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Development of Anhydrous Ethanol Purification: Reduction of Acetal Content and Vapor−Liquid Equilibrium Study of the Ethanol−Acetal Binary System

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ABSTRACT: Acetaldehyde diethyl acetal (herein called acetal) is an important pollutant of anhydrous ethanol. Isobaric vapor−liquid equilibrium (VLE) of an ethanol−acetal binary system was measured using a vapor condensate and liquid circulation VLE still. The experimental data were correlated with Wilson, nonrandom two-liquid (NRTL), and universal quasichemical (UNIQUAC) activity coefficient models, which were found suitable for representing the VLE data. Proper agreements between experimental and calculated VLE data were obtained, which were then confirmed with consistency tests. The applicability of the novel VLE data was demonstrated during an investigation of an anhydrous ethanol purification column. Reduction of the concentration of acetal and other pollutants was examined and optimized in a flowsheet environment. The modeling results were verified in a laboratory with an experimental distillation column, confirming a correct agreement between the results. It must be highlighted that the developed method is suitable for the production of pharmacopeial quality anhydrous alcohol, based on reliable, verified VLE data. The results show the importance of accurate VLE data in critical compositions (low pollutant content); moreover, aiming at high product purity, experimental validation has paramount importance. The consistency between the three platforms (VLE and distillation experiments and flowsheet simulation) confirms the accuracy of the developed method.
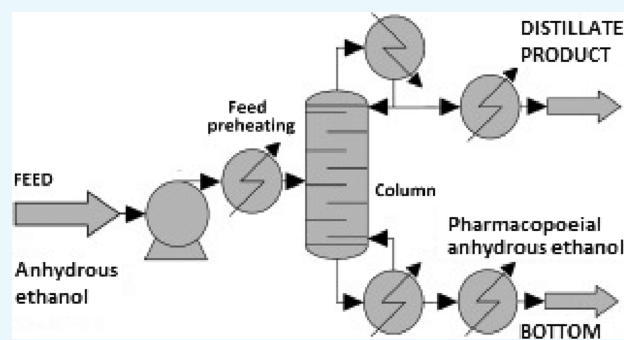
1. INTRODUCTION

Certain industries, for example, pharmaceutical and fine chemical sectors, need high purity chemicals. Such chemicals are frequently produced by distillation. In the case of pharmacopeial anhydrous alcohol, there are strict requirements regarding polluting compounds. For the reliable production of such ethanol, a proper process should be designed. Nowadays, the process design activities are strongly based on professional flowsheeting software programs. These software programs must operate on a reliable database, rigorous modeling tools, and accurate calculation based on thermodynamic equilibria. The accuracy of these tools is generally sufficient; however, in a research focused on obtaining high purity chemicals, special attention must be paid to the evaluation of the computed results.

A typical example for the application of distillation is the production of ethanol, as a precious chemical in fine chemical industry.[1] Basically, ethanol production is performed through a biological process, resulting in bioethanol, obtained in different qualities/purities depending on its application.[2−5]

Anhydrous ethanol has an alcohol content of at least 99.7 v/v % and thus an extremely low water content.[6] The extremely low water content makes it suitable for use by fuel manufacturers to make mixed fuel.[7] By mixing with traditional petrol in fuel production, the proportion of biocomponents has increased,

thus reducing traffic emissions of environmentally harmful greenhouse gases.[8−10] Pharmacopeial anhydrous alcohol is a premium quality anhydrous alcohol which, besides conforming to the relevant EU and Hungarian specifications, also meets the strict requirements of the PHHg VIII, EU Pharma 4 pharmacopeial regulations.[11,12] The major aim of this work is to develop the conversion process from anhydrous ethanol produced on a biological source to pharmacopeial anhydrous alcohol using distillation.

The required level of purity is extremely difficult to achieve as raw anhydrous alcohol contains a wide variety of contaminants, albeit only in small concentrations. Examples of ethanol contaminants include acetal, acetaldehyde, acetone, benzene, cyclohexane, methanol, ethyl methyl ketone, isobutyl methyl ketone, propanol, isopropyl alcohol, butanols, furfural, 2-methylpropan-2-ol, and 2-methylbutan-2-ol.[13] During the distillation process, polluting compounds have to be removed

to obtain the high purity bottom product, considered pharmacopeial anhydrous alcohol.

