LIQUID-VAPOR EQUILIBRIUM THERMODYNAMICS OF THE FUSEL OIL: A CASE STUDY

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ABSTRACT

Fusel oil is a by-product of the process of recovering hydrated ethanol, consisting of a mixture of superior alcohols, ethanol, water, among other components. Its commercial interest is mainly due to the presence of isoamyl alcohol, one of the raw materials used in the synthesis of esters, which compounds are relevant for the chemical industry. The recovery of this superior alcohol involves unit operations based on phase equilibrium, which for multicomponent systems can be studied in software that simulates the operation of equipment, in order to present predictions of interactions between its components, reducing errors, time and costs of design. In the industrial, academic and scientific fields, there are numerous challenges regarding the design of separation processes and the monitoring of mixing effects in typical operations, and the Aspen Plus process simulation and optimization platform excels in solving these issues. The current study aims to predict the Liquid-Vapor Equilibrium of the fusel oil, which was considered as a mixture of five components, from the behavioral analysis of each of the binaries that compose it. Several models were investigated, observing the deviations of the ideality as well as the azeotrope formation. The most suitable model to describe the behavior of the studied mixture was determined with the aid of literature data for the Liquid-Vapor Equilibrium of the Isoamyl alcohol/Water binary. The results show that the Wilson modeling presented better adjustment to the experimental data, although modeling with modified Wilson also showed appreciable adjustments.

KEYWORDS: Aspen Plus, Isoamyl alcohol, Wilson modeling.

TERMODINÂMICA DO EQUILÍBRIO LÍQUIDO-VAPOR DO ÓLEO FÚSEL: UM ESTUDO DE CASO

RESUMO

O óleo fúsel é um subproduto do processo de recuperação de etanol hidratado, constituído por uma mistura de alcoóis superiores, etanol, água, dentre outros componentes. Seu interesse comercial se deve principalmente à presença do álcool isoamílico, uma das matérias-primas utilizadas na síntese de ésteres, compostos estes relevantes para a indústria química. A recuperação deste álcool superior envolve operações unitárias baseadas no equilíbrio de fases, que para sistemas multicomponentes pode ser estudada em *softwares* que simulam o funcionamento de equipamentos, de forma a apresentar previsões das interações entre os seus componentes, reduzindo erros, tempo e custos de projeto. No âmbito industrial, acadêmico e cientifico, existem inúmeros desafios acerca do dimensionamento de processos de separação e acompanhamento dos efeitos de mistura em operações típicas, e a plataforma de simulação e otimização de processos *Aspen Plus* se destaca na solução destas questões. O presente trabalho tem como objetivo prever o equilíbrio Líquido-Vapor do óleo fúsel, que foi considerado como uma mistura de cinco componentes, a partir da análise comportamental de cada um dos binários que o compõe. Foram investigadas modelagens diversas, observando os desvios da idealidade e também quanto à formação de azeótropos. O modelo mais adequado para descrever o comportamento da mistura estudada foi determinado com o auxílio dos dados experimentais da literatura para o equilíbrio Líquido-Vapor do binário Álcool Isoamílico/Água. Os resultados apontam que a modelagem Wilson apresentou melhor ajuste aos dados experimentais, embora as modelagens com Wilson modificado também apresentassem ajustes apreciáveis.

PALAVRAS-CHAVE: Álcool isoamílico, Aspen Plus, Modelagem de Wilson.

INTRODUCTION

The worldwide concern to seek clean and renewable sources of energy has boosted Brazil, the world's largest sugarcane producer, by making continuous efforts in its sugar and alcohol industry, with a purpose to become it sustainable and to promote ethanol from sugar cane as an imminent substitute for fossil fuels. The Brazilian production of this bio-fuel is considered as a world reference due to its superior productivity rates and its cogeneration system; as a result the country consolidates as one of the leaders in this market, and maintains its commitment to reduce the gases that cause the greenhouse effect (BATISTA et al., 2011; PEDROZA et al., 2015; IPEA, 2016; BENITES-LAZARO et al., 2017; CONAB, 2018). Besides, the advances in the sugar and alcohol industry interfere directly in the national economy, with job creation and the valuation GDP (Gross Domestic Product) (BRINKMAN et al., 2018).

In the Brazilian production of ethanol, the sugary solution extracted from sugar cane is fermented to obtain a wine that consists of a hydro alcoholic mixture. It is possible to notice the distillation of this mixture in a large part of the chemical industries in order to recover hydrated ethanol (composed of up to 7.5% of water by mass), used as bio-fuel for flex fuel cars. Anhydrous ethanol (composed of up to 0.7% water by mass) used as a supplement to gasoline (in the proportion of 27%) is recovered in the dehydration units. The use of ethanol can also be seen in the

productive chains of pharmaceuticals, cosmetics, paints, varnishes, solvents, beverages, among others (BATISTA et al., 2012; DIAS et al., 2015; IPEA, 2016; CONAB, 2018; COPERSUCAR, 2018; EUSTÁCIO et al., 2018).

During the total obtaining of this bio-fuel some by-products are generated, among them the fusel oil, which deserves special attention, since its presence in the mixture is associated to the deterioration of the bio-fuel quality and consequent reduction of the distillation process yield. In addition, direct disposal of fusel oil into the environment is not recommended in view of this action may cause undesirable environmental impacts. Therefore, one of the concerns of the sugar-alcohol industry is to seek sustainable ways to use this by-product, which has already proved to be a potential fuel, because its calorific value is similar to that presented by other alternative fuels (FERREIRA et al., 2013; CALAM et al., 2014; EUSTÁCIO et al., 2018).

According to Ferreira et al. (2013) the Brazilian production of fusel oil is approximately 2.5 liters for every 1000 liters of ethanol produced. On this scale, and with the forecast made in 2018 by the Companhia Nacional de Abastecimento (CONAB) for a record production of 32.3 billion liters of total ethanol in the 2018/2019 harvest, the production of fusel oil can reach a value of 80,75 million liters in this same period. This byproduct sugar cane processing consists of an ethanol, water, and superior alcohols (such as propanol, isobutanol and isoamyl alcohol) mixture. The latter being its main component, and also responsible for its great commercial appeal. This superior alcohol has a market value of approximately three times the value of fuel ethanol, and its main destination is the production of esters to be used as flavoring agents, industrial solvents and plasticizers (BATISTA; MEIRELLES, 2011; FERREIRA et al., 2013; CALAM et al., 2014; DIAS et al., 2015; MAYER et al., 2015; PEDROZA et al., 2015).

