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SIMULATION OF THE MULTICOMPONENT DISTILLATION OF SPEARMINT ESSENTIAL OIL BY A PREDICTIVE SOAVE-REDLICH-KWONG EQUATION OF STATE AND COMPARISON WITH EXPERIMENTS

Article Highlights

- Pilot scale of separation of spearmint oil components was carried out in a column
- The results are compared to predictions based on a computer simulation
- For the simulation of the multicomponent distillation studied, a BP method is used
- The consistency between the experiments and simulations was good
- The distillation was found to be sensitive to the number of trays and reflux ratio

Abstract

In this study, enrichment in major component of spearmint oil has been investigated by continuous multicomponent distillation. A mathematical model was evaluated to predict the enrichment by multicomponent distillation of spearmint oil. The aim of the work was to obtain simulation data to compare with experimental data of spearmint oil enriching. The simulation model is based on the bubble point method, the Wang-Henke algorithm and predictive Soave-Redlich-Kwong (PSRK) equation. In this method, MESH equations are solved and a diagonal matrix method for solving equations is used. The model was validated by experimental data obtained from a pilot-plant system, using a continuous distillation column with 1-5 trays. The simulation was able to predict satisfactory the experimental data. The results of simulation and experiments show that the major component of spearmint essential oil is enriched from 31 to 62% by the distillation column with five trays. The results show that the addition of a tray to the distillation column with a low number of trays is more effective relative to addition of a tray to the distillation column with a higher number of trays. The results indicate that increasing of reflux ratio from 2 to 3 increases separation of the major component from 62.04 to 67.04%.

Keywords: spearmint essential oil, simulation, separation, multicomponent distillation, bubble point method, PSRK equation.

A large number of plant species contain volatile chemical compounds that can be extracted as an essential oil. The main components 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]. Due to its high taste and smell, it is widely used in spices and cultivated in several countries [2].

Although it seems relatively simple to separate such a component from oils, the yield of the main component may vary to a large extent depending on the separation method used. The advantages and disadvantages of some methods such as solvent extraction, simultaneous distillation-extraction, supercritical carbon dioxide extraction and the use of microwave ovens have been discussed extensively [3]. None of these processes is universal; in fact, each process presents particular advantages and disadvantages when used for a particular material. A literature survey indicated a lack of published data on the main component separation of spearmint essential oil by multicomponent distillation.

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The main objective of this article is to obtain a better understanding of spearmint multicomponent distillation. The paper is subdivided into two specific parts:

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

2. The development of a numerical model able to predict 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 will be used in future work to optimize process conditions and product quality.

EXPERIMENTS

The experimental pilot plant is shown in Figure 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 column was insulated in order to minimize heat losses. The column was equipped with a total condenser, an electrically heated thermosyphon reboiler and a protection heating to ensure adiabatic operation.

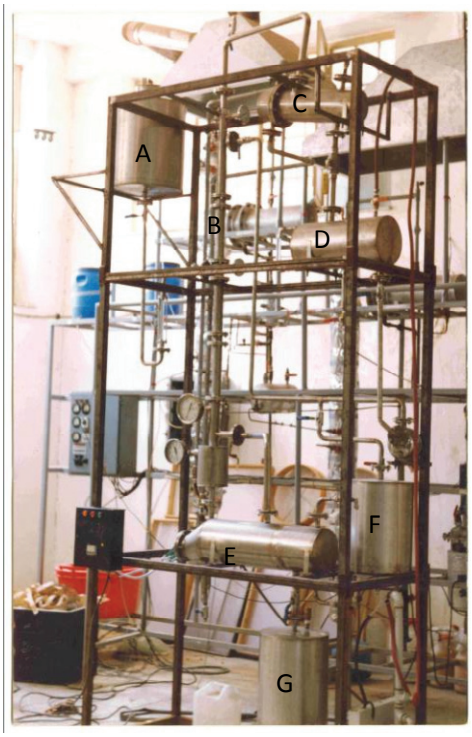

Figure 1. Picture of the distillation pilot plant: A - feed vessel; B - distillation column; C - condenser; D - decanter; E - reboiler; F - vessel for product from top of column; G - vessel for product from bottom of column.