One of the most important pollutant compounds is acetal, as it belongs to the most common contaminants. Acetaldehyde diethyl acetal (1,1-diethoxyethane) is a major flavoring component of distilled beverages, especially of sherry[14] and malt whisky.[15] In spite of being one of many compounds containing the acetal functional group, this specific chemical is often simply referred to as acetal.

Acetal is applied in the design of synthetic perfumes to increase the resistance to oxidation, therefore the lifetime of perfumes. Acetals have been under consideration as oxygenated additives to diesel fuel because they drastically decrease the emission of nitrogen oxides and other particles while retaining or improving the cetane number and helping in the combustion of the final products, without decreasing the ignition quality.[16−19]

1,1-Diethoxyethane production involves the reversible reaction of acetaldehyde and ethanol in acid medium, according to the following: acetaldehyde + 2 ethanol ↔ acetal + water (see Figure 1).[20−22] However, acetaldehyde could be replaced by
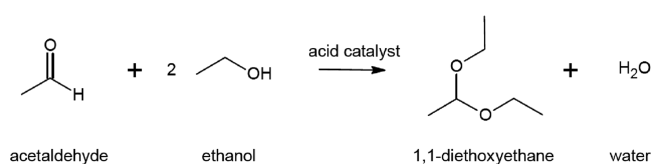

Figure 1. Acetalization of acetaldehyde and ethanol.

ethylene, acetylene, or vinyl ether.[23] The advantage of using acetaldehyde and ethanol as reactants is that ethanol is produced from renewable sources (mainly from the sugarcane industry) and acetaldehyde can be produced by dehydrogenation of ethanol or direct ethylene oxidation.[19,24,25]

The reaction shown in Figure 1 is slightly exothermic; at a temperature of 25 °C, a 59% conversion can be achieved with a sulfonic acid catalyst. The acetal formed can be used as an additive to diesel fuels as it increases the cetane number and promotes combustion of the mixture.[26]

In order to increase the purification efficiency, it is essential to know the exact vapor−liquid phase equilibrium data of the mixture. Ionescu et al.[27] have presented the vapor−liquid equilibrium (VLE) data and nonrandom two-liquid (NRTL), Wilson, and Gothard model parameters of ethanol−diethyl acetate and i-propanol−diethyl acetate binary mixtures. In contrast, the VLE data and main thermodynamic models for other contaminant components of anhydrous ethanol have already been explored in detail.[28,29] Consequently, a further goal of this work is to experimentally determine the VLE data of this binary mixture for universal quasichemical (UNIQUAC) model parameters too and to verify the VLE data with laboratory distillation experiments and in a flowsheet environment.

The purpose of VLE analysis is to determine equilibrium-related data and the boiling-dew point, in addition to thermodynamic data. Today, these can be calculated with fairly high accuracy using process simulators, various state equations, and activity coefficient models, but the basis of the calculations lies in the knowledge of reliable and accurate measurement data and physicochemical parameters. It is not possible to perform accurate calculations with thermodynamic relations alone, as it requires knowledge of appropriate measurement data and parameters derived from them.

These can be used to explore the possible azeotropic behavior of liquid mixtures; furthermore, separation possibilities of liquid mixtures can also be modeled on the basis of this data. Simulation programs often determine the state of a multi-component mixture from the parameters of the pure components, which can cause discrepancies with their actual behavior. For example, they show an azeotrope, or a liquid−liquid distribution, where it does not actually occur, or they do not reveal it where it is in fact present. However, knowledge of azeotropes is essential in the design of a separation unit, as they require different technologies and special design considerations.

VLE data and the resulting pair interaction parameters can be used to model the separation of different mixtures, as well as for the design of separation systems. In the context of industrial implementation, the economic aspects are also taken into account in which case different separation models can also be used for cost calculation.

During the measurements, it is necessary to examine the equilibrium phases of vapor and liquid under the same conditions. VLE points can be determined in two ways. Either the operation is carried out at constant temperature and the pressure is changed point by point or vice versa. By these means, it is possible to perform isothermal or isobaric measurements.

Since the vast majority of columns in industrial separation units operate under constant pressure, in the present work, the vapor−liquid phase equilibrium of the various mixtures is also measured at constant pressure.

