Chemical Engineering & Processing: Process Intensification 163 (2021) 108329

Contents lists available at ScienceDirect

Chemical Engineering and Processing - Process Intensification

journal homepage: www.elsevier.com/locate/cep

Recovery of alcohol industry wastes: Revaluation of fusel oil through intensified processes

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ARTICLE INFO

Keywords:
Optimization
Fusel oil
Isoamyl alcohol
Dividing wall column
Energy savings

ABSTRACT

Fusel oil is a mixture obtained as a side cut during ethanol distillation, mainly composed of i-amyl alcohol, water, ethanol, isobutanol, and other alcohols. Currently, fusel separation into the constitutive alcohols is accomplished by batch or continuous distillation involving different columns in an energy-intensive process. Moreover, fusel oil presents a particular thermodynamic behavior projected in several azeotropes, making the purification of fusel oil a challenging process. In this work is proposed a novel distillation scheme to purify isoamyl alcohol from other fusel alcohols by using a dividing wall column scheme. In order to determine the benefits of using such intensified technology, a comparison with the conventional scheme was carried out. In order to accurately represent the thermodynamic equilibrium, data for phase equilibrium was needed to the correctly design of the purification process. Both, the traditional distillation scheme and the dividing wall column were modeled using Aspen Plus and optimized by using a hybrid stochastic algorithm. Results indicate that the dividing wall column is not only more efficient in term of energy intensity (2785 kJ/kg Amyl alcohol) against (3497 kJ/Kg Amyl alcohol) the conventional scheme, but also it offers large economic savings compared with the conventional scheme (27 % savings).

1. Introduction

Currently, agro-industrial waste is a valuable resource in the search for renewable sources of energy. Additionally, they can be used to produce a wide range of chemical building blocks. The latter products can later be transformed into high added-value compounds, with the potential to replace petroleum-derived compounds. A clear example is the obtaining of alcohols by fermentation.

Through the years, the industrial production of ethanol by fermentation has increased due to the rising global demand for biofuels. The current market size is approximately USD 33.7 billion, and it is expected to grow to USD 64.8 billion by 2025. Moreover, global production is continuously growing, for example, fuel ethanol grew by 191 % from 55,700 million liters produced in 2007 up to 162.000 million in 2015. The continuous interest in ethanol is due to its the high number of applications. Consequently, the generation of by-products and residues of this industry has increased at the same pace, becoming a major concern for its sustainability, see an example of the ethanol process in Fig. 1. The by-products obtained from agro-industrial biomass obtained after a manufacturing process can be revalued. This valorization process has become a major issue to improve sustainability in the production chain. The possibility of using by-products of agro-industrial waste treatment has created a wide margin for waste reduction, as well as the generation of direct income [1].

Among the different fuel ethanol by-products, fusel oil (also known as fusel alcohol or just fusel) stands out as an interesting source of higher added value chemicals. Fusel oil is a mixture obtained as a side cut during ethanol distillation, mainly composed of i-amyl alcohol, water, ethanol, *iso*butanol, and other alcohols (C3-C5) in an average composition of 41–87 % wt, 1–20 % wt, 1–15 % wt, 0–6 %wt, and 0–6% wt respectively [2,3]. All these alcohols are side products generated during ethanol biosynthesis, so the nature and quantity of fusel oil produced

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https://doi.org/10.1016/j.cep.2021.108329
Received 30 October 2020; Received in revised form 28 January 2021; Accepted 4 February 2021

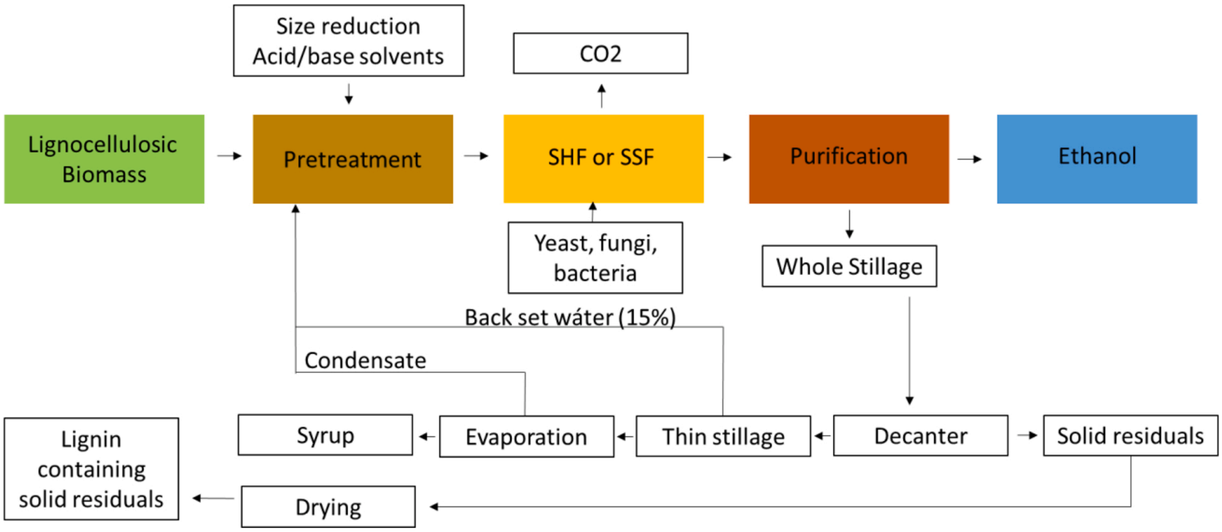

Fig. 1. Second-generation ethanol from lignocelluloses, adapted from [39] (SHF, separate hydrolysis and fermentation; SSF, simultaneous saccharification and fermentation).

Table 1
World fusel oil production by country in Million litres [38].

Country	2009	2011	2013	2015	2017	2019
USA	207	264	251	280	299	299
BRAZIL	124	105	118	134	133	163
Europe Union	20	22	26	26	27	27
China	10	10	13	15	17	17
Canada	5	9	10	8	9	9
Rest of World	4	14	24	22	27	35
Total	**384**	**423**	**467**	**485**	**511**	**550**

depend largely on the fermentation operating conditions and its performance.

The yields of fusel oil in commercial plants may vary between 1 and 11 L per 1000 L of ethanol produced (absolute basis) [2]. Because of the low production volume compared with ethanol, fusel oil has been considered as liquid waste, and it has been generally used as an energy source within the distilleries where it is burned in the steam generators.

The world production of fusel oil by country is shown in Table 1. The production of fusel oil is highly concentrated geographically. The United States produces more than half of the world's fusel oil (54.36 %), followed by Brazil (29.63 %). Fusel oil production in the European Union was stable in 2019 at 27 million liters. China ranks fourth in the production of fusel oil globally during 2009–2019 and produced around 17 million liters.

Even when this waste is considered for energy production, possibly purifying fusel oil compounds will generate high value-added compounds. In other words, fuse oil is not a good fuel and the collateral damage produced is greater than the benefit acquired [4]. Moreover, the current needs for sustainable processes for the future of society, need an approach that goes beyond basic engineering work. In that sense, the circular economy is a philosophy that was initially presented by MacArthur et al. [5]. The general concept of the circular economy is based on closing circles through different sources and levels of recovery, as well as the ability to transform materials into goods and services using raw materials and renewable materials. A key aspect is the prevention of industrial waste materials, thus avoiding an environmental impact greater than that generated by the industry [6].