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 min. Measurements were made after at least 25 min 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 enriched vapor of essential oil at the column outlet was condensed in a stainless steel condenser, which was designed to cope with various operating conditions of flow rates and pressures. The condensate was collected in a sealed vessel and partially refluxed to the column.

Concentrations and temperatures were also measured in the feed, bottom product and distillate. For five experiments, the feed location was above the first tray for column with one tray, above the first tray for column with two trays, above the middle tray for column with three trays, above the second tray for column with four trays, above the middle tray for column with five trays, respectively. 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 PU 4500 gas chromatograph with equipped with packed SE-30 (1.52 m×4 mm) column. Nitrogen was used as carrier gas at a flow rate of 30 mL/min. The temperature program was from 55 (6 min) to 210 °C, at a rate of 4 °C/min. Carvone and limonene were identified by comparing their retention times with those of standard compounds. The percentage composition of carvone and limonene was calculated using a calibration curve with components injected at different concentrations.

All experiments were conducted at the same conditions and showed reproducible results. The relative error for each of the major component separation results is typically below 2%.

COMPUTER SIMULATION

Spearmint essential oil has a narrow boiling point range (160 to 240 °C). When the feed(s) to the distillation column contains components of a narrow boiling-point range, the bubble point (BP) method is very efficient [4,5].

In the bubble-point (BP) method, a new set of stage temperatures is computed at each iteration from bubble-point equations. In the method, all equations are partitioned and solved sequentially except for the modified M-equations, which are solved sepa-

rately for each component by the tridiagonal matrix technique [5].

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 enthalpy balances around the j^{th} tray of the model (see Figure 2).

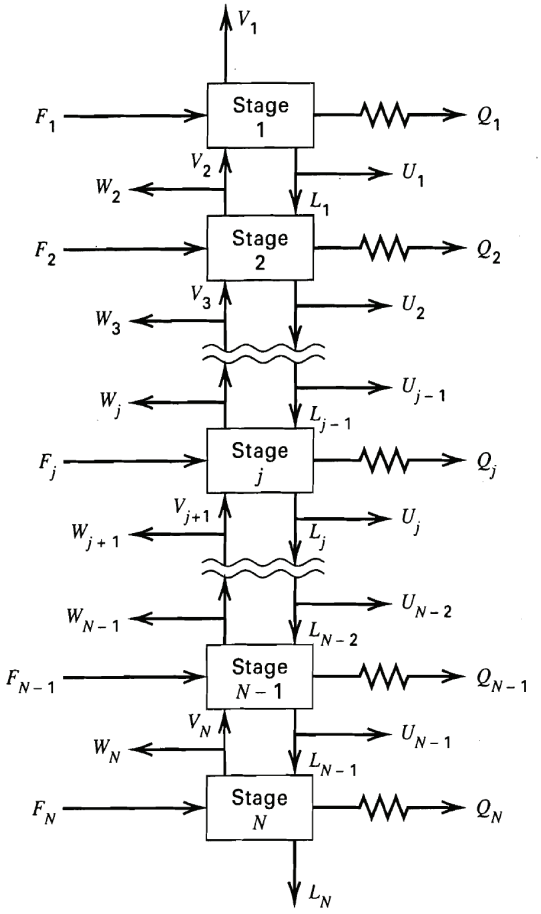

Figure 2.. General countercurrent cascade of N stages [5].