Isoamyl alcohol, such as ethanol, can be recovered by distillation. Although the amount of energy required by this kind of operation is high, this is the most common one of separation in the chemical industry. In this operation, which is based on the volatility differences, there is the intimate contact between the liquid phase and the vapor phase, which seek to be in equilibrium, in order to promote the increase of the interfacial mass transfer and the recovery of the more volatile component in the vapor, and the least volatile in the liquid. In this way, knowledge about the thermodynamics of the Vapor Liquid Equilibrium is needed to understand the mixing effects to Project and to lead satisfactorily the recovery processes from interest compounds (MCCABE et al., 2000; MAYER et al., 2015).

The use of unitary operations in distillation equipment, just like the use of Vapor-Liquid separation flash drum, is a form that chemical engineers use to study equilibrium. This kind of equipment consists of a single Liquid-Vapor Equilibrium stage, and is widely used for petroleum fractionation. Because of the limitations found in flash drum associated with thermodynamics, its use focuses on pre-processing and pre-separation of mixtures before they are led by more strict operations (MCCABE et al., 2000; SMITH et al., 2011).

In the flash drum, the liquid feed has its pressure reduced to below the bubble point, and is partially evaporated to become two phases, liquid and vapor, in equilibrium. The study of this equilibrium determines the quantities recovered from each component in each phase. The equality of the fugacities of the saturated phases (Equation (1)), at the same temperature, helps in the calculations of the

Liquid Vapor balance of each component (*i*) (POLING et al., 2000; SMITH et al., 2011):

$$\hat{f}_i^L = \hat{f}_i^V \quad (1)$$

Where: *f* corresponds to fugacity; *L* corresponds to the liquid; *V* corresponds to the vapor.

However, the relation described by Equation (1) must be expanded by means of the fugacity coefficients ($\hat{\Phi}_i$) and activity coefficients (γ_i). As the present study attempts to understand the mixing effects by quantifying the non-idealities in the liquid and vapor phase, at low and modeled pressure, the approach to be followed is *gamma-phi*, Equations (2) and (3), respectively (SMITH et al., 2011).

$$\gamma_i = \frac{\hat{f}_i^L}{x_i f_i} \quad (2)$$

$$\hat{\Phi}_i = \frac{\hat{f}_i^V}{y_i P} \quad (3)$$

Where: y_i e x_i correspond, respectively, to the molar fraction of component (*i*) in the vapor; and in the liquid; *P* corresponds to the total pressure of the system; f_i corresponds to the fugacity of the pure liquid (*i*) under the system temperature and pressure conditions, which is represented by Equation (4) (SMITH et al., 2011).

$$f_i = \Phi_i^{sat} P_i^{sat} \exp\left(\frac{1}{RT}\int_{P_i^{sat}}^{P} V_i dP\right) \quad (4)$$

Where: Φ_i^{sat}correspond of the fugacity coefficient of the pure component (*i*) in the saturation; P_i^{sat}corresponds to the vapor or saturation pressure.

With the substitution of Equations (2), (3) and (4) in Equation (1), it results in:

$$y_i P = \gamma_i x_i P_i^{sat} \frac{\Phi_i^{sat}}{\hat{\Phi}_i} exp\left(\frac{1}{RT}\int_{P_i^{sat}}^{P} V_i dP\right) \quad (5)$$

The exponential term that appears in Equation (5) and (4) corresponds to the correction factor of Poynting and represents the effects of the pressure in the fugacity of the liquid phase. For situations where the pressure is adopted as low or moderate, the liquid is taken as incompressible, so the Poynting factor and the term Φ_i^{sat}can be considered as equal to the unit value (SMITH et al., 2011). So, Equation (5) becomes:

$$y_i \hat{\Phi}_i P = \gamma_i x_i P_i^{sat} \quad (6)$$

Equation (6) consists of the modified Raoult's Law (in the *gamma-phi* approach) which considers the non-idealities in the liquid phase (γ_i), and in the vapor phase ($\hat{\Phi}_i$), being the Equation (6) adopted by the literature as a typical modeling for distillation of the sugar and alcohol industry (BATISTA; MEIRELLES, 2011; EUSTÁCIO et al., 2018; MATUGI et al., 2018).

When it comes to an ideal situation, there are no deviations for the activity coefficient (γ_i), nor for the fugacity coefficient ($\hat{\Phi}_i$), and both correspond to the unit value. In this way, the vapor phase is treated as an ideal gas, and the liquid phase, as an ideal solution (POLING et al., 2000; SMITH et al., 2011). With this, it is obtained Equation (7) for Raoult's Law:

$$y_i P = x_i P_i^{sat} \quad (7)$$

However, for real situations that have deviations for both vapor and liquid phase, some corrections are required. For the vapor phase, the fugacity coefficient

($\widehat{\phi}_i$) can be obtained by means of PVT equations to adequately describe the situation to be modeled. These equations can be Virial, Soave-Redlich-Kwong, among others (POLING et al., 2000; BATISTA; MEIRELLES, 2011; SMITH et al., 2011; FERREIRA et al., 2013; EUSTÁCIO et al., 2018; MATUGI et al., 2018). For the liquid phase, the activity coefficient (γ_i) depends on all the components of the mixture in question and can be calculated by the excess Gibbs energy (SMITH et al., 2011).

Equation (8) consists of a form of representing this greatness:

$$\frac{G^E}{RT} = \sum_i x_i ln\gamma_i \quad (8)$$

In this kind of equation models are used to obtain the necessary parameters. These models may be locally composed (for example NRTL, UNIQUAC and WILSON) or from group contributions (for example UNIFAC) (POLING et al., 2000; BATISTA; MEIRELLES, 2011; SMITH et al., 2011; FERREIRA et al., 2013; EUSTÁCIO et al., 2018; MATUGI et al., 2018).

