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Bioethanol Production Optimization: A Thermodynamic Analysis

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Abstract In this work, the phase equilibrium of binary mixtures for bioethanol production by continuous extractive process was studied. The process is composed of four interlinked units: fermentor, centrifuge, cell treatment unit, and flash vessel (ethanol-congener separation unit). A proposal for modeling the vapor–liquid equilibrium in binary mixtures found in the flash vessel has been considered. This approach uses the Predictive Soave–Redlich–Kwong equation of state, with original and modified molecular parameters. The congeners considered were acetic acid, acetaldehyde, furfural, methanol, and 1-pentanol. The results show that the introduction of new molecular parameters r and q in the UNIFAC model gives more accurate predictions for the concentration of the congener in the gas phase for binary and ternary systems.

Keywords Bioreactors · Fermentation · Phase equilibria · Predictive Soave–Redlich–Kwong

Nomenclature

φ_i	Fugacity coefficients of component i
q	Area molecular parameters in the UNIFAC model
r	Volume molecular parameters in the UNIFAC model
x_i	Mole fraction in the liquid phase
y_i	Mole fraction in the vapor phase
P	Pressure of the system
T	Temperature of the system

Introduction

The global demand for ethanol is increasing very quickly. In Brazil, the growth of the internal market is due to the new technology used in flex fuel vehicles (vehicles with the

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ability to operate with pure either ethanol or gasoline or even with any alcohol/gasoline blend) and the increase in oil prices. The growth of the foreign market is expected because of the enactment of the Kyoto Protocol and the implementation of environmental protection laws in many countries. Thus, there is an intensified interest in the study of all the steps involved in ethanol production and especially in the more intensive process as the extractive fermentation.

High concentrations of ethanol inhibit the fermentation process, particularly when a fermentative medium with high substrate concentration is used, as is the case in the majority of the industrial processes. Considering this, Silva et al. [1] studied a process of fermentation combined with a flash vessel, which selectively extracts ethanol from the medium as soon as it is produced. These authors have shown that this scheme presents many positive features and better performance than conventional industrial processes [2]. Cardona and Sanchez [3] point out that the reaction–separation integration is a particularly attractive alternative for the intensification of bioethanol production. When bioethanol is removed from the culture broth, its inhibition effect on the growth rate is diminished or neutralized. However, the performance of the whole process is significantly influenced by separation unit, and that means that thermodynamic knowledge of the mixture is required.

Most of the substances found in the culture broth to be separated are polar components. Besides, the very low concentration of many other components (apart from ethanol and water), called congeners, lead to difficulties to correlate and predict the concentration of the distilled product in the continuous extractive fermentation. Some of these substances (acetic acid, furfural, and methanol) are considered as a source of valuable co products [3], so that further downstream separation is justifiable.

Knowledge of the vapor–liquid equilibrium (VLE) behavior in these mixtures is necessary to design and to optimize the separation in the flash vessel, which is part of the extractive process considered in this work, described in the next section. The problem of phase equilibrium consists on the calculation of some variables of the set (T, P, x, and y) when some of them are known.

The flash vessel in the continuous extractive process operates under vacuum, but, in this study, the atmospheric pressure is considered, as no significant changes are expected to occur because of values of the used operating conditions. The classic thermodynamic models require knowledge of binary interaction parameters, which are usually determined from experimental data for binary systems.

In this study, the phase equilibrium in the binary mixtures that are expected to be found in the flash distillation was modeled with the Predictive Soave–Redlich–Kwong (PSRK) equation of state [4], using modified molecular parameters r and q. Five binary ethanol + congener mixtures were considered for new yield values for parameters r and q. The congeners considered were acetic acid, acetaldehyde, furfural, methanol, and 1-pentanol. Subsequently, the model was validated with the water + ethanol binary system, and the 1-pentanol + ethanol + water, 1-propanol + ethanol + water, and furfural + ethanol + water ternary systems.