The equations are often referred to as the MESH equations after Wang and Henke [6]. These equations are:

1. *M-equations*. material balance for each component (C equations for each stage):

$$M_{i,j} = L_{j-1}x_{i,j-1} + V_{j+1}y_{i,j+1} + F_j z_{i,j} - \\ -(L_j + U_j)x_{i,j} - (V_j + W_j)y_{i,j} = 0 \quad (1)$$

where $x_{i,j}$, $y_{i,j}$, and $z_{i,j}$ are the mole fractions of component i on stage j, respectively, in the liquid phase, vapor phase, and feed stream; L_j, V_j, U_j, W_j and F_j are liquid, vapor, liquid side stream, vapor side stream flow rates leaving or entering stage j and feed molar flow rate entering stage j.

2. *E-equations*. phase-equilibrium relation for each component (C equations for each stage):

$$E_{i,j} = y_{i,j} - K_{i,j}x_{i,j} = 0 \quad (2)$$

where $K_{i,j}$, is the phase equilibrium ratio.

3. *S-equations*. mole-fraction summations (one for each stage):

$$(S_y)_j = \sum_{j=1}^{C} y_{i,j} - 1.0 = 0 \quad (3)$$

$$(S_x)_j = \sum_{j=1}^{C} x_{i,j} - 1.0 = 0 \quad (4)$$

4. *H-equation*. energy balance (one for each stage):

$$H_j = L_{j-1}H_{L_{j-1}} + V_{j+1}H_{V_{j+1}} + F_i H_{F_j} - \\ -(L_j + U_j)H_{L_j} - (V_j + W_j)H_{V_j} - Q_j = 0 \quad (5)$$

where kinetic and potential energy changes are ignored.

A total material balance equation can be used in place of Eqs. (3) or (4). It is derived by combining these two equations and using $\Sigma z_{i,j} = 1.0$ with Eq. (1) summed over the C components and over stages 1 through j to give:

$$L_j = V_{j+1} + \sum_{m=1}^{j}(F_m - U_m - W_m) - V_1 \quad (6)$$

Solution of governing equations

In the BP methods, the MESH equations are grouped by types. With this approach, stage temperatures and flow rates are estimated. The M-equations, Eq. (1), are combined with the E-equations, Eq. (2), to form the first subset of equations. These equations are linearized by holding the values of the flow rates and separation factors invariant and then solved component-wise for stage composition, using the Thomas algorithm (see, for instance, work by Chapra and Canale [7]). Using the calculated composition, the S-equations, Eqs. (3) and (4), and the H-equations, Eq. (5), are then solved separately for the new values of tray temperatures and flow rates. The boiling range of spearmint oil is chosen for the first iteration. The entire procedure is repeated until convergence is achieved [5,6].

The following five components: carvone, dihydrocarvone, cineol, limonene and α-pinene, represents 93 to 98 mass% of spearmint essential oil, so calculations are performed for these five components.

Pure component physical properties required in the calculation were taken from Chemstations [8] and/or the work by Daubert *et al.* [9], Poling *et al.* [10], and Valderrama and Silva [11].

K-values

To solve equations by the Thomas method, $K_{i,j}$ values are required. When they are composition-dependent, initial assumptions for all $x_{i,j}$ and $y_{i,j}$ values are needed. Ideal K-values, employed for the first iteration, are computed from:

$$K_{\text{ideal}} = \frac{\Phi_{\text{iL}}^{\text{o}}}{\Phi_{\text{iV}}^{\text{o}}} \tag{7}$$

where $\Phi_{\text{iL}}^{\text{o}}$ and $\Phi_{\text{iV}}^{\text{o}}$ are the pure-species fugacity coefficients which were computed from PSRK equation of state. The PSRK equation of state is widely applied in process calculations, particularly for saturated vapors and liquids [5,11,12].

The *K*-values are updated between iterations using Chao-Seader K-value:

$$K_{\text{i}} = \frac{\gamma_{\text{iL}}\Phi_{\text{iL}}^{\text{o}}}{\hat{\Phi}_{\text{iV}}^{\text{o}}} \tag{8}$$

where γ_{iL} and $\hat{\Phi}_{\text{iV}}^{\text{o}}$ are the activity coefficient of a species in a liquid and partial fugacity coefficient of a species in a vapor, respectively.

