages
P	Pressure
T	Temperature
τ	Convergence criterion
γ	Activity coefficient

Subscripts and Superscripts

i	Particular species or component
j	Stage number
L	Liquid phase
V	Vapor
°	Pure species
^	Partial

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