A valorization alternative for fusel oil could be the purification and esterification of alcohols. Esters from C2 to C8 alcohols are widely used at the industrial scale as a high value-added flavor and fragrance components for food, beverage, cosmetic and pharmaceutical industries [7]. Specifically, isoamyl acetate is extensively used as "green solvent" (methyl ethyl ketone substitute), as an additive in nitrocellulose lacquers, and as banana- or pear-like flavoring agent [8,9].

As can be seen, the mixture has great potential when is analyzed separately as pure components. However, a great challenge to overcome is the thermodynamic interactions present in fusel oil. Particularly, there are four heterogeneous azeotropes between EtAc-H_2O, *n*BOH-H_2O, *iso*-BOH-H_2O, *iso*AOH-H_2O, respectively.

The separation of this mixture has not gone unnoticed by the scientific community. Due to the importance of isoamyl alcohol. Whitmore and Olewine [10] built an experimental distillation column to obtain isoamyl alcohol. Several cuts were made in his column, however, due to the thermodynamic interactions, high purities could not be obtained in simple cuts.

On the other hand, Ferreira et al. [4] proposed three schemes based on distillation columns for the purification of fuse oil. Taking a slight advantage of the presence of several heterogeneous azeotropes, the authors proposed using decanters at various positions in the process. Although it was possible to separate the compound of greatest interest, isoamyl alcohol; the purity obtained is not high compared to a conventional reactive grade product (81.8 % mol).

According to industrial experiences, an interesting alternative for fusel separation is the addition of water. Through water addition to fusel oil helps triggering phase splitting, obtaining a C6-alcohols-rich organic phase, and an aqueous phase where miscible alcohols (methanol, ethanol, propanol, isopropanol) are partially removed. Afterward, the organic phase is processed in several distillation columns obtaining, isoamyl alcohol as a bottom stream. In other processes, the whole fusel oil stream is directly introduced as feed in the distillation train. In both separation approaches, distillation stages are energy-intensive, increasing the final costs of the isolated alcohols.

Please note so far, the separation hurdles associated with thermodynamic interactions. A relatively well-known strategy to overcome mass transfer problems is through process intensification (PI)philosophy. Even there are several PI definitions, most of them converge in some characteristics associated with an intensified process. For example, PI strategies allow achieving enhancing phenomena in a process through the integration of operations, phenomena, and functions. In the same manner, through the application of PI, a process has the potential to increase its efficiency via the reduction in energy requirements, waste generated, and volumes handled without sacrifice product quality [11].

Among the PI technologies proposed for improving distillation, the most promising ones are in the functional (synergy) domain, as they integrate functions and steps into a single unit, thus taking advantage of synergistic effects to overcome equilibrium limitations, leading to

Table 2
Azeotropes in fusel mixture.

Components	Temperature °C	Category
Ethanol Water	78.15	homogeneous
Isoamyl alcohol Water	94.83	heterogeneous
Isoamyl alcohol n-butanol Water	94.48	heterogeneous
n-butanol water	94.52	heterogeneous
Isobutanol water	90.49	heterogeneous
2-ethyl hexanol water	99.14	heterogeneous

Table 3
Model composition of fusel oil used in this study.

Component	Composition (% w)
Ethanol	12.6
Water	14.3
*iso*amyl alcohol	70.4
*n*butanol	1.4
*iso*butanol	1.3

compact equipment and increase of overall efficiency. Hybrid technologies based on process intensification principles can pave the way to more efficient integrated distillation processes, such as DWC. It is applicable to many processes, with a large range of industrial applications and many key players including: BASF, Julius Montz, Linde, Uhde, Lonza, UOP, Sulzer, Koch-Glitsch [12]. It has been estimated that there are at least 125 operating DWCs, with over 70 units belonging to BASF. DWCs clearly represent a successfully first level process intensification [13]. Moreover, DWC has proven its efficiency in separating azeotropic mixtures [14,15]. Additionally, implementing DWC technology has been reported a reduction in investment cost by 25 %, operating cost by 35 %, and space requirements by 40 %, as compared to the conventional column system [16].

With all background mentioned, it is clear the two biggest challenges so far, i) the thermodynamic modeling and validation for this complex mixture, ii) the energy requirements associated with the purification process. This work aims to propose an intensified alternative for the separation and purification of fusel oil. The intensified alternative will be based on a DWC. Numerous industrial applications are known today, mainly concerning separations of ternary mixtures using DWC. The development and implementation efforts focus nowadays on the separation of more than three components or applications in the purification of complex mixtures (azeotropic mixtures, close boiling point mixtures, among others) using DWC [12]. Few works have been reported on the design and optimization of DWC in the purification of mixtures with azeotropes with industrial application. As far as the authors are aware, the use of DWC for the purification of fusel oil has not been reported. Therefore, the design strategy and optimization are necessary for a possible real successful implementation of this intensified configuration in the fusel industry and hence the novelty and contribution of this work. To assess this intensified proposal, a direct comparison will be performed with the conventional process. Moreover, for correct thermodynamic modeling, a validation process of experimental was also developed.

2. Problem statement and case of study

A recent study [17] established the composition of six different samples of fusel oils from different sugar mills in Colombia. From this report, a model composition for a typical fusel oil sample was obtained and it is presented in Table 2. This composition is considered in the modeling and design of the proposed separation schemes. Due to the presence of water in fusel oil, heterogeneous azeotropes form between water and most of the higher alcohols. The separation of a heterogeneous azeotrope mixture is much easier than that of a homogeneous azeotrope mixture because the liquid–liquid equilibrium that occurs in the decanter can be used to facilitate this separation. As mentioned, there are four heterogeneous azeotropes between EtAc-H2O, nBOH-H2O, isoBOH-H2O, isoAOH-H2O, respectively (Table 2).

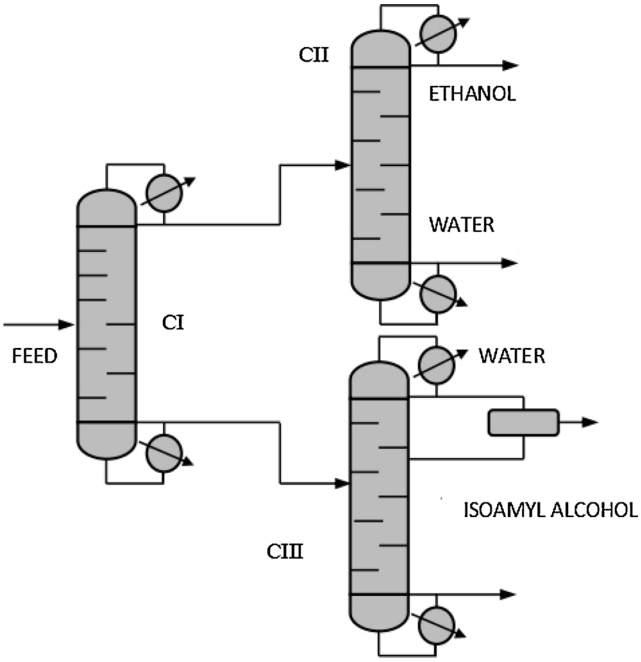

Fig. 2. Conventional distillation system for fusel purification.