The PSRK equation

The PSRK equation is in the following form [11]:

$$P = \frac{RT}{V - b} - \frac{a_{\text{c}}\alpha(T_{\text{r}})}{V(V+b)} \tag{9}$$

$$a_{\text{c}} = 0.42748\frac{R^2T_{\text{c}}^2}{P_{\text{c}}} \tag{10}$$

$$b = 0.08664\frac{R^2T_{\text{c}}^2}{P_{\text{c}}} \tag{11}$$

$$\begin{aligned} &T_{\text{r}} < 1:\ \alpha(T_{\text{r}}) = [1 + c_1(1 - T_{\text{r}}^{0.5}) + c_2(1 - T_{\text{r}}^{0.5})^2 + \\ &\quad + c_3(1 - T_{\text{r}}^{0.5})^3]^2 \\ &T_{\text{r}} > 1:\ \alpha(T_{\text{r}}) = [1 + c_1(1 - T_{\text{r}}^{0.5})]^2 \end{aligned} \tag{12}$$

where c_1, c_2 and c_3 are empirical constants given in the literature [8].

$\Phi_{\text{iL}}^{\text{o}}$ and $\Phi_{\text{iV}}^{\text{o}}$ are obtained from PSRK equation [5,11] and γ_{iL} is computed from Flory-Huggins equation [5]. The complete expression for the activity coefficient of a species including the Flory-Huggins correction is:

$$\gamma_{\text{iL}} = \exp\left[\frac{v_{\text{iL}}(\delta_i - \sum_{i=1}^{C}\Phi_i\delta_i)^2}{RT} + \ln\left(\frac{v_{\text{iL}}}{v_{\text{L}}}\right) + 1 - \frac{v_{\text{iL}}}{v_{\text{L}}}\right] \tag{13}$$

where v_{iL}, δ_i, Φ_i, v_{l}, R and T are the molar volume in liquid phases, solubility parameter, volume fraction, molar volume of a species, universal gas constant and temperature, respectively.

Simulation convergence criterion

The following convergence criterion based on successive sets of the stage temperatures was considered [4,5]:

$$\tau = \sum_{j=1}^{N}\left[T_j^{(k)} - T_j^{(k-1)}\right]^2 \le 0.01N \tag{14}$$

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 min.

RESULTS AND DISCUSSION

Comparison between the model predictions and the experimental data

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 values.

a) Carvone enriching

The enriched carvone exits from a reboiler connected to the bottom of the column. Table 1 shows the experimental and simulation results of the car-

Table 1. Experimental and simulation results for carvone enriching with reflux ratios of 2 and 3 for the pilot plant considered in this study

Reflux ratio	Results (weight percent)	One tray	Two trays	Three trays	Four trays	Five trays
2	Experiment	37.42	44.46	49.50	58.40	62.04
	Simulation	42.96	55.55	58.90	67.92	71.81
3	Experiment	38.93	48.51	52.91	59.89	67.04
	Simulation	46.53	58.14	67.46	72.60	74.77

vone enrichment for reflux ratios of 2 and 3. In addition, the results are presented in Figure 3.

The predicted profiles of simulation are in qualitative agreement with the experimental data. Deviations, however, occur in the predictions of the carvone concentration for greater number of trays. The relative error is shown in Figure 4 and is about 20%. The deviations can be interpreted as a result of the use of PSRK equations. Another source of deviation from exponential results is the plat efficiency. The plate efficiency is taken as 100% but it is always lower in real columns. The real plate efficiency should be taken into account in the future version of the model.

Furthermore, the slope of the lines shows that the value of separation is reduced for large 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 [5].