In order to reduce costs, errors and calculation times, it is increasingly important to use industrial process simulators to analyze how operating conditions interfere with performance, for example, distillation operations. In the Chemical Engineering field, Aspen Plus is widely used software for the development, planning, simulation and optimization of a series of steady state processes. This software, by means of mass and energy balance equations, associated with the phase equilibrium data obtained by thermodynamic models, predict precisely under specific conditions the behavior of real systems of several processes in the industry (AHMED et al., 2015; COUTO et al., 2015; HAN et al., 2017).

The aim of the current study consists of analyzing the best model to predict the Liquid-Vapor Equilibrium of the fusel oil. In this way, to provide reliable results that will base future projects of recovery processes of isoamyl alcohol, from this industrial by-product.

MATERIAL AND MÉTHODS

Mixture determination

Although the composition of the fusel oil depends on factors such as the raw material used for its production, and the conditions of the fermentation medium (CALAM et al., 2014; AWAD, et al., 2018; EUSTÁCIO et al., 2018), the system was modeled according to the compatibility between mixtures of the literature that summarize actual compositions processed by the Brazilian sugar and alcohol sector. In this way, the fusel oil was considered as a mixture of ethanol, water, propanol, isobutanol and isoamyl alcohol (BATISTA; MEIRELLES, 2011; FERREIRA et al., 2013; CALAM et al., 2014; MAYER et al., 2015). The assertions of the aforementioned authors and of Pedroza et al. (2015) were the basis for the determination of the fractions of each of these components (Table 1).

TABLE1 – Oil Composition Studied (Adapted from PEDROZA et al., 2015)

Compounds	Composition (molar fraction)
Water	0.14300
Ethanol	0.12580
Isoamyl Alcohol	0.70470

Isobutanol	0.01325
Propanol	0.01325

Environment for the study accomplishment

The computational platform Aspen Plus served as an environment for the study of the Liquid-Vapor Equilibrium of the fusel oil, through the simulation of pre-separation operations, in an adiabatic flash drum from the type V- DRUM1, which received as feed stream mixture described in Table 1, at a flow rate of 100kmol/h, at a pressure of 1.01325 bar and at 25°C of temperature.

Adopted models for the Equilibrium Liquid-Vapor

Due to the formation of two phases in a saturated state, distillation operations depend on the characteristics of the mixture. Thus, phase equilibrium analysis is crucial to provide reliable projects development of interest product recovery (MCCABE et al., 2000; SMITH et al., 2011; FERREIRA et al., 2013). In this way, the mixture behavior was investigated in several thermodynamic models of Raoult's Law correction, based on the *gamma-phi* approach. These models, listed in Table 2, were selected according to the *Aspen User Guide* (ASPEN TECHNOLOGY, 2000) and Poling et al. (2000), and with the adopted models for alcoholic systems by Sanz and Gmehling (2008), Batista and Meirelles (2011), Smith et al. (2011), Batista et al. (2012), Ferreira et al. (2013), Eustácio et al. (2018), Matugi et al. (2018), Machado et al. (2019).

TABLE 2 – Analyzed Thermodynamic Models (Adapted from *ASPEN TECHNOLOGY*, 2000)

Analyzed Models	Activity Coefficient (γ_i)	Fugacity Coefficient ($\widehat{\Phi}_i$)
NRTL-HOC	NRTL	Hayden-O'Connel
UNIF-DMD	Dortmund-Modified UNIFAC	Redlich-Kwong Soave
WILSON	WILSON	Ideal gas
WILSON-RK	WILSON	Readlich Kwong
WILSON-HOC	WILSON	Hayden-O'Connel
WILSON-NTH	WILSON	Nothnagel
UNIQUAC	UNIQUAC	Ideal gas

Considering that the fusel oil is a multicomponent system, this behavioral analysis was made considering each of the binaries that constitute it, since the literature only describes experimental data of equilibrium for binary (or ternary) systems.

The Liquid-Vapor Equilibrium data generated by Aspen Plus were transferred to Excel, where they were transformed into answers profiles that were evaluated in relation to the azeotrope formation and deviations from ideality.

Determination of the most appropriated model

The answer profiles for the 3-Methyl-1-Butanol/Water binary in the studied models were compared with the experimental data of Cho et al. (1984), for the same binary, and in the same pressure condition. Thus, the model that best fit the experimental data was chosen as being the most appropriate to describe the behavior of the studied multicomponent system.

RESULTS AND DISCUSSION

Type of studied graph

The graphs generated for the study of the Liquid-Vapor Equilibrium were of type T-xy, with constant pressure, because this is a situation of practical interest. It is more plausible to conduct a distillation process at constant pressure than the constant temperature (SMITH et al., 2011).

Binaries that approximate to ideality

Figures 1, 2, 3, 4 and 5 show the binaries with equilibrium profiles that are closest to the ideal behavior. For each of them, the several analyzed models are practically confused with one another and even with the ideal situation. In addition, the pairs: Figure 1 (1-Propanol/Ethanol) - Figure 3 (3-Methyl-1-Butanol/Isobutanol) and Figure 4 (3-Methyl-1-Butanol/Propanol) - Figure 5 (Isobutanol/Ethanol) present similarities to the shapes of phase envelopes.