Process Description and Modeling

Extractive Continuous Alcoholic Fermentation Process

The extractive fermentation process for bioethanol production proposed by Silva et al. [1] is shown in Fig. 1. The process is composed of four interlinked units: fermentor (ethanol

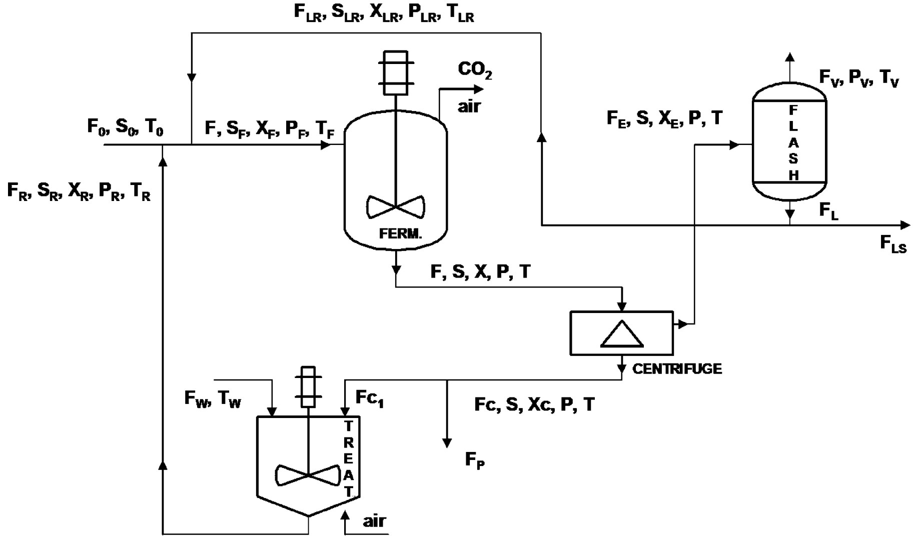

Fig. 1 Extractive alcoholic fermentation scheme

production unit), centrifuge (cell separation unit), cell treatment unit, and flash vessel (ethanol–water separation unit). This scheme attempts to simulate industrial conditions [2], with the difference that only one fermentor is used instead of a cascade system, and a flash vessel is used to extract part of the ethanol.

The flash vessel is an equipment where a close contact between a liquid and a vapor phase takes place to separate components based on the volatility difference among them. Thus, the liquid becomes rich with the less volatile components and the vapor with the most volatile components. The flash vessel is a single-stage distillation column.

The fermentation broth, without yeast, is led to the distillation flash, where the separation of the ethanol–water mixture occurs. The flash vessel must work in a temperature and pressure range to meet two main goals: cooling the broth in the fermentor to eliminate the necessity of heat exchangers in the industrial process and consequently diminishing the operational cost; and maintaining the ethanol concentration in the fermentor in levels such as it can act as antiseptic, around of 40 g/L, to prevent propagation of contaminants, typically bacteria [1]. The vapor phase pass through a condenser at 5°C to condense the rich ethanol vapor, and the liquid phase, poor in ethanol, returns to the fermentor.

The mathematical modeling of the process consists of mass and energy balance equations. All equipment, except the fermentor, are modeled assuming the hypothesis of “pseudo” steady state.

Assuming constant volume, the mass and energy balance equations for the fermentor can be written by using the intrinsic model [5, 6], with parameters adjusted as functions of the temperature from experimental data; the equations are given in Atala et al. [7]. A detailed description of the process and the mathematical model can be found in Costa et al. [8].

The Predictive Soave-Redlich-Kwong (PSRK) Equation of State: A Proposal for Modeling the Flash Vessel

The idea of combining simple cubic equations of state with excess Gibbs free energy (g^E) models, to describe the intermolecular interactions derived from the behavior of the liquid and vapor phases, is well-known. Since Huron and Vidal [9] published their mixing rule for the attractive parameter "*a*" of a cubic equation of state (EoS), numerous publications have appeared, with more or less similar approaches [10].

The PSRK model was first proposed by Holderbaum and Gmehling [4] and considers the Soave–Redlich–Kwong equation of state [11] and the UNIFAC model for the excess free energy and the activity coefficient in the mixing rules, as shown below:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)} \tag{1}$$

$$a_i = 0.42748\frac{R^2 Tc_i^2}{Pc_i}\alpha(T) \tag{2}$$

$$b_i = 0.08664\frac{RTc_i}{Pc_i} \tag{3}$$

For polar components, the expression proposed by Mathias and Copeman [12] is used to evaluate $\alpha(T)$ in the PSRK equation:

$$\alpha(T) = \left[1 + c_1\left(1 - T_\mathrm{r}^{0.5}\right) + c_2\left(1 - T_\mathrm{r}^{0.5}\right)^2 + c_3\left(1 - T_\mathrm{r}^{0.5}\right)^3\right]^2 \quad for \quad T_\mathrm{r} < 1 \tag{4a}$$

$$\alpha(T) = \left[1 + c_1\left(1 - T_\mathrm{r}^{0.5}\right)\right]^2 \quad for \quad T_\mathrm{r} > 1 \tag{4b}$$

In these equations, T_r is the reduced temperature and T_c is the critical temperature, whereas c_1, c_2, and c_3 are empirical parameters.