However, the measurement data must be examined to determine whether they are in accordance with the relevant thermodynamic laws, for which the so-called thermodynamic consistency tests, derived from thermodynamic relationships, are used.[30] Thermodynamic theorems provide a deeper understanding of different physical, physicochemical, and thermal processes. The equations derived from these are still used today to quantitatively describe chemical systems and phase equilibria. In order to make sure that the measured data comply with the laws of thermodynamics, consistency tests can serve as a tool for verification.[31] It is important to check if the measured equilibria correspond to reality, that is, whether the measurement points are consistent or inconsistent.[32,33] If they are shown to be consistent, they meet the thermodynamic theorems and the data set can be considered reliable.

2. RESULTS AND DISCUSSION

First, the modified equipment and VLE measurement procedure were tested with the acetaldehyde−ethanol binary mixture as a well-known and studied system. Good reproducibility and correlation with published results were obtained for the VLE data[29] at 101 kPa (Supporting Information: Table S1, Figures S1 and S2). It can be stated that the equilibrium still was suitable for measurements.

The refractive indexes were experimentally determined in the whole concentration range for the ethanol (1)−acetal (2) system at T = 293.2 K. The data are shown in Table 1. The concentration versus refractive index plots are shown in Figure 2.

The isobaric VLE of ethanol (1)−acetal (2) was measured at p = 101 kPa. With the experimental data, NRTL, Wilson, and UNIQAC parameters were regressed. The experimental and calculated data are presented in Table 2 and Figures 3 and 4. The activity coefficients presented were calculated by eq 1.

Table 1. Experimental Refractive Indexes (n_D) of the Ethanol (1)−Acetal (2) Mixture at 293.2 K, p = 101 kPa[a]

ethanol content		n_D [−]	ethanol content		n_D [−]
[mol/mol]	[g/g]	(293.15 K)	[mol/mol]	[g/g]	(293.15 K)
0.0000	0.0000	1.3805	0.5527	0.3251	1.3753
0.0180	0.0071	1.3805	0.5964	0.3655	1.3747
0.0485	0.0195	1.3802	0.6461	0.4158	1.3737
0.0976	0.0405	1.3800	0.6867	0.4608	1.3727
0.1521	0.0654	1.3798	0.7509	0.5402	1.3711
0.2104	0.0941	1.3795	0.8014	0.6114	1.3697
0.2477	0.1138	1.3790	0.8437	0.6779	1.3682
0.3092	0.1486	1.3786	0.8995	0.7773	1.3660
0.3510	0.1741	1.3782	0.9520	0.8855	1.3647
0.4009	0.2069	1.3775	0.9898	0.9743	1.3615
0.4598	0.2491	1.3767	1.0000	1.0000	1.3611
0.5044	0.2840	1.3760			

[a]Standard uncertainty u is $u(n_D)$ = 0.0001, $u(p)$ = 2 kPa, $u(T)$ = 0.1 K; $u(x_1)$ = 0.0001.

$$\gamma_i = \frac{y_i \times p}{x_i \times p_i^*} \tag{1}$$

The minimization of ChemCAD's objective function was utilized to obtain model parameters[34] with eq 2.

$$OF_{VLE} = \sum_{i=1}^{N} (y_{\exp,i} - y_{cal,i})^2 + \sum_{i=1}^{N} (T_{\exp,i} - T_{cal,i})^2 \tag{2}$$

The calculated mean and maximum deviation results can be found in Table 3.

As it can be seen, the maximum deviation is lower than 1.00 for NRTL, Wilson, and UNIQUAC models and no significant difference is revealed in the accuracy of the models.

The volume and area structural parameters applied in UNIQUAC modeling are demonstrated in Table 4.

It can be determined that ethanol forms a minimal boiling azeotropic mixture with acetal in the investigated concentration range. The calculated binary parameters are presented in Table 5.

The thermodynamic consistency test for ethanol−acetal data was performed according to Herrington's area test for isobaric data.[30,34] D_H and J_H values are calculated according to the following equations.

$$D_H = 100 \times \left| \frac{\int_{x_1=0}^{x_1=1} \ln(\gamma_1/\gamma_2)\,dx_1}{\int_{x_1=0}^{x_1=1} |\ln(\gamma_1/\gamma_2)|\,dx_1} \right| \tag{3}$$

$$J_H = 150 \times \frac{|\Delta T_{max}|}{T_{min}} \tag{4}$$

$$D_H - J_H \leq 10\% \tag{5}$$

The D_H value was 18.3% and the J_H value was found to be 9.5%; therefore, $D_H - J_H$ is 8.8%. It can be concluded that the measured data is suitable for application in a flowsheet environment. The elaborated ethanol−acetal binary model can be used for simulation of the ethanol purification column.