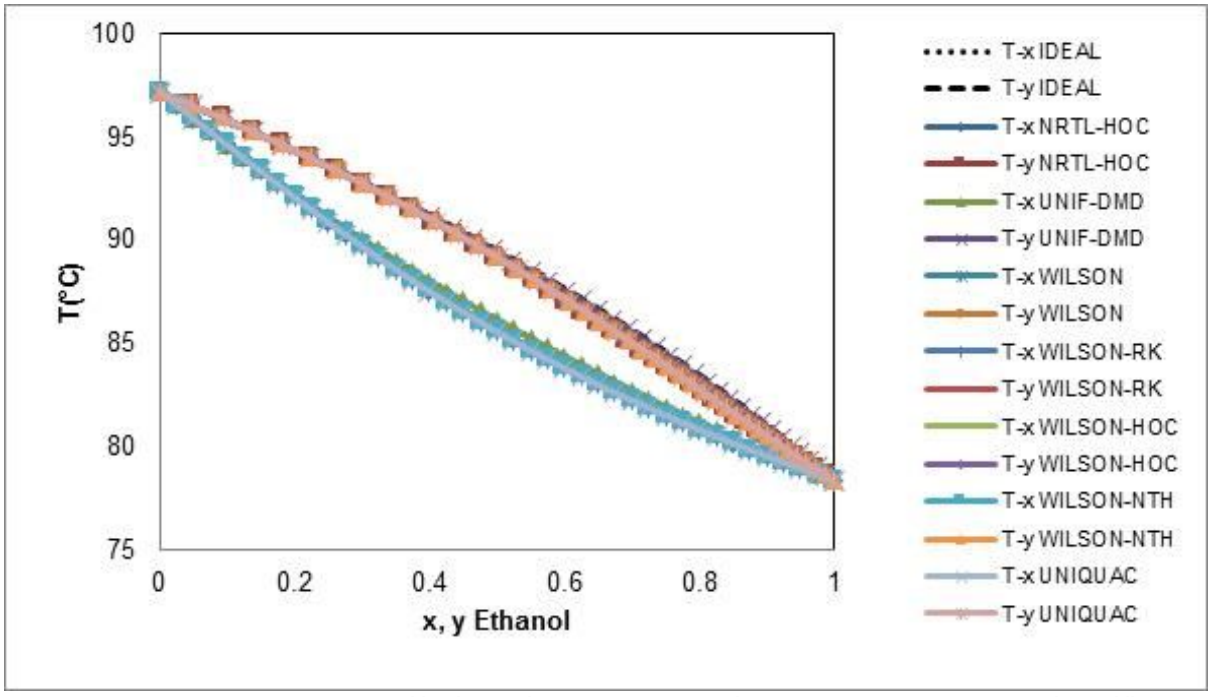

FIGURE 1 – T-xy 1-Propanol/Ethanol, P = 1.01325 bar, T = 25°C, F = 100kmol/h.

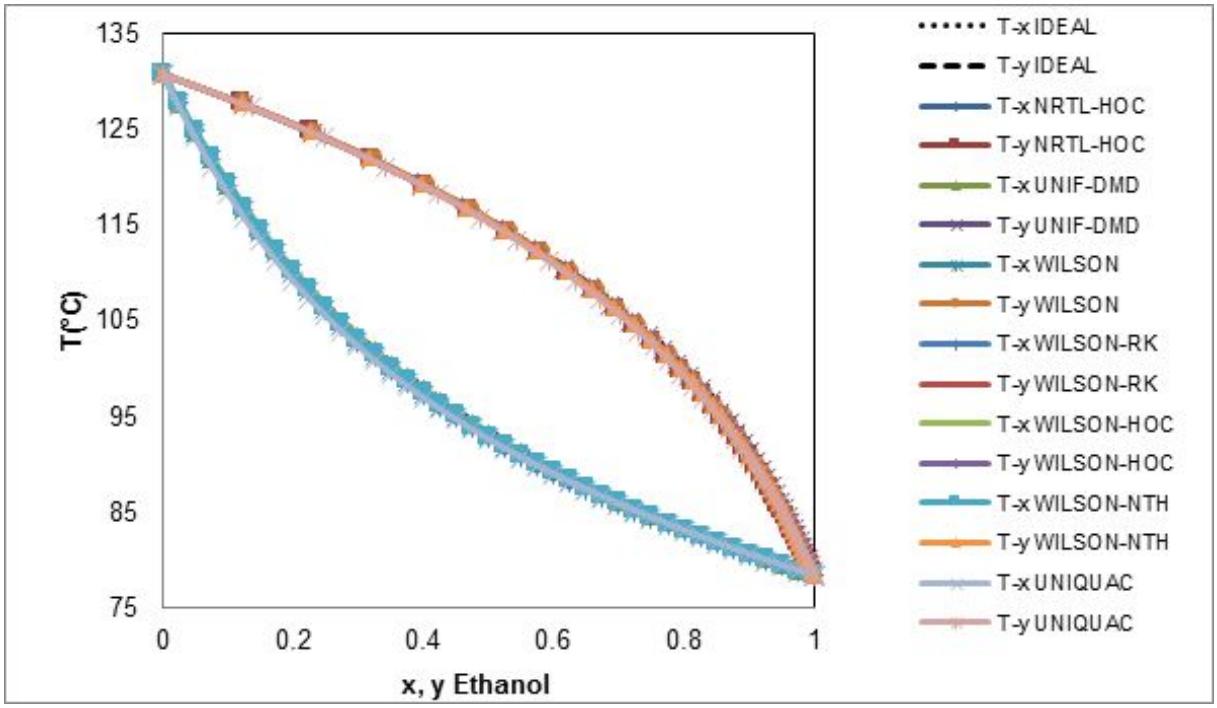

FIGURE 2 – T-xy 3-Methyl-1-Butanol/Ethanol, P = 1.01325 bar, T = 25°C, F = 100kmol/h.