Table 1 UNIFAC functional groups and molecular parameters *r* and *q*.

Components	Subgroup Contribution		*R*	*q*
Acetic acid	CH3	1	2.2024	2.0720
	COOH	1		
Acetaldehyde	CH3	1	1.8991	1.7960
	CHO	1		
Furfural	Furfural	1	3.1680	2.4810
Methanol	CH3OH	1	1.4311	1.4320
1–pentanol	CH3	1	4.5987	4.2080
	CH2	4		
	OH	1		
Ethanol	CH3	1	2.5755	2.5880
	CH2	1		
	OH	1		
Water	H2O	1	0.9200	1.4000
1–propanol	CH3	1	3.2499	3.1280
	CH2	2		
	OH	1		

Table 2 Properties for all substances involved in this study.

Components	M	T_b/K	T_c/K	P_c/MPa	V_c/m^3 kmol^{-1}	ω	Z_c
Acetic acid	60.1	391.05	591.95	5.786	0.180	0.46652	0.211
Ethanol	46.1	351.44	514.0	6.137	0.168	0.64356	0.241
Methanol	32.0	337.85	512.5	8.084	0.117	0.56583	0.222
1-pentanol	88.2	410.95	588.1	3.897	0.326	0.57314	0.260
Acetaldehyde	44.1	294.00	466.0	5.55	0.154	0.29073	0.221
Furfural	96.1	434.85	670.15	5.66	0.252	0.36778	0.256
Water	18.0	373.15	647.13	22.055	0.056	0.34486	0.229
1-pentanol	88.15	410.95	588.10	3.897	0.326	0.57314	0.260
1-propanol	60.10	370.35	536.8	5.169	0.218	0.62043	0.252

The mixing rules, which arise from combining the equation of state and a model for the excess Gibbs free energy [9, 13] are:

$$a = b\left[\frac{g^E}{A_1} + \sum x_1 \frac{a_i}{b_i} + \frac{RT}{A_1}\sum x_i \ln\frac{b}{b_i}\right] \tag{5}$$

where A_1 is a constant equal to −0.64663. Equation 5 is used together with the UNIFAC model for g^E [14] and the classical mixing and combination rule for the volume parameter b is assumed:

$$b = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_{ij} \quad b_{ij} = \frac{b_i + b_j}{2} \tag{6}$$

In these equations, a_i and b_i are the pure component constants in the equation of state as defined by Eqs. 2 and 3. A survey about the current status and potential of the PSRK equation of state has been recently presented by Horstmann et al. [15]. Different fields of

Table 3 Ranges of temperature, liquid-phase mole fraction, and vapor-phase mole fraction.

Systems	Temperature Range ΔT (K)	Liquid-Phase Fraction Δx_1	Vapor-Phase Fraction Δy_1
Ethanol (2)+			
Acetic acid	351–386	0.076–0.945	0.010–0.893
Acetaldehyde	315–339	0.100–0.450	0.495–0.959
Furfural	352–407	0.0201–0.9800	0.0048–0.35
Methanol	339–351	0.012–0.91	0.026–0.95
1-pentanol	353–406	0.083–0.985	0.012–0.875
Water	351–363	0.05–0.95	0.0526–0.6628
Ethanol (2) + water (3)			
1-pentanol	354–360	0.07–0.092	0.009–0.043
1-propanol	359–360	0.005–0.500	0.0263–0.350
Furfural	360–361	0.005–0.509	0.008–0.054

application are discussed by the authors, but applications to mixtures such as those discussed in this paper were not included. Details on how to calculate the different contributions and molecular parameters in the UNIFAC model are given in Table 1.

Modified PSRK Model

The PSRK model includes two molecular parameters, a volume parameter, *r*, and a surface area parameter, *q*. In this work, these molecular parameters are modified for ethanol, assuming them to be adjustable parameters. The VLE data for the binary systems acetic acid + ethanol, acetaldehyde + ethanol, furfural + ethanol, methanol + ethanol, and 1-pentanol + ethanol were used to obtain optimum values of *r* and *q*. This empirical approach tries to explain the modification of the molecular physical structure of ethanol mixed with some congener. An analogous empirical approach was applied for temperature-dependent variables in UNIFAC-Dortmund [16]. Then the method was validated with the binary system ethanol + water and three ternary systems, 1-pentanol + ethanol + water, 1-propanol + ethanol + water, and furfural + ethanol + water.