Figure 5 shows the optimization of ethanol purification. The red line represents the acetal target concentration in the bottom product, which is 10 ppm. Acetaldehyde did not occur in the bottom product in any of the cases. The feed was close to the
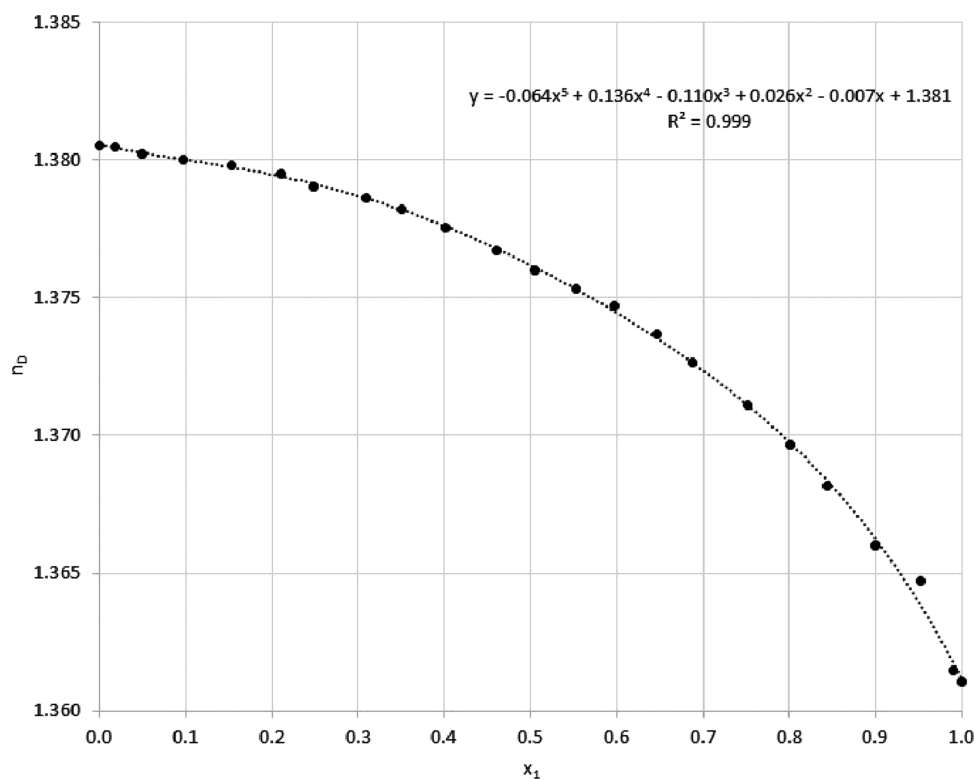

y = -0.064x⁵ + 0.136x⁴ - 0.110x³ + 0.026x² - 0.007x + 1.381
$$y = -0.064x^5 + 0.136x^4 - 0.110x^3 + 0.026x^2 - 0.007x + 1.381$$
$$R^2 = 0.999$$

Figure 2. Experimental refractive indexes of the system ethanol (1)−acetal (2) at T = 293.2 K (black solid circle) x_1: mole fraction of ethanol

Table 2. VLE Data (T, Temperature; x, Liquid Mole Fraction; y, Vapor Mole Fraction) of Ethanol (1)−Acetal (2) at p = 101 kPa[a]