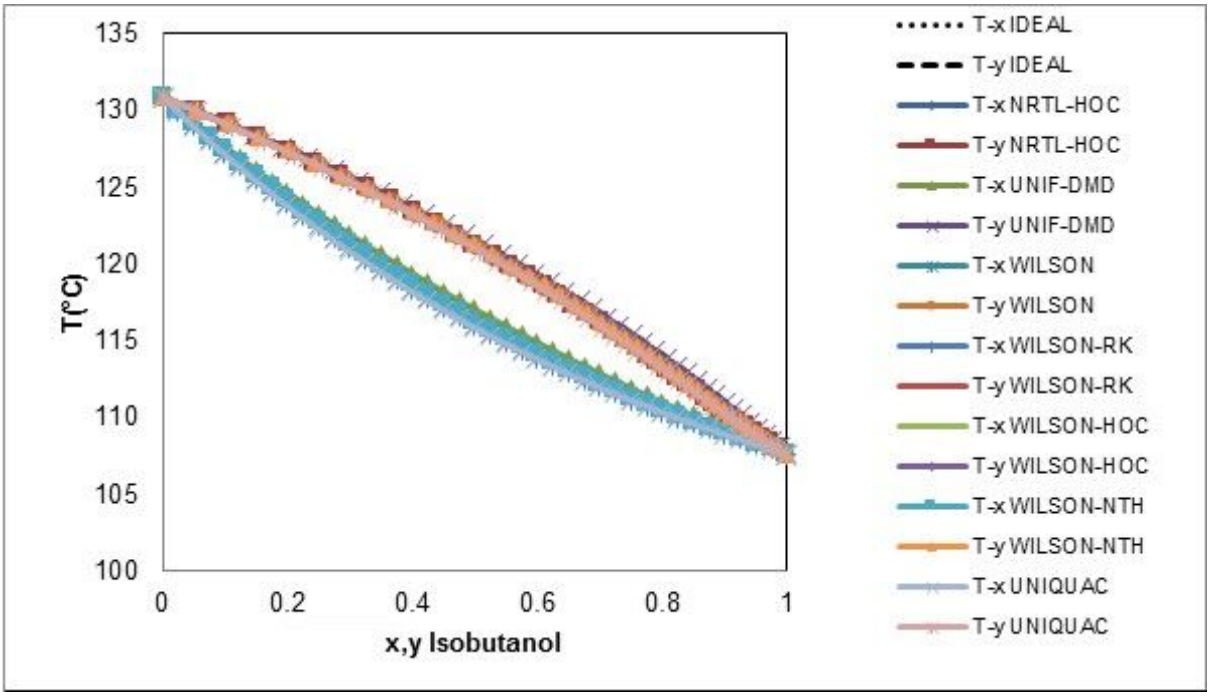

FIGURE 3 – T-xy 3-Methyl-1-Butanol/Isobutanol, P = 1.01325 bar, T = 25°C, F = 100kmol/h.

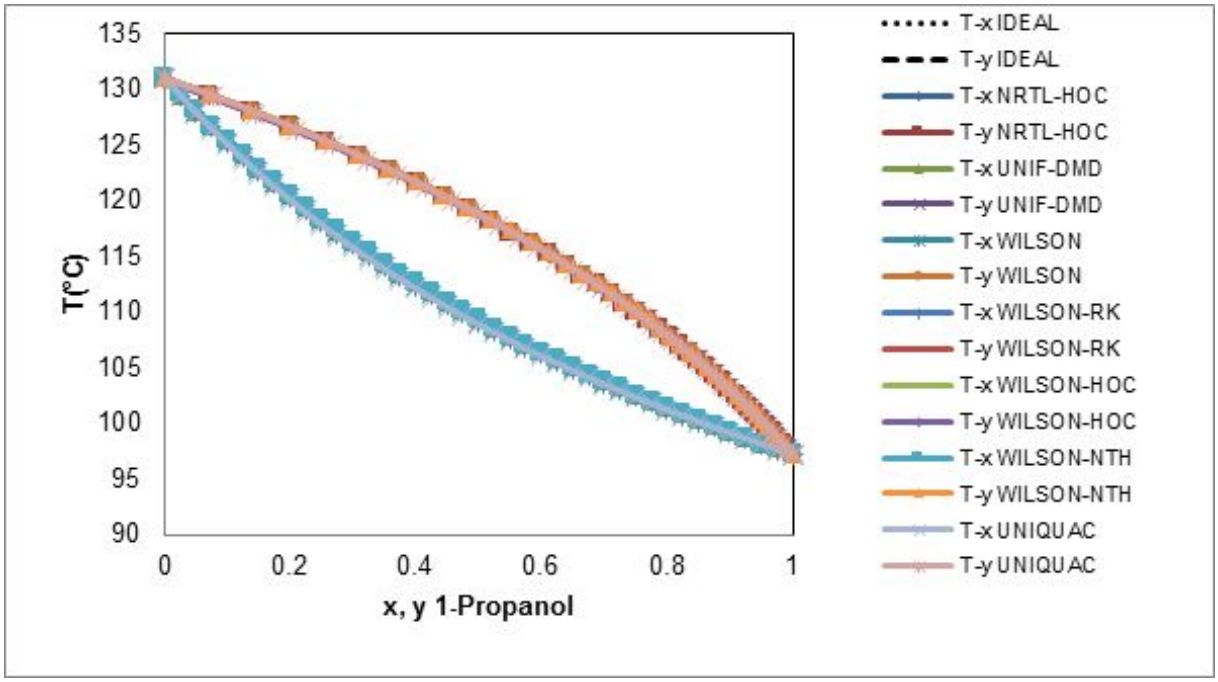

FIGURE 4 – T-xy 3-Methyl-1-Butanol/Propanol, P = 1.01325 bar, T = 25°C, F = 100kmol/h.