Table 2 shows the pure component properties of all the substances involved in this study. Here, M is the molecular weight, T_c is the critical temperature, T_b is the normal boiling temperature, P_c is the critical pressure, V_c is the critical volume, and ω is the acentric factor. Data were obtained from Diadem Public [17].

Table 3 gives some details on the experimental data used in the study. The simpler mixtures of VLE data were taken from Gmehling et al. [18].

Results and Discussion

Table 4 shows the average absolute deviations for the temperature, $\%|\Delta T|$, and for the vapor-phase concentration, $\%|\Delta y_i|$, comparing predicted and experimental values for all studied systems. These deviations are defined as follows:

$$\%|\Delta y_i| = \frac{100}{N}\sum\frac{|y_{\mathrm{cal}} - y_{\mathrm{exp}}|}{y_{\mathrm{exp}}} \quad \%|\Delta T| = \frac{100}{N}\sum\left[\frac{T_{\mathrm{cal}} - T_{\mathrm{exp}}}{T_{\mathrm{exp}}}\right] \tag{7}$$

The VLE data were analyzed using the PSRK model considering the molecular parameters *r* and *q* as adjustable parameters. To evaluate these parameters, a Genetic Algorithm optimization procedure, implemented and fully explained in Alvarez et al. [19]

Table 4 Percent deviations for the temperature and congener vapor-phase mole fraction used for the correlation developed in Equations 9 and 10.

Ethanol (2)+	Original. $r = 2.5755$, $q = 2.5880$		Optimized				Correlation	
	$\%\lvert\Delta T\rvert$	$\%\lvert\Delta y_1\rvert$	r	q	$\%\lvert\Delta T\rvert$	$\%\lvert\Delta y_1\rvert$	$\%\lvert\Delta T\rvert$	$\%\lvert\Delta y_1\rvert$
Acetic acid	0.3	24.4	2.8591	2.6304	0.2	22.8	0.2	22.7
Acetaldehyde	0.7	4.4	2.7217	2.4872	0.4	4.8	0.4	4.7
Furfural	0.4	22.8	2.4014	2.5911	0.5	14.6	0.5	13.3
Methanol	0.2	6.7	2.7675	2.6299	0.2	5.9	0.2	6.1
1-pentanol	0.4	7.9	2.3088	2.5764	0.3	9.3	0.3	9.2

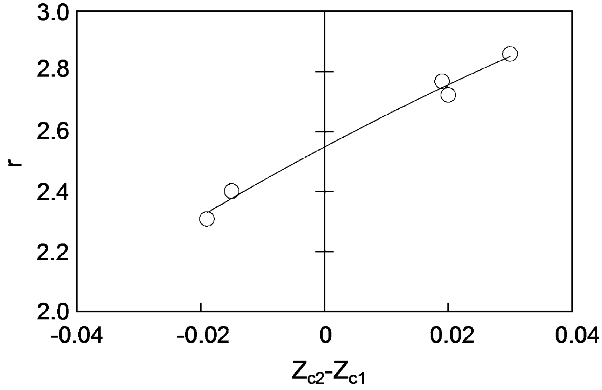

Fig. 2 Optimum molecular parameter *r* for the congener component in the PSRK model

was used. Thus, the optimization programs developed for this study used the objective function O_f:

$$O_f = \sum_{1}^{N} \left(y_1^{\exp} - y_1^{cal}\right)^2 \tag{8}$$

In this equation, N is the number of data points in the experimental data set and y_1 is the congener mole fraction in the vapor phase.

Results with the PSRK equation using original values for the molecular parameters *r* and *q* for ethanol in all mixtures congener (1) + ethanol (2) are shown in Table 4. As observed in this table, the PSRK model give good values for the boiling temperature, but reproduces the congener concentration in vapor phase with mean absolute deviations ranging from 4.4% to 24.4%.

The binary systems with acetic acid, acetaldehyde, furfural, methanol, and 1-pentanol congeners were used to obtain optimized molecular parameters for ethanol. The molecular parameters for ethanol, *r* and *q*, were optimized for each binary system resulting in different values for *r* and *q*, as shown in Table 4.

In the same way, the molecular *r* and *q* parameters for ethanol were optimized for each binary system, and so results in different values for these parameters.