The variation of the reflux has an important influence on the column performance. By increasing the

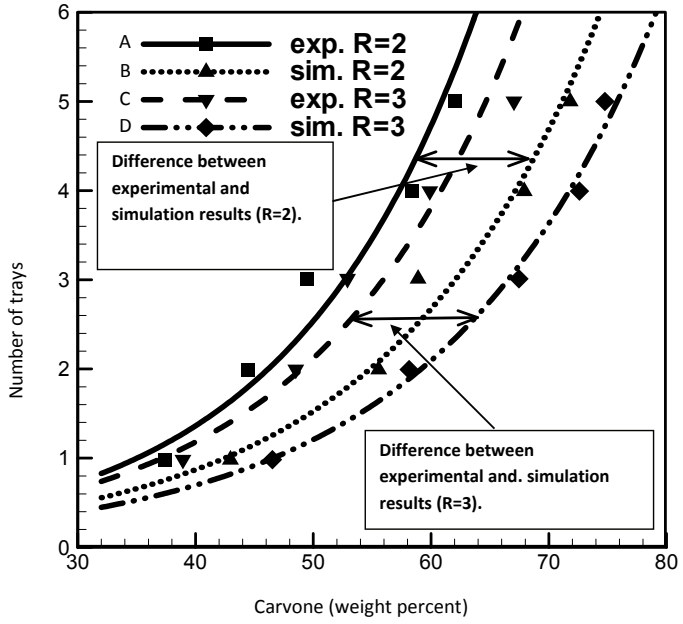

Figure 1. A comparison between experimental and numerical results for the evolution of carvone separation (exit concentration vs. number of trays and reflux R): A - experimental results (R = 2); B - numerical results (R = 2); C - experimental results (R = 3); D - numerical results (R = 3).

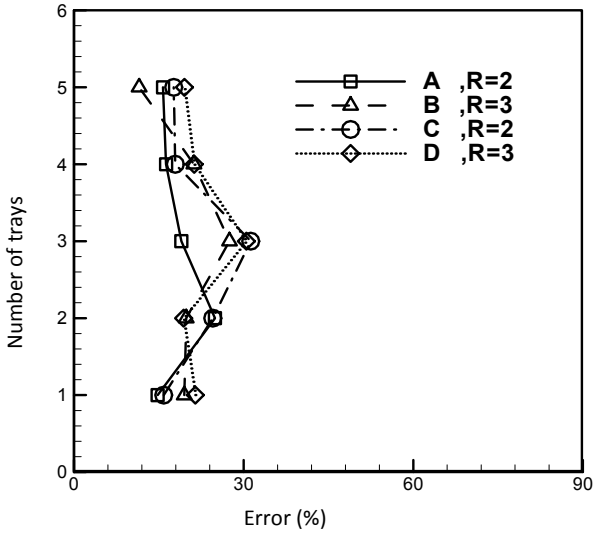

Figure 2. The relative deviation between the results of computer simulations and the experimental results: A - carvone enrichment with R = 2; B - carvone enrichment with R = 3; C - limonene removal with R = 2; D - limonene removal with R = 3.

reflux ratio the internal flows in the column are increased, so that enriching in the column performance is improved. Figure 3 shows results of the carvone separation, which was carried out with reflux ratios equal to 2 and 3.

b) Limonene removal

Table 2 shows the experimental and simulation results on the limonene concentration in the exit from a reboiler connected to the bottom of the column. The results are also presented in Figure 5 for reflux ratios of 2 and 3.

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 Figure 4. Also, these deviations can be interpreted as a consequence of the effect of the PSRK equation.

CONCLUSION

Pilot scale experiments of multicomponent distillation of spearmint oil were carried out in a column of 270 cm height equipped with a condenser and reboiler. The influence of different number of trays (1 to 5 trays) with reflux ratio of 2 and 3 was studied. The results are compared to predictions based on a computer simulation. For the simulation of the multicomponent distillation studied in the present work, the BP method is used. With MESH equations and PSRK state equation, the multicomponent distillation model is entirely predictive. The results of the model were compared and validated with the experiments. The results of model show satisfactory agreement with experimental data.