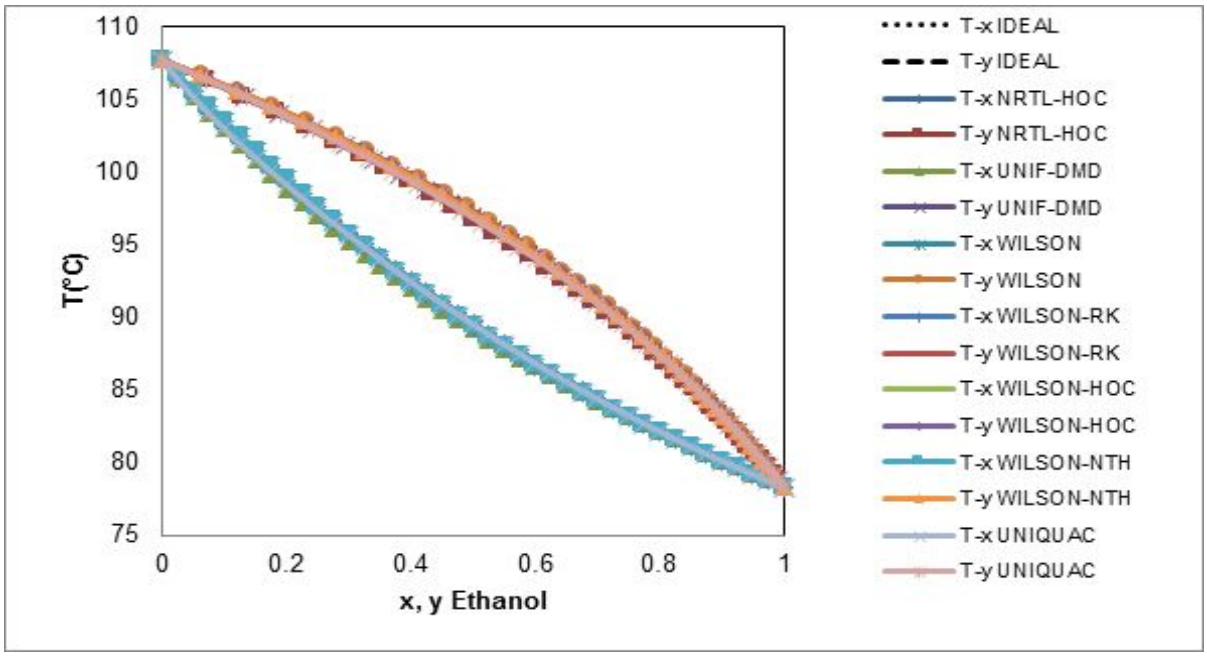

FIGURE 5 – T-xy Isobutanol/Ethanol, P = 1.01325 bar, T = 25°C, F = 100kmol/h.

According Pedroza et al. (2015) 98% (molar fraction) of the fusel oil composition consists of ethanol, water, and isoamyl alcohol. Mayer et al. (2015) claims this superior alcohol corresponds to approximately 60% (% w/w) of this blend. There are some studies in the literature that only consider these three components to characterize the fusel oil. In this way, Figure 2, which represents the 3-Methyl-1-Butanol/Ethanol binary, deserves special attention because this involves

two of the three major components of Brazilian fusel oil. In this binary (Figure 2) the least volatile and the most volatile component of the entire studied multicomponent system ($t_{n,Ethanol}$ = 78.3°C, $t_{n,3\text{-}Methyl\text{-}1\text{-}Butanol}$ = 130.9°C, data from Aspen Technology, 2000). Therefore, in distillation operations of the fusel oil there will be a greater recovery of the ethanol in the vapor phase and the isoamyl alcohol in the liquid phase. It is also possible to notice that the saturation temperatures at the pressure of 1.01325 bar (t_1^{sat} = 78.3°C; e t_2^{sat} = 130.9°C) are corresponding to the normal boiling temperatures, this being one of the principles for the construction of equilibrium diagrams T-xy (SMITH et al., 2011).

Binaries that form azeotrope

The binaries: 3-Methyl-1-Butanol/Water, Isobutanol/Water, Water/1-Propanol and Water/Ethanol present the formation of azeotrope, already expected behavior, due to the presence of water (FERREIRA et al., 2013). The temperature ranges (in °C) and composition ranges (in molar fraction) where this kind of behavior occurs, for each of the aforementioned binaries (Figures 6, 7, 8 and 9) are shown in Table 3.

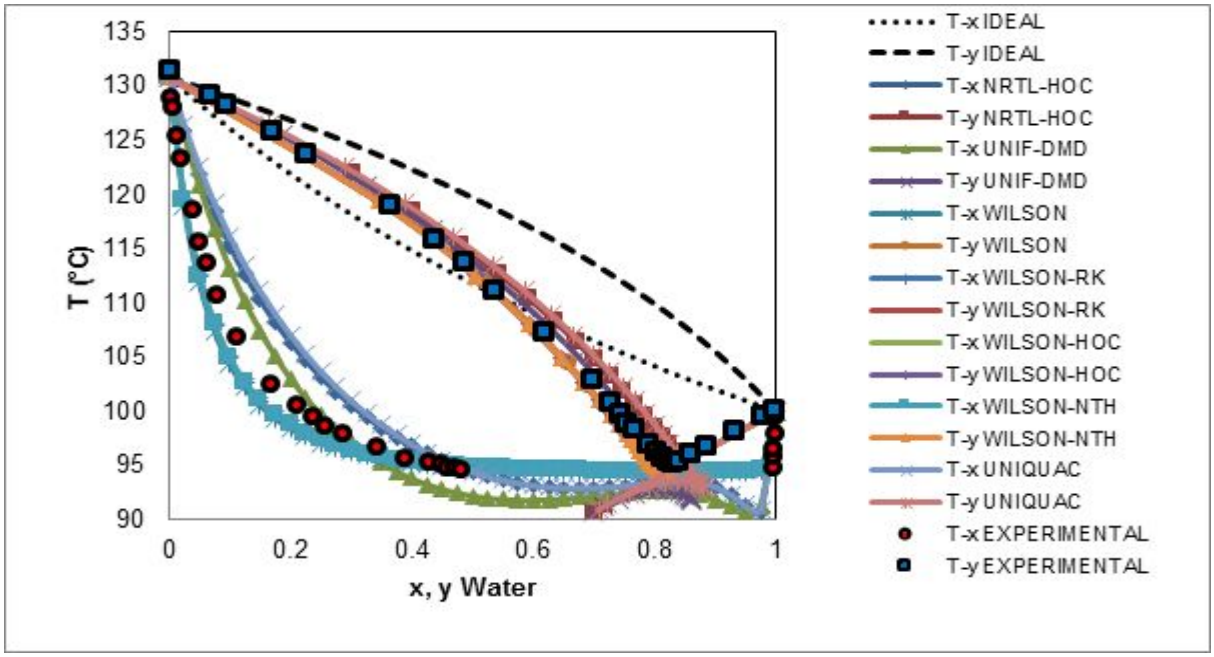

FIGURE 6 – T-xy 3-Methyl-1-Butanol/Water, P = 1.01325 bar, T = 25°C, F = 100kmol/h.