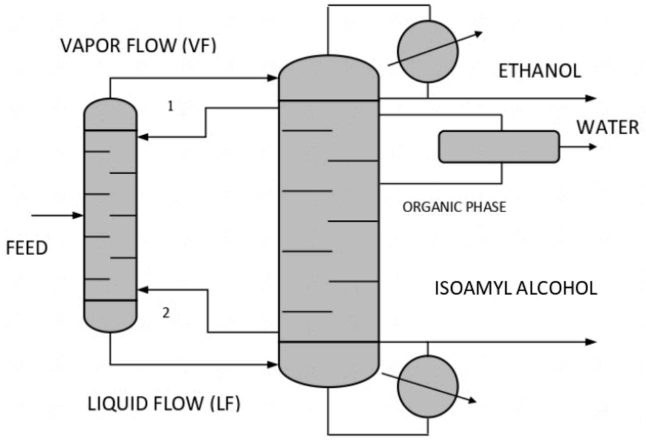

Fig. 3. Dividing wall column distillation scheme for fusel purification.

Considering the compositions of Table 3, the simplified distillation train of Fig. 2 can represent the traditional method for fusel oil separation [17,18]. Ethanol and water are removed as a distillate of the first column (CI), while the C5-C6 alcohols and some water are removed from bottoms. In the second column (CII), azeotropic ethanol is recovered as distillate, and water is removed from the reboiler as a waste. Finally, the bottoms from the first column are sent to a third distillation column (CIII) connected to a decanter. Here, isoamyl alcohol is obtained as a pure product from bottoms and the aqueous phase from the decanter removes most of the water carrying the C5 alcohols out of the system.

To purify fusel oil, a DWC is presented here as an intensified alternative (see Fig. 3) that can be adopted [19]. The components distribution in DWC is carried out as follows, azeotropic ethanol is obtained as

Table 4
Binary systems used for NRTL-HOC parameter regression.

VLE	
Component (1)	Component (2)
Ethanol	*n*-butanol
Ethanol	*iso*butanol
Ethanol	*iso*amyl Alcohol
Ethanol	Water
n-butanol	*iso*butanol
n-butanol	*iso*amyl Alcohol
n-butanol	Agua
*iso*butanol	*iso*amyl Alcohol
*iso*butanol	Water
Isoamyl Alcohol	Water

LLE	
Component (1)	Component (2)
*iso*butanol	*iso*amyl Alcohol
n-butanol	Water
*iso*amyl Alcohol	Water

the top product of the main column, while isoamyl alcohol is removed from bottoms. Water is removed as a side stream from a decanter connected to the intermediate sections of the column. Here the liquid phase immiscibility is an advantage because it helps the selective removal of water. As in the previous scheme, most C5 alcohols are removed together with the aqueous stream of the decanter, and if required, they could be recovered in subsequent separations.

In order to assess the advantages of using an intensified alternative in fusel oil separation, this work will be evaluated both alternatives, the conventional and intensified alternatives. The evaluation was performed through a robust and rigorous optimization framework. The optimization procedure considered the same recovery and purity constraints for both separation alternatives. This evaluation methodology has proved to be able of handling highly non-linear, non-convex, and with have several degrees of freedom.

3. Thermodynamic modeling

Both, traditional and DWC distillation schemes were modeled using the equilibrium stage approach implemented in Aspen Plus. As the design of the different distillation sequences is heavily dependent on the accurate representation of phase equilibria, a validation of the thermodynamic models used to describe fusel oil Vapor-Liquid (VL) and Liquid-Liquid (LL) equilibria was performed. Considering the nature of the components listed in Table 3 there is a need for a model able to capture the non-ideality of the mixture. Phase equilibria of mixtures involving isoamyl alcohol have been recently studied [20–22], and it was found that a NRTL activity-based model fits well most experimental observations [22].

Despite some default parameters were available in the Aspen plus database, after a preliminary verification of the predicted phase equilibria, it was found that the model was not able to predict correctly VLE and LLE of some binary and ternary mixtures. To obtain a correct set of thermodynamic parameters, NIST equilibrium data incorporated within Aspen Plus database, together with literature reports were collected and regressed. Using the regression tool included in the same software, VLE and LLE data were simultaneously fit. As the source of experimental data were diverse, the area test was applied to ensure thermodynamic consistency during parameter fitting, and only those regressions that passed the tests were accepted. The binary systems used for parameter estimation are listed in Table 4. The complete set of binary interaction parameters obtained from the regression is presented in Table 5. The Antoine equation parameters to calculate vapor pressure of pure components are included in the Appendix A (Table A1). A comparison between predicted and reported azeotropes, and the whole set of experimental VLE and LLE are reported in Table A2. The corresponding representation with the NRTL-HOC model is also included in the appendix (Figs. A1–A6). The plots showed good compromise and a reasonably good agreement of model predictions concerning the experimental data. In summary, several tests were performed to select the thermodynamic model that best represents the experimental data, also evaluating the libraries of the parameters present in the simulator. A similar procedure is presented in the work of Ferreira et al. [4]with very reliable results for a mixture similar to the one studied in this work. It is important to highlight that according to the thermodynamic data reported by Tamir and Wisniak [23], Aucejo et al., [24,25], Ferreira et al. [4], among others, the data used in this paper to estimate the liquid - vapor and liquid - liquid equilibrium (as well as to estimate all the azeotropes) are adequate to represent the integral behavior of the mixture at despite its complexity.

4. Optimization methodology

According to the state of the art for fusel separation, the biggest challenge to overcome in this operation is the isoamyl alcohol purity. In other words, all previous works concluded that is quite difficult to obtain isoamyl alcohol at high purity in conventional separation schemes. Moreover, in a circular economy framework, it is desirable a zero-waste process. Additionally, there is a large number of variables to manipulate and a highly complex scheme.

With such consideration, two objective functions were set during optimization: the total annual cost (TAC) and the maximization of both isoamyl alcohol and ethanol purities. The optimization was subjected to a certain minimal recovery of the required products. The objective

Table 5
Thermodynamic parameters for NTRL-HOC model for the evaluation of phase equilibria in fusel mixtures.