The distillation process was found to be sensitive to the number of trays and the value of reflux ratio. The results show that increasing the number of trays has an impact on the carvone separation.

Acknowledgments

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Table 2. Experimental and simulation results for limonene removal with reflux ratios of 2 and 3 for the pilot plant considered in this study

Reflux ratio	Results (weight percent)	One tray	Two trays	Three trays	Four trays	Five trays
2	Experiment	15.31	12.75	10.68	7.865	7.310
	Simulation	12.88	9.617	7.342	6.457	6.023
3	Experiment	14.53	10.31	9.410	6.960	6.595
	Simulation	11.41	8.311	6.542	5.483	5.313

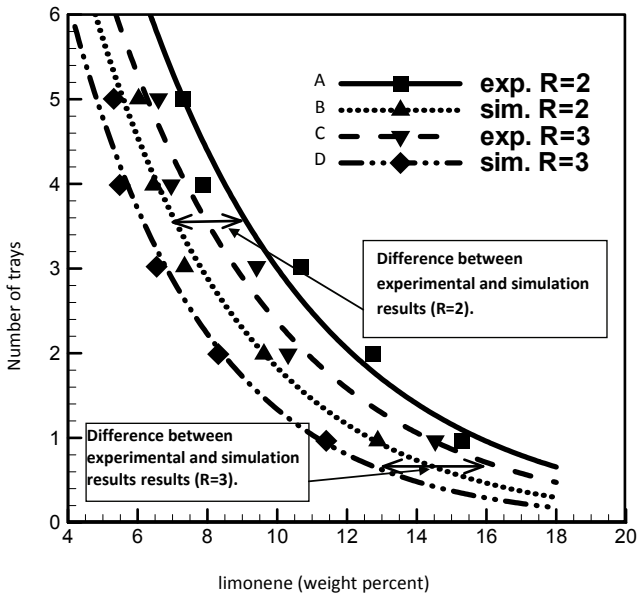

Figure 3. A comparison between experimental and numerical results for the evolution of limonene separation (exit concentration vs. number of trays and reflux R): A -experimental results (R = 2); B - numerical results (R = 2); C - experimental results (R = 3); D - numerical results (R = 3).

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NAUČNI RAD

SIMULACIJA VIŠEKOMPONETNE DESTILACIJE ETARSKOG ULJA NANE PRIMENOM SOAVE-REDLICH-KWONG JEDNAČINE STANJA I POREĐENJE SA EKSPERIMENTOM

U ovom radu je ispitano povećanje koncentracije glavnih komponenti etarskog ulja nane kontinualnom višekomponentnom destilacijom. Za predviđanje povećavanje koncentracije glavnih komponenti etarskog ulja nane korišćen je matematički model. Cilj rada je bio dobijanje simulacionih podataka da bi se poredili sa eksperimentalnim podacima. Simulacioni model je zasnovan na tačkama ključanja, Wang-Henkel algoritmu i Soave-Redlich--Kwong. U ovoj metodi, MESH jednačine su rešene, a korišćena je metoda dijagonalne metrije. Model je validiran eksperimentalnim podacima dobijenim iz pilot postrojenja sa kolonom za kontinualnu destilaciju sa jednim do pet podova. Simulacijom je moguće zadovoljavajuće predvideti eksperimenatlne podatke. Rezultati simulacije i eksperimenti pokazuju da se destilacijom u koloni sa pet podova glavne komponente etarskog ulja nane obogaćuju od 31 do 62%. Rezultati pokazuju da dodatak jednog poda destilacionoj koloni sa malim brojem podova ima mnogo veći efekat u odnosu na dodatak poda destilacionoj koloni sa većim brojem podova. Rezultati ukazuju da povećanje refluksnog odnosa od 2 na 3 povećava separaciju glavnih komponenti od 62,04 do 67,04%.

Ključne reči: etarsko ulje nane, simulacija, separacija, multikomponentna destilacija, metoda tačke ključanja, PSRK jednačina.