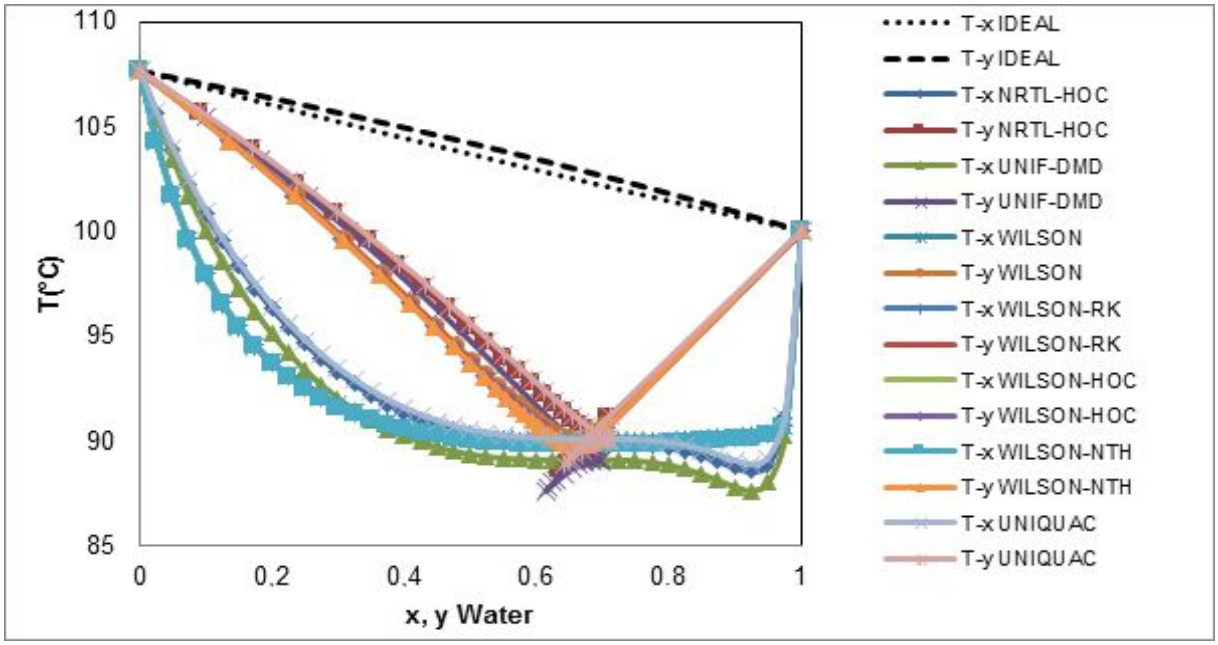

FIGURE 7 – T-xy Isobutanol/Water, P = 1.01325 bar, T = 25°C, F = 100kmol/h.

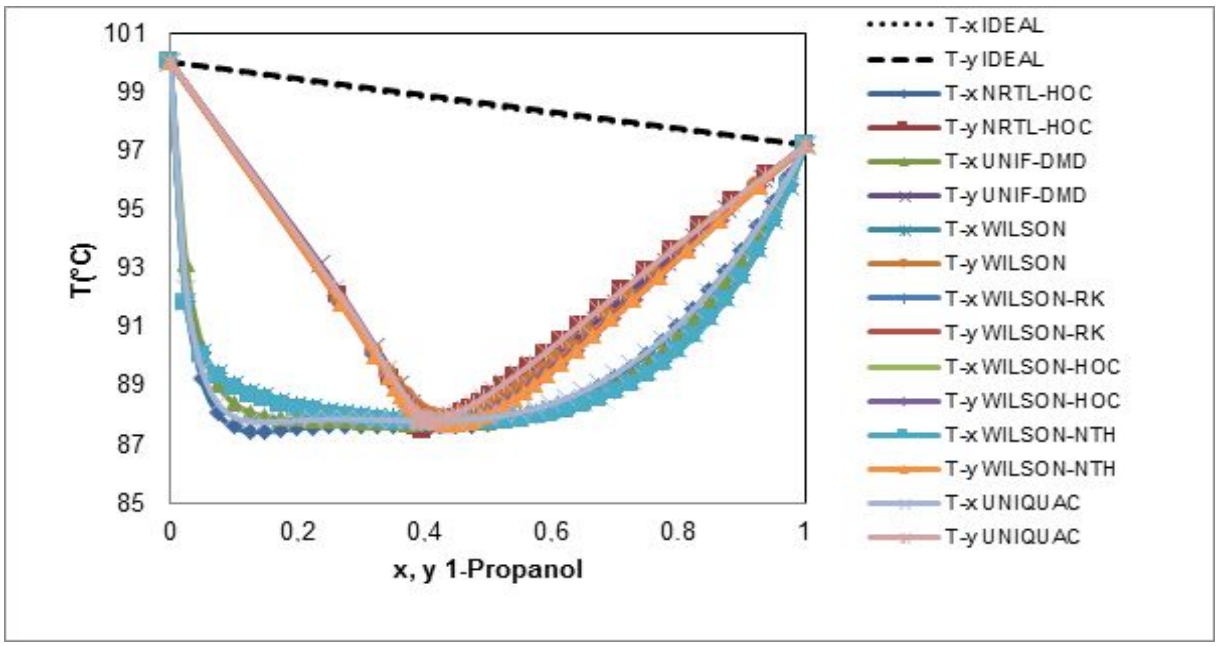

FIGURE 8 – T-xy Water/1-Propanol, P = 1.01325 bar, T = 25°C, F = 100kmol/h.