NRTL binary interaction parameters

	H_2O EtOH	H_2O *iso*AOH	H_2O *n*BOH	H_2O *iso*BOH	EtOH *iso*AOH	EtOH *n*BOH	EtOH *iso*BOH	isoAOH *n*BOH	isoAOH *iso*BOH	*n*BOH *iso*BOH
aij	3,7555	34,3401209	16,974830	5.3185014	−3.8946	0.32390439	−1.0129191	−10.453029	0	2.0859561
aji	−0,9852	−2,2072582	61,011038	−1.925482	2.2125	0.45490009	0.42494674	10.1845183	0	−1.608747
bij	−676,0314	−9986,34	−750,2012	−564.2319	1529.4836	−188.034772	233.255074	4026.06936	506.8193	−165.7742
bji	302,2365	1040,16	−2438,486	822.72797	−848.1124	−79.6324553	53.9798985	−3896.7943	−324.331	219.3191
cij	3,0	0,3	0,3	0.4	0.3	0.3	0.3	0.3	0.3	0.3

Hayden O'Connell interaction parameters for the vapor phase

	H_2O	EtOH	*iso*AOH	*n*BOH	*iso*BOH
H2O	1,7	1,55		1,55	1,55
EtOH	1,55	1,4			
*iso*AOH					
*n*BOH	1,55	1,55		2,20	1,55
*iso*BOH	1,55	1,55		1,55	1,90

function is expressed according to:

$$Min\ (TAC, -isoAOH, -etOH) = f\left(N_{tn}, N_{fn}, R_n, F_n, D_n\right)$$
$$\text{Subject to}: \ \overrightarrow{y_m} \geq \overrightarrow{x_m}$$

Here, the subscript n refers to the column number. N_{tn} and N_{fn} are the total number of stages and the feed stages, R_n is the reflux ratio, F_{rn} is the distillate flow, and D_{cn} is the column diameter. $\overrightarrow{y}_m$ and $\overrightarrow{x}_m$ are required recovery vectors of the m components, respectively. To calculate the total costs of the schemes studied various correlations and parameters were used. As the base cost, the pressure factor, and the cost of the bare module for each team. To calculate the total annual cost (TAC), it is used the method proposed by Guthrie [26] and modified by Ulrich [27] where the cost of an industrial plant is estimated by separating the units from the process.

$$TAC = \frac{\sum_{i=1}^{n} C_{TM,\,i}}{n} + \sum_{j=1}^{n} C_{ut,j} \tag{1}$$

Where TAC is the total annual cost, CTM is the capital cost of the plant annualized to n number of years, Cut, is the cost of services, respectively. In this work, the capital cost was annualized to 5 years.

Note that TAC minimization is connected to energy reduction. Additionally, with the target of waste reduction, this optimization problem tries to accomplish some of those sustainable metrics highlighted by Jimenez-Gonzalez et al. [28] to encourage process design in a circular economy framework.

Together, the model of these separation processes is represented by highly non-linear multivariate equations. Additionally, they present both continuous and discontinuous variables. Considering also the potentially non-convex equation that makes up the objective function, it is likely that together several local optimums are subject to constraints.

This type of relatively complex model can be optimized using two methodologies: deterministic or stochastic. The first is a technique that ensures that you find the global minimum of the model. However, it has a strong dependency on the initial search points, as well as a correct subrogation of the model, in order to prevent the search being trapped in the local optimums. Regarding stochastic methodologies, it is not necessary to subrogate the model using stochastic methods. In other words, the whole model can be configured with all the ambiguity that it implies. Many studies report that these approaches are capable of achieving the global optimum [29,30]. There are several stochastic optimization algorithms, for example, genetic algorithms, simulated annealing, PSO, Differential Evolution (DE), etc. Particularly the hybrid methods have shown better performance than the conventional version because they bring together the strengths of various methods. Srinivas and Rangaiah [31] showed that the use of some concepts of the meta-heuristic tabu can improve the performance of DE algorithm. In particular, the tabu list (TL) can be used to avoid the revisit of search space by keeping a record of recently visited points, which can avoid unnecessary function evaluations. Based on this fact, Srinivas and Rangaiah [31] proposed the hybrid method DETL. Note, that this type of method has been previously used to optimize complex separation schemes, relatively similar to the one addressed in this study [32–34].

This minimization procedure implies the manipulation of continuous and discrete variables of each scheme, and 5 variables are used for the design of each column. Since the product stream flows are manipulated, the recoveries of the key components in each product stream must be included as a restriction for the optimization problem. A complete list of manipulated variables for both schemes is listed in Table 6.

As mentioned, the optimization methodology is carried out using a stochastic hybrid method, Differential Evolution with Tabu List. The stochastic strategy is coupled to Aspen Plus process simulator. This link allows one to obtain the rigorous Pareto front of both schemes: a set of non-dominated, optimal, and rigorous designs that satisfied the purities and recoveries required. The term “non-dominated” means that there is no other design that can improve one objective without worsening another. The term “rigorous” means that all designs presented were obtained considering the complete set of MESH equations along with the phase equilibrium calculations, using the Radfrac module of Aspen ONE Aspen Plus. The link between Aspen Plus and the optimization procedure was realized with ActiveX Control Technology, which allows the manipulation and information exchange between applications. The evolutionary algorithm works as follows: for each run, a feasible initial design of the reactive scheme is given as an initial solution to the algorithm; from this initial solution, the algorithm generates N individuals to make up the initial population. The manipulated variables of each of the N individuals are sent to Aspen Plus to perform the simulation; then, the algorithm retrieves, from Aspen Plus, the values of objective functions and constraints for each individual. With the retrieved information, the population is divided into subpopulations according to the number of satisfied constraints; at this time, the best individuals are those that satisfy c constraints, followed by those individuals that reach c-1 constraints, and so on. Inside each subpopulation, the individuals are ranked based on the value of the fitness function. The classification of the population makes it possible to optimize the original objective functions but also minimizes the difference between the required and obtained constraints (recoveries and purities). In the end, a set of non-dominated optimal designs of the schemes of distillation arrangements is obtained [30,31]. It is worthy of mention that an infinite heat duty is assigned by the algorithm to the individual where the simulation converges with errors; if the simulation does not converge, the algorithm also settles, as zero, the values of purities and recoveries. The flowchart of this stochastic approach is shown in Fig. 4.

Table 6
Manipulated variables during process optimization.

Manipulated variable	Conventional scheme			DWC	
	CI	CII	CIII	Pref.	Petlyuk
Number of stages in column *n*, N_{Cn}	x	x	x	x	x
Feed stage in column *n*, $N_{F,Cn}$	x	x	x	x	x
Distillate streamflow of column *n*, F_{Cn}	x	x			x
Reflux ratio in column *n*, R_n	x	x	x		
Bottoms streamflow of column *n*, B_{Cn}			x		x
Feed stage of liquid interconnection Flow FL in column C_i, N_{FL},C_i					x
Feed stage of liquid interconnection Flow FV in column C_i, N_{FL},C_i					x
Feed stage of liquid interconnection Flow FL in column C_i, N_{FL},C_i					x
Vapor interconnection flow, VF					x
Liquid interconnection flow, VL					x

5. Results and discussion

The typical design problem for distillation processes is to find the configuration with the minimum total annual cost that produces on-spec products from a given feed mixture of components. The results generated during the optimization of the two schemes studied for the purification of fusel oil are shown below.

5.1. Conventional scheme

The Pareto front displayed in Fig. 5 for the conventional scheme shows that at high purities of ethanol and isoamyl alcohols, the total annual costs (TAC) are increased greatly and where the purity of both is lower, the total annual costs (TAC) decrease drastically. Analyzing the results of each scheme, a direct connection between some of the manipulated variables and the results generated can be observed. For example, in the conventional sequence, it was observed that column I has the highest energy requirements compared to columns II and III.