					calculated data					
	experimental data				NRTL		Wilson		UNIQUAC	
T [K]	x_1	y_1	γ_1	γ_2	T [K]	y_1	T [K]	y_1	T [K]	y_1
373.19	0.0258	0.1089	2.0077	1.0421	375.65	0.0000	375.65	0.0000	375.65	0.0000
369.12	0.0738	0.2595	2.0294	1.1005	371.42	0.1720	371.46	0.1706	371.45	0.1712
365.85	0.1356	0.3721	1.8188	1.1438	368.01	0.2986	368.08	0.2966	368.04	0.2977
364.98	0.1552	0.4224	1.8107	1.0804	365.22	0.3957	365.30	0.3932	365.24	0.3948
360.86	0.2718	0.5389	1.5094	1.2832	362.88	0.4726	362.98	0.4696	362.89	0.4715
360.23	0.2836	0.5607	1.6563	1.2109	360.91	0.5350	361.03	0.5315	360.92	0.5336
358.67	0.3291	0.5853	1.5045	1.2831	359.24	0.5866	359.37	0.5828	359.25	0.5850
357.12	0.3746	0.6297	1.4735	1.3282	357.82	0.6301	357.96	0.6261	357.83	0.6282
356.32	0.4201	0.6567	1.4045	1.3640	356.60	0.6673	356.75	0.6633	356.62	0.6652
355.23	0.4563	0.6818	1.3916	1.3393	355.56	0.6995	355.71	0.6957	355.58	0.6973
354.34	0.5273	0.7206	1.3197	1.4058	354.67	0.7278	354.82	0.7245	354.69	0.7257
353.87	0.5719	0.7474	1.2702	1.4908	353.92	0.7531	354.05	0.7505	353.93	0.7512
353.12	0.6382	0.7779	1.2003	1.5846	353.27	0.7762	353.39	0.7743	353.29	0.7745
352.64	0.6796	0.7939	1.1741	1.7034	352.73	0.7978	352.82	0.7968	352.73	0.7964
352.12	0.7076	0.8092	1.1501	1.7394	352.26	0.8185	352.34	0.8184	352.26	0.8175
351.56	0.7367	0.8219	1.1359	1.8367	351.87	0.8392	351.92	0.8399	351.86	0.8386
351.23	0.7702	0.8325	1.1188	1.8934	351.54	0.8610	351.58	0.8622	351.53	0.8606
351.11	0.8309	0.8646	1.0862	2.1243	351.27	0.8850	351.30	0.8865	351.26	0.8849
351.01	0.8517	0.8785	1.0769	2.1912	351.09	0.9136	351.10	0.9148	351.08	0.9135
350.99	0.9410	0.9381	1.0528	2.5918	351.01	0.9499	351.01	0.9504	351.00	0.9498
350.95	0.8976	0.9009	1.0644	2.3976	351.13	1.0000	351.13	1.0000	351.13	1.0000
350.91	0.9620	0.9556	1.0534	2.8931						

[a]Standard uncertainties: $u(T) = 0.1$ K; $u(p) = 1$ kPa

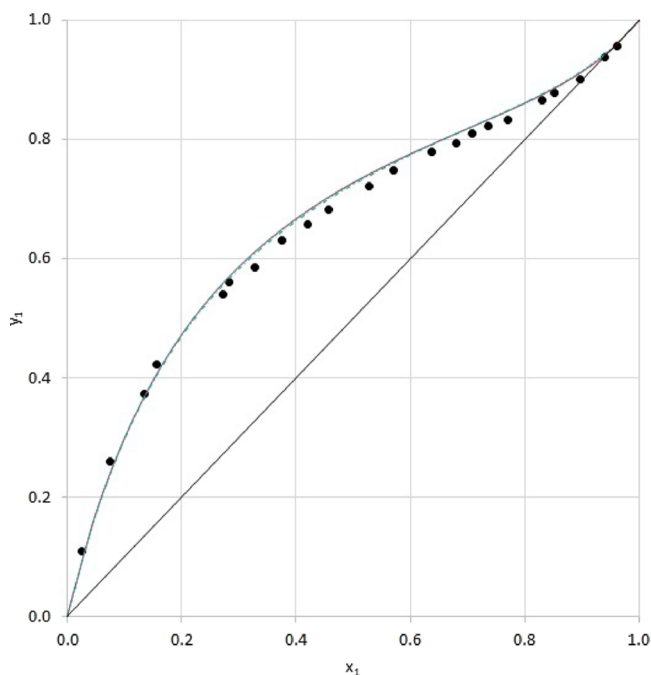**Figure 3.** y−x diagram for the ethanol (1)−acetal (2) system at p = 101 kPa with experimental data (black solid circle), Wilson (green line), UNIQUAC (blue line), and NRTL (red line) activity coefficient models
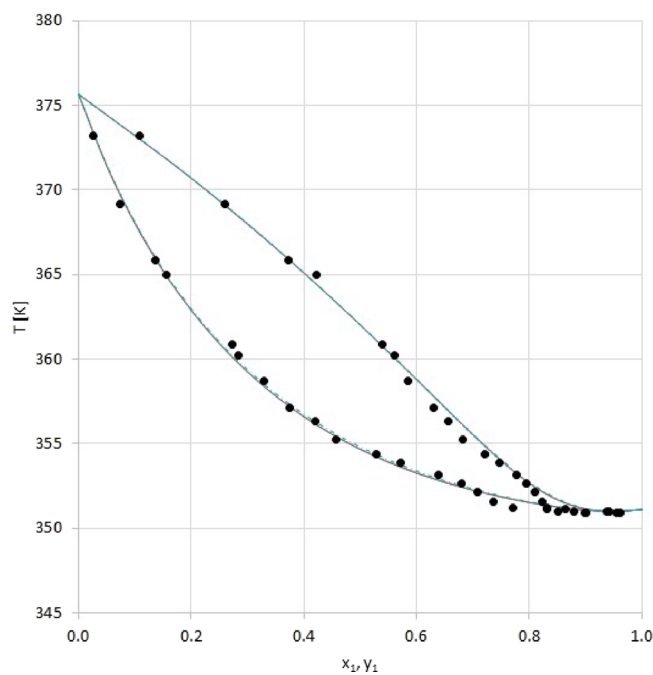