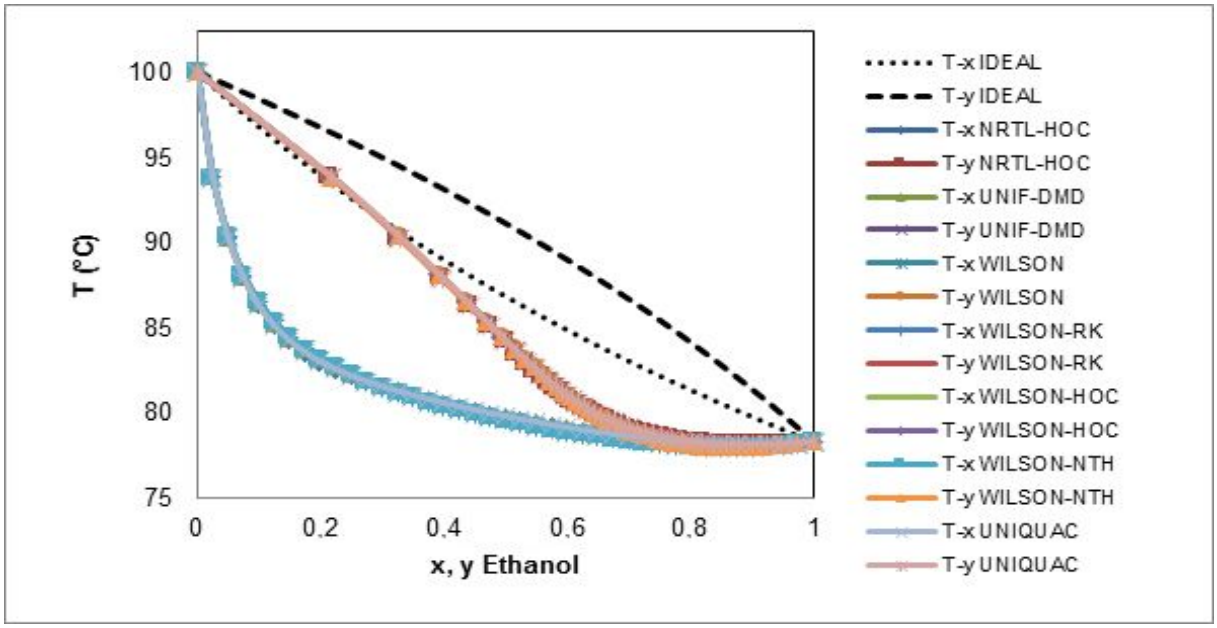

FIGURE 9 – T-xy Water/Ethanol, P = 1.01325 bar, T = 25°C, F = 100kmol/h.

TABELA 3 – Azeotrope Formation Ranges

Binary System	Molar Fraction	Temperature (°C)
3-Methyl-1-Butanol/Water	0.80 – 0.85	92.7 – 94.5
Isobutanol/Water	0.65 – 0.71	89.1 – 90.1
Water/1-Propanol	0.40 – 0.45	87.6 – 87.8
Water/Ethanol	0.89 – 0.93	77.9 – 78.2

Both the azeotrope formed for the 3-Methyl-1-Butanol/Water binary (Figure 6) as the azeotrope formed for the Isobutanol/Water binary (Figure 7) are constituted by two liquid phases and one vapor phase, due to the fact that the components involved present low miscibility at room temperature. This type of Vapor-Liquid-Liquid Equilibrium (VLLE) behavior is not provided for by the modified Raoult's Law, but the mixture effects re-establish the Liquid-Vapor Equilibrium (LVE) to the binaries.

The profiles represented by Figures 6 and 9 (together involve the three major components of the fusel oil) are the ones that represent, respectively, more and less discrepancies between the studied models. In a rough analysis of the Water/Ethanol binary (Figure 9), it can be considered that the analyzed models are confused with each other, and show the same deviations from the ideality. Therefore, the curves resulting from the predictive models of the Liquid-Vapor Equilibrium for the 3-Methyl-1-Butanol/Water binary (Figure 6) are the most suitable to be compared with experimental data, and to promote the definition of the model that best describes the fusel oil equilibrium.

The group contribution models are very useful for describing the thermodynamic parameters of liquid-vapor equilibrium systems such as fusel oil in a wide way. The UNIFAC model (group contribution model) is very common in the chemical industry to estimate equilibrium, as well as the NRTL model (local composition model) are complex equations that fit well with actual mixtures such as those processed by industry of ethanol. It is due to this that commonly the literature

uses the predictive models NRTL-HOC and UNIF-DMD for the modeling of fusel oil (POLING et al., 2000; SANZ; GMEHLING, 2008; FERREIRA et al., 2013; EUSTÁCIO et al., 2018; MATUGI et al., 2018; MACHADO et al., 2019).

According to Poling et al. (2000) in the binary mixtures modeling, which present moderated no-idealities, the utilization of any model to calculate the excess Gibbs energy guarantees satisfactory results. Thus, although according to the literature the UNIF-DMD and NRTL HOC models seem to be suitable for the fusel oil study, the choice of one model to the detriment of the others is due to the better representation of the experimental equilibrium values. In this case, it is possible to notice that the UNIF-DMD, NRTL-HOC and UNIQUAC models (being this a model of a great focus in the study of thermodynamics, according Machado et al. (2019)) are the most distant from the experimental data, while the WILSON model shows good adjustments for both Tx and Ty curves, which is the best predictive model Liquid-Vapor Equilibrium of the considered fusel oil. Its variations (WILSON-RK, WILSON-HOC and WILSON-NTH) also have appreciable adjustments and can predict the equilibrium of the mixture.

CONCLUSION

Although the NRTL-HOC, UNIF-DMD and UNIQUAC models show deviations from the experimental data, their presence in the literature is strong, and because of this, they can be used in the predictions of the interactions among mixtures components such as fusel oil, a fact evidenced by the identification of the azeotrope formation in the same region as the other studied models.

However, the WILSON model and its variations show themselves to be more indicated to predict the behavior of the studied multicomponent system. Among all the studied models, the WILSON model has been the one that has adjusted the most to the experimental data, is the one that has the simplest algebraic manipulation, therefore it is an equation of robust results of interest for thermodynamic studies, and practical application in the chemical industries field.

It is worth mentioning that, for a more detailed study, it is also necessary to analyze the Vapor-Liquid-Liquid Equilibrium for the 3 Methyl 1 Butanol/Water and Isobutanol/Water binaries.

The results obtained for the analysis of the mixing effects caused in the fusel oil system showed that the Aspen Plus commercial platform and the used methodology are feasible options for the monitoring of the Liquid-Vapor Equilibrium on an industrial scale.

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