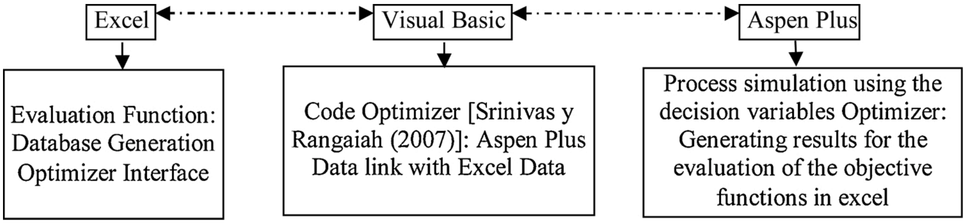

Fig. 4. Tool implemented to perform optimization of the proposed schemes.

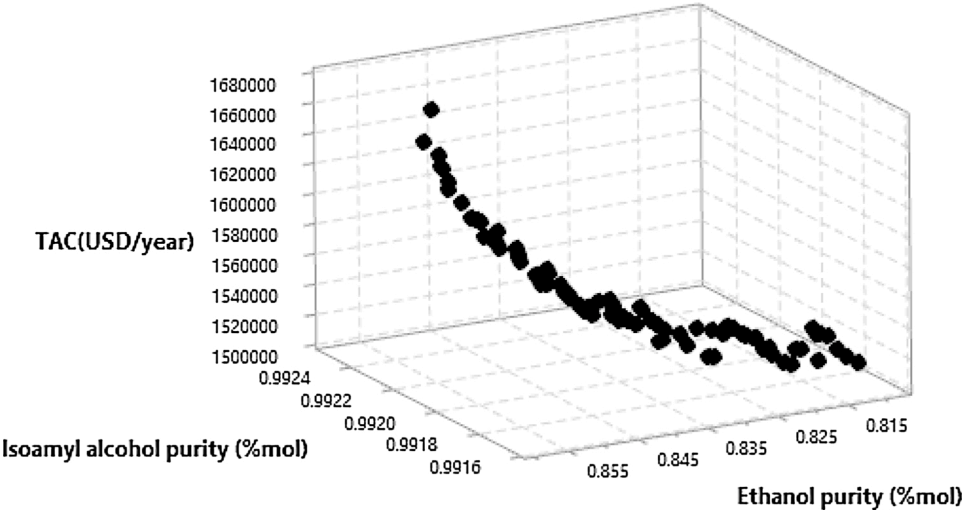

Fig. 5. Pareto front Conventional scheme.

Table 7
Design specifications of proposed schemes.

Design specifications						
		DWC		Conventional Configuration		
Equipment		Pref	Main Column	CI	CII	CIII
Stages		10	29	16	21	7
Feed stage		8	22	11	15	5
Distillate flow (Kmol/hr)			11.1469	13.6996	2.4652	11.1442
Reflux ratio			9. 820	6. 190	8. 395	9.83
	VF		6.4489			
Streams (Kmol/hr)	VL		12.8996			
	Organic Phase		8.9123			
Products	Ethanol		0.453		0.453	
(Kmol/hr)	Isoamyl Alcohol		11.778		11.778	
	Water		9.966		9.966	
Interconnection Flows (Kmol/hr)	1		7.4124			
	2		59.5364			
	Ethanol		0.84		0.84	
Composition	Water		0.71		0.72	
	Isoamyl		0.99			0.99
Energy consumption (kW)		2382.85		2993.62		
Costs (USD/year)		430 231.31		1 573 677.43		

That is, column I contributes 83 % of the total thermal load of the three columns reported in Table 7.

This was expected since the separation is performed in this column: water and higher alcohols in the fusel oil mixture, ethanol, and isoamyl alcohol. Concerning the analysis of column II, the dependence of the manipulated variables reveals that there is a connection between the total number of stages and the feed stage with the purity of ethanol, therefore, the total number of stages equals 21, and the feed stage equals to 15, the scheme presented a higher purity of ethanol. Finally, regarding Column III, there is not an evident relationship between energy consumption and the purity of isoamyl alcohol obtained in the bottoms of the distillation column. The energy consumption in this column is approximately 4% of the total of the scheme and, therefore, represents the lowest energy consumption of the distillation column.

5.2. Divided wall column configuration

The main parameters for the best alternative obtained after optimization are shown in Table 6. This design satisfied all restrictions. When comparing both schemes, savings of 73 % in the total annual costs (TAC)

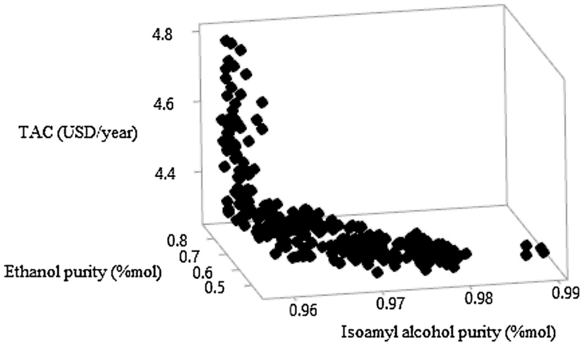

Fig. 6. Pareto front Petlyuk scheme.

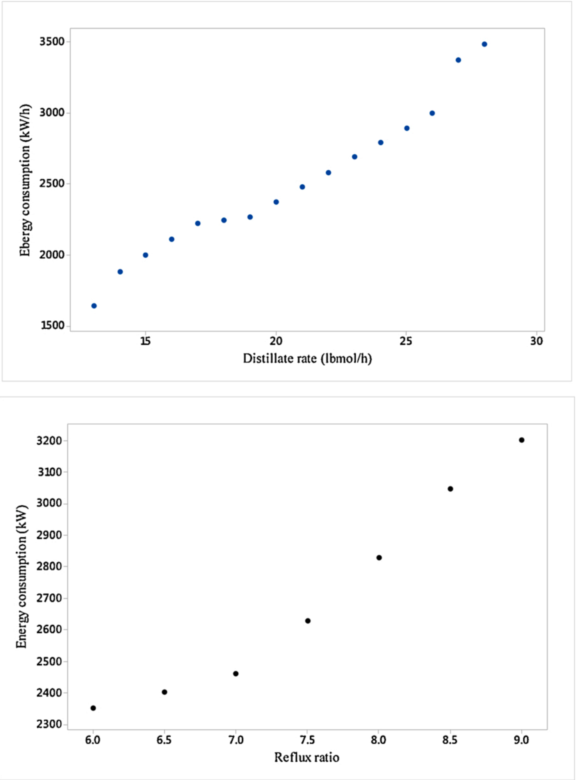

Fig. 7. Dependence between energy consumption, distillate flow and the reflux ratio.

and 27 % of energy consumption are obtained. By analyzing the results from the divided wall column scheme, it can be observed that the feed stage has no connection with the energy consumption, and it does not affect the purity of the alcohols of interest. Some relations between manipulated variables and their effect on the output variables are presented below.

Fig. 6 shows that there is a connection between total annual cost (TAC) and the purity of ethanol as high purity ethanol considerably increases the cost and low purity of this alcohol low cost. Reverse, at high purity isoamyl alcohol, the total annual cost (TAC) is low. This behavior can be understood because ethanol exits at top of the distillation column and its purity is related to the reflux. In Fig. 7 this dependence is observed, high values of reflux ratio and flow distillate provokes increments in both the energy demand and the total annual cost.