Figure 4. T−y−x diagram for the ethanol (1)−acetal (2) system at p = 101 kPa with experimental data (black solid circle), Wilson (green line), UNIQUAC (blue line), and NRTL (red line) activity coefficient models

boiling point in every case. Studying Figure 5, the following optimized parameters can be determined: 40 theoretical stages, feed into the eighth stage, the reflux ratio is 26, and column pressure must be kept at 10 kPa. The relatively high values can be considered realistic because extreme purity ethanol was the

goal. It must be mentioned that 10 kPa has to be achieved in feed and column pressure to reach the corresponding acetal concentration in the bottom product. Under a pressure value of 10 kPa, it is difficult to keep up the working pressure in the laboratory column apparatus; therefore, computer calculations were not performed below this value.

Table 3. Accuracy of NRTL, Wilson, and UNIQUAC Models

	NRTL		Wilson		UNIQUAC	
	T [K]	y_1	T [K]	y_1	T [K]	y_1
mean deviation	0.39	0.0099	0.39	0.0102	0.34	0.0103
max. deviation	0.92	0.0209	0.91	0.0189	0.92	0.0221

Table 4. Structural Parameters for Pure Components (R: Volume Parameter and Q: Area Parameter)

parameter	acetal	ethanol
R	4.9868	2.1054
Q	4.332	1.972

Table 5. Calculated Binary (Ethanol and Acetal) Interaction Parameters of Wilson (λ_{12}, λ_{21}, Adjustable Parameters), NRTL (B_{ij}, B_{ji}, Dimensionless Interaction Parameters; α, Constant Characteristic of the Nonrandomness of the Mixture), and UNIQUAC (ΔU_{ij}, ΔU_{ji}, Binary Interaction Parameter) Models

NRTL			Wilson		UNIQUAC	
B_{ij}	B_{ji}	α	λ_{12}	λ_{21}	ΔU_{ij}	ΔU_{ji}
559.08	−168.65	0.296	525.002	213.742	16.25	269.9

The reboiler duty value was 2278 MJ/h in the optimum. Figure 6 shows the influence of reboiler duties (Q-RD) on the acetal concentration of the bottom product (W-Acetal).

The experiments were carried out according to the optimized results of the simulations. The reflux ratio was 26 and the distillate/feed ratio was the same as that of the simulation, 10%. The feed flow rate was 3 kg/h in the case of laboratory experiments. The trap flow rate was 0.05 kg/h, which was analyzed together with the distillate product due to its nearly identical composition. In this evaluation part, the best available results are presented. Table 6 shows the optimized simulation results and their control laboratory measurement results. The simulation verification can be taken with the objective function ($OF_{Distillation}$), which presents minimized deviation of the simulated and the measured values (see eq 6).[35]

$$OF_{Distillation} = \sum_{i=1}^{n} \left(\frac{D \text{ or } W_{Experiment} - D \text{ or } W_{Modeling}}{D \text{ or } W_{Experiment}} \right)^2$$

(6)

The prespecified purification requirements can be achieved in both laboratory and simulation cases as shown in Table 6. As it can be seen, low objective function values can be achieved due to the accurate assembly of laboratory apparatus. Furthermore, the laboratory experiments justified the accuracy of VLE data, especially ethanol−acetal measurements, which also proved to be valid under vacuum conditions.

3. CONCLUSIONS

VLE data for the ethanol−acetal binary system were measured using a modified Gillespie still. Experimental data were