The optimum parameters found for each of the five mixtures have been correlated with the critical compressibility factor (Z_c) for *r* and the acentric factor (ω) for *q*, as shown in

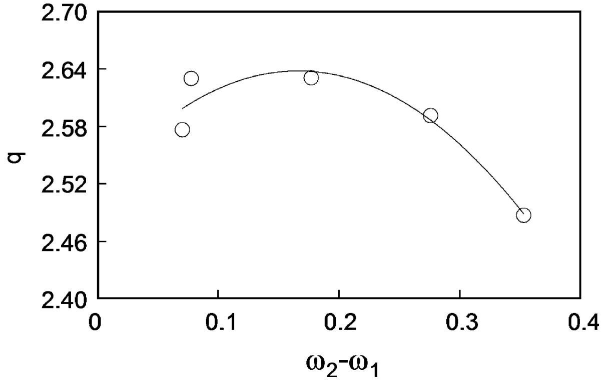

Fig. 3 Optimum molecular parameter *q* for the congener component in the PSRK model

Table 5 Percent deviations for the temperature and congener vapor phase mole fraction for a new binary system using original and modified PSRK model.

Ethanol (2)+	Original r=2.5755, q=2.5880			Correlation		
	$\%\|\Delta T\|$	$\%\|\Delta y_1\|$	$\%\|\Delta y_2\|$	$\%\|\Delta T\|$	$\%\|\Delta y_1\|$	$\%\|\Delta y_2\|$
Water	0.2	3.9	2.2	0.1	2.4	1.4

Figs. 2 and 3, respectively. These parameters have been fitted to quadratic functions as follows:

$$r = -30.325166(Z_{c2} - Z_{c1})^2 + 10.975229(Z_{c2} - Z_{c1}) + 2.548474 \tag{9}$$

$$q = -4.2758(\omega_2 - \omega_1)^2 + 1.4213(\omega_2 - \omega_1) + 2.5196 \tag{10}$$

In these equations, ω_2 and Zc_2 are the properties for the ethanol, and ω_1 and Zc_1 are the properties for each one of the congeners.

It can be noted that with the proposed modifications, the PSRK model becomes more empirical, but keeps the predictive capabilities of the model and, at the same time, improves its accuracy, which is demonstrated in Table 4. In addition, the model could be used for VLE in mixtures of interest for ethanol fuel.

In ternary systems, the structural parameters r and q of ethanol were calculated with the functions:

$$r = \omega_1 r_1 + \omega_2 r_2 \tag{11}$$

$$q = \omega_1 q_1 + \omega_2 q_2 \tag{12}$$

where r_i is the structural parameter r for ethanol with the congener i, and q_i is the structural parameter q for ethanol with the congener i. The experimental data for ternary systems were taken from Gmehling et al. [18].

Tables 5 and 6 showed the results of the percent deviations for the temperature and congener vapor phase mole fraction for binary and ternary systems. It can be seen that the results for the modified PSRK model are better than for the original model. In addition, different components were used as water and 1-propanol.

Table 6 Percent deviations for the temperature and congeners vapor-phase mole fraction for ternary system using original and modified PSRK model.

Ethanol (2) + water (3)	Original r=2.5755, q=2.5880				Equations 11 and 12			
	$\%\|\Delta T\|$	$\%\|\Delta y_1\|$	$\%\|\Delta y_2\|$	$\%\|\Delta y_3\|$	$\%\|\Delta T\|$	$\%\|\Delta y_1\|$	$\%\|\Delta y_2\|$	$\%\|\Delta y_3\|$
1-pentanol	0.3	34.7	4.9	10.2	0.9	28.7	4.4	8.2
1-propanol	0.1	19.2	4.0	3.0	0.4	19.9	3.5	2.6
1-furfural	0.5	42.1	7.4	13.8	1.8	43.4	4.3	7.3

Concluding Remarks

This work proposed the use of the Predictive Soave–Redlich–Kwong (PSRK) model to describe the phase equilibria in the flash distillation, using modified molecular parameters r and q for ethanol. In this way, the PSRK equation of state becomes more empirical, but keeps the predictive capabilities of the model. Furthermore, the introduction of new molecular parameters r and q in the UNIFAC model gives more accurate predictions for the concentration of the congener in the gas phase for binary and ternary systems.

The development presented in this work is important to be able to better understand the behavior of the flash distillation, which is a component of the extractive fermentation process. This allows the investigation of suitable operating strategies to achieve high operational performance.

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