Fig. 8 shows the dependence of energy consumption and the purity of ethanol, we can conclude that the energy demand is directly dependent on the purity of ethanol only. In Fig. 9, the connection between energy consumption, purity isoamyl alcohol, and interconnection flow is observed.

If the interconnection flows increase, also increase alcohol purities. However, the reboiler duty also increases with high interconnection flows. When the interconnection flow has larger values (60 Lbmol / h) isoamyl alcohol has a high purity and simultaneously the scheme has high energy consumption. In this way, the results from the Pareto front allow us to establish the best compromise between all design parameters.

Fig. 10 shows the concentration profile of the DWC scheme, which confirms high purities of the isoamyl alcohol and the ethanol. This behavior of the divided wall column is projecting itself as a good alternative in fusel purification due to the energy savings and consequently costs savings.

When analyzing the total annual costs for both schemes, we note that the conventional scheme represents a 70 % higher cost compared to the divided wall column. Regarding energy consumption, the DWC scheme generates a saving of 20 % compared to the conventional scheme. Note in the conventional scheme, columns CI and CII have more stages compared to DWC scheme. On the other hand, the diameters of both schemes are very similar. According to the results contained in Table 7, we can ensure that there is a connection between energy consumption and total annual cost (TAC) directly. Therefore, the scheme of divided wall column represents an attractive alternative in its implementation in the industry, because of its low total annual cost (TAC) is a combination of efficiency and low cost of the operation and infrastructure. Thus, in this paper, to calculate the cost, diameter of each of the sections of DWC shall be calculated based on the vapor rate. Depending upon the change in diameter, one can choose either to use a single diameter or step diameter (the top section with a smaller diameter). In the former case, the larger diameter of all the three sections should be used. Premkumar and Rangaiah [35] have presented a similar assumption for the design and costing of a DWC. The amount of impurities in the product streams is reduced by increasing the energy consumption and the number of stages, the objective functions are in conflict. As lower the impurities as higher the TAC. In order to obtain the preferable operating condition of each scheme, the set of solutions must be analyzed in terms of a Pareto front. In this analysis, a Pareto front represents all the optimal operating conditions of the feasible designs; from a minimum number of stages (total reflux ratio) to minimum reflux ratio (infinite number of stages), and all designs in between these limiting conditions. This set of optimal solutions allows the engineer to choose among them by doing a compromise among the three goals (TAC, $x_{iso\mathrm{AOH}}$, x_{EtOH}). It is important to note that in both configurations the same purity is achieved for ethanol and isoamyl alcohol (Table 7). In the particular case of isoamyl alcohol, it is obtained in high purity (99 % mole). There is growing interest in adding value to isoamyl alcohol increasing the economic viability of fusel oil. Isoamyl alcohol can be used to produce isoamyl acetate via both enzymatic and chemical catalytic esterification routes. As high-purity isoamyl acetate is used in the fragrance, food, and pharmaceutical industries, much of the focus has been on this product [36].

Also, it is important to mention that the total number of stages involved in the optimal design of the DWC is less than the total number of stages in the conventional configuration. This impacts on the decrease in the total operating cost of the intensified system. And also this smaller size of the configuration would be impacted on environmental indicators such as eco-indicator 99, which will be reflecting a sustainable purification of isoamyl alcohol [37].

In summary, when comparing the optimal designs for the conventional case and the intensified case, it can be observed that DWC technology offers key advantages such as improved thermodynamic efficiency (associated with the reduction of the total energy consumption of the configuration), with high purity for the bottom product stream (main product), compact configuration (2 columns in 1 shell), around 20 % energy savings (due to no remixing effect), lower capital investment (reduction greater than 50 %). A point to highlight, based on the results, as the main drawbacks are that DWC allows only one operating pressure for the whole separation, leading to a higher pressure drop and temperature span along the column. Although less energy is

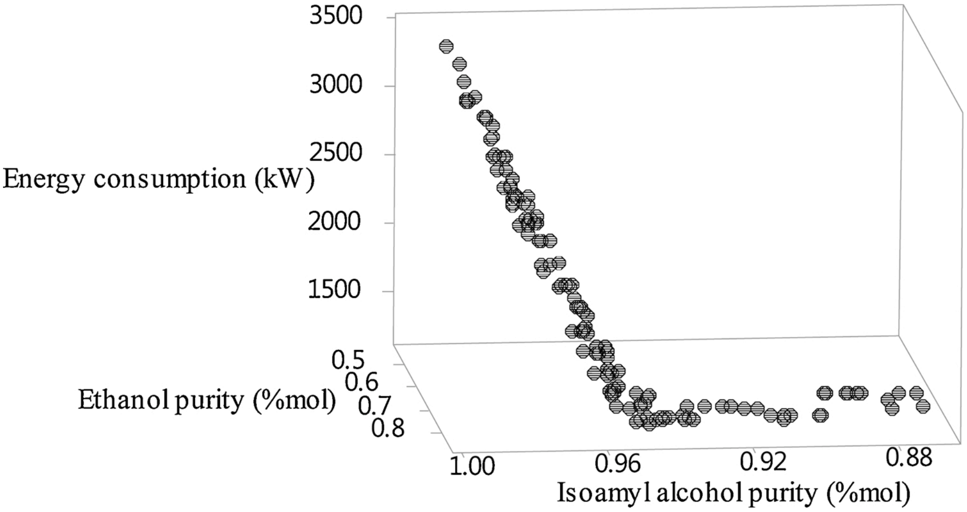

Fig. 8. Relationship between energy consumption and purity of ethanol.

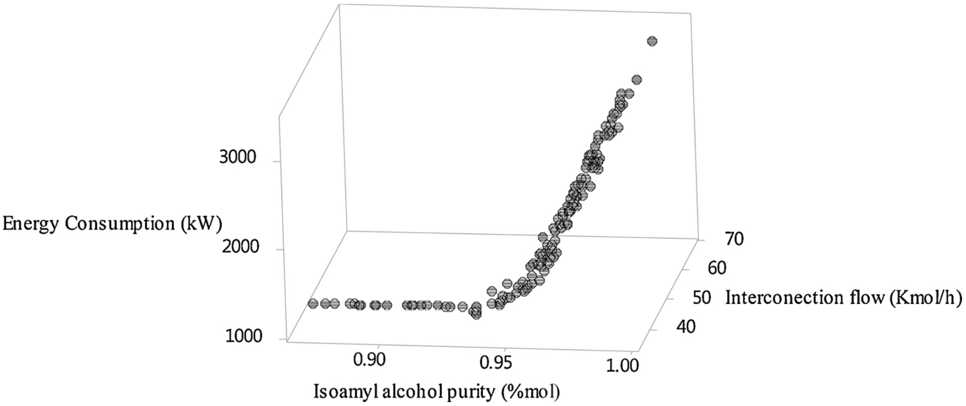

Fig. 9. Relationship between the flow interconnection, energy consumption and purity of isoamyl alcohol.

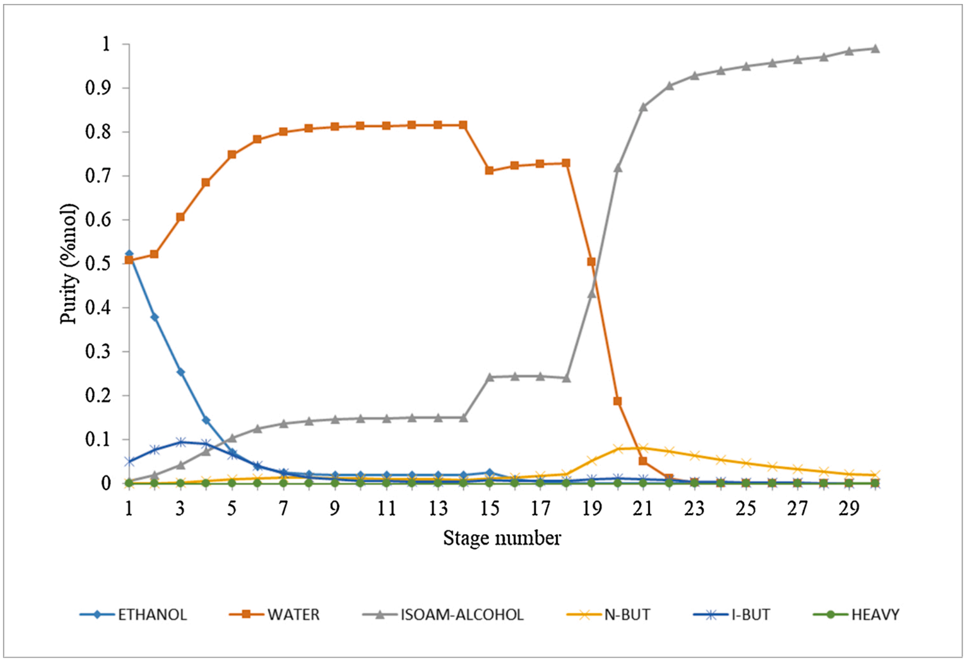

Fig. 10. Concentration profile (DWC) scheme.

required, this energy is overall added and rejected at more extreme temperatures than a conventional arrangement. A complementary point to discuss is that the environmental problems in the distillation process are mainly pollutant emissions and energy consumption. High energy consumption can increase CO_2 emissions. From the perspective of CO_2 emissions, DWC is more attractive due to the reduction in energy consumption in the intensified system compared to the conventional system. In this sense, the use of DWC for the purification of fusel oil is not only relevant from the economic point of view but also from the objective of environmental sustainability. As a preliminary conclusion, it should be highlighted that, as long as authors are aware, this is the first intensified proposal for obtaining high purity alcohol from fusel oil in a single equipment. DWC has the potential to add value in chemical processes involving complex multicomponent separations compared to traditional process equipment.

6. Conclusions

In this work, an intensified alternative is presented for the separation of fusel oil. An investigation of phase equilibrium (vapor–liquid equilibrium and liquid–liquid equilibrium) was carried out for the components involved in this mixture. The results show that a divided wall column represents a good option for fusel oil distillation due to the benefits in terms of reduction in the total annual cost (TAC) over the traditional distillation that is used in the industry. Contrary to other previous works, in this proposal was possible to obtain high purity alcohols. The separation of isoamyl alcohol, at high purity and low cost using a dividing wall column, represents an excellent option for the purification of fusel oil in the industry. The divided wall column presents a 20 % savings in energy consumption and 72 % in total annual cost (TAC). These results represent a new vision in regard to highly nonideal mixtures, where heterogeneous azeotropes are present in multicomponent systems. Moreover, this kind of proposal highlights intensified separation schemes capable of being embedded in a circular economy framework. In other words, a process able of generating high added-value components from wastes to be further attached in the production-consumption circle.

Authorship contributions

Category 1: Conception and design of study: J.J. Mendoza-Pedroza, J.G. Segovia-Hernandez, A. Orjuela; acquisition of data: J.J. Mendoza-Pedroza, A. Orjuela, analysis and/or interpretation of data: J.J. Mendoza-Pedroza, J.G. Segovia-Hernandez, A. Orjuela.

Category 2: Drafting the manuscript: J.J. Mendoza-Pedroza, J.G. Segovia-Hernandez, A. Orjuela, E. Sanchez-Ramirez, S. Hernandez revising the manuscript critically for important intellectual content: J.J. Mendoza-Pedroza, J.G. Segovia-Hernandez, A. Orjuela, E. Sanchez-Ramirez, S. Hernandez.

Category 3: Approval of the version of the manuscript to be published (the names of all authors must be listed): J.J. Mendoza-Pedroza, J.G. Segovia-Hernandez, A. Orjuela, E. Sanchez-Ramirez, S. Hernandez.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors acknowledge financial support received from CONACyT, Universidad Nacional de Colombia and Universidad de Guanajuato, México.

Appendix A

$$\mathrm{LnP(bar)} = A + B/T(^{\circ}C) + C\ln(T) + DT^{E} \tag{B.1}$$

Table A1
Antoine equation coeficients [40,41].

Parameter	H2O	ETOH	HAC	ETAC	DEE
A	61.0371	61.7911	41.7571	55.3111	125.3871
B	−7206.7	−7122.3	−6304.5	−6227.6	−6954.3
C	−7.1385	−7.1424	−4.2985	−6.41	−19.254
D	4.05E-06	2.89E-06	8.89E-18	1.79E-17	0.024508
E	2	2	6	6	1
Min Temp (°C)	0.01	−114.1	16.66	−83.55	−116.3
Max Temp (°C)	374.14	240.85	318.8	250.15	193.55

Table A2
Predicted azeotropes from NRTL-HOC model at 1 atm and experimantal reports [42–45].

Components	Experimental Temp (°C)	Computed Temp (°C)	Classification	Type *	No. Comp.	Experimental Mole Fraction			Computed Mole Fraction		
						xH2O	xEtOH	xEtAc	xH2O	xEtOH	xEtAc
EtAc-H2O	70,38	70,37	Saddle	Hete	2	0,3115	0	0,6885	0,3131	0	0,6869
						xH2O	x*n*BOH	x*n*BOH Ac	xH2O	x*n*BOH	xnBOH
*n*BOH-H2O	95,12	94,28	Saddle	Hete	2	0,3988		0,6012	0,3303		0,6697
						xH2O	isoBOH	xisoBOH Ac	xH2O	xisoBOH	xisoBOH
*iso*BOH-H2O	90,48	94,46	Saddle	Hete	2	0,5069		0,5654	0,3303		0,4346
						xH2O	isoAOH	xisoAOH Ac	xH2O	xisoAOH	xisoAOH
*iso*AOH-H2O	94,74	95,26	Saddle	Hete	2	0,8384		0,1616	0,8385		0,1615

[*] Hom=Homogeneous, Het=Heterogeneous.

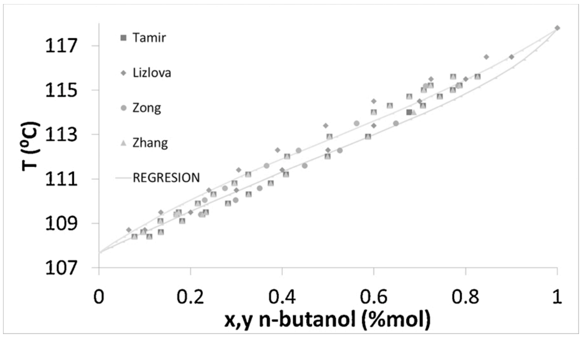

Fig. A1. Vapor-Liquid equilibrium curve, system ethanol - *n* butanol, taken from [4,40–45].

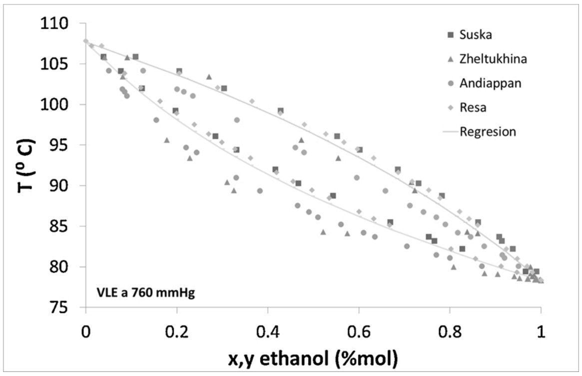

Fig. A2. Vapor-Liquid equilibrium curve, system ethanol – *iso*butanol, taken from [4,40–45].

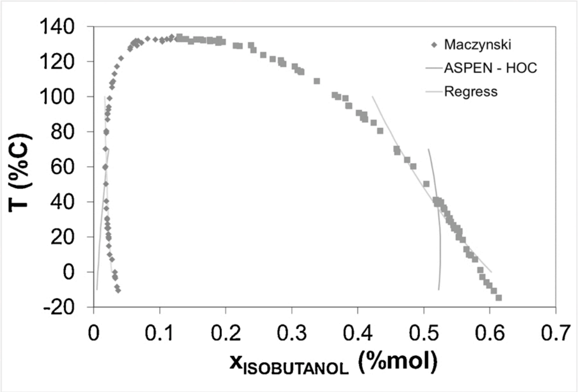

Fig. A3. Liquid-Liquid Equilibrium curve, system *iso*butanol – water, taken from [4,40–45].

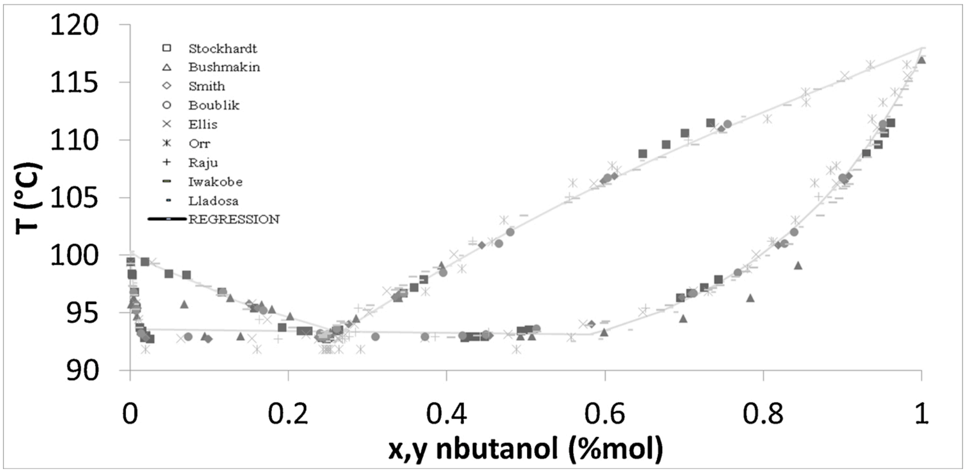

Fig. A4. Vapor-Liquid equilibrium curve, system *iso*butanol – water, taken from [4,40–45].

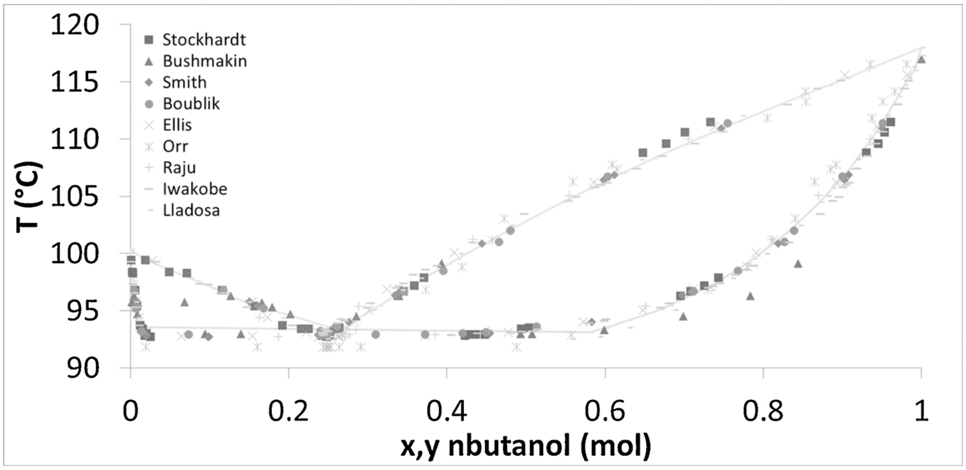

Fig. A5. Vapor-Liquid equilibrium curve, system *n* butanol – water, taken from [4,40–45].

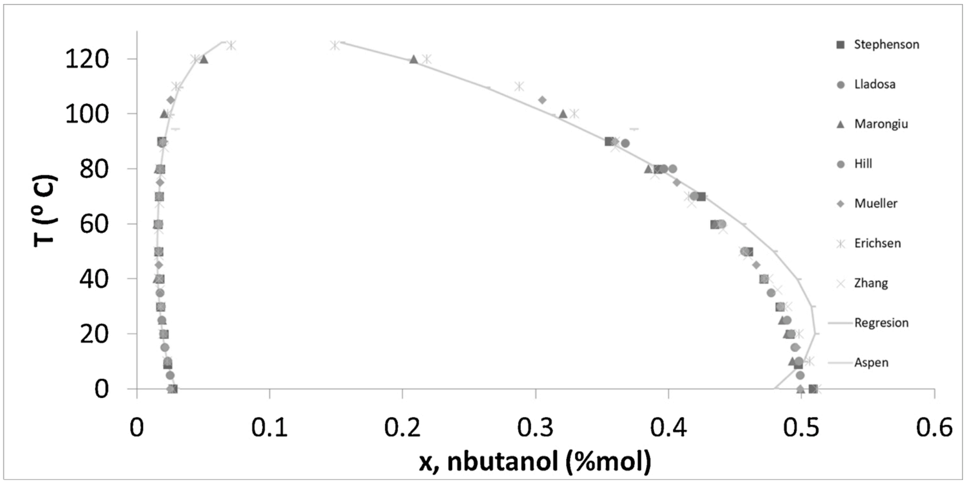

Fig. A6. Liquid-Liquid equilibrium curve system, *n* butanol – water, taken from [4,40–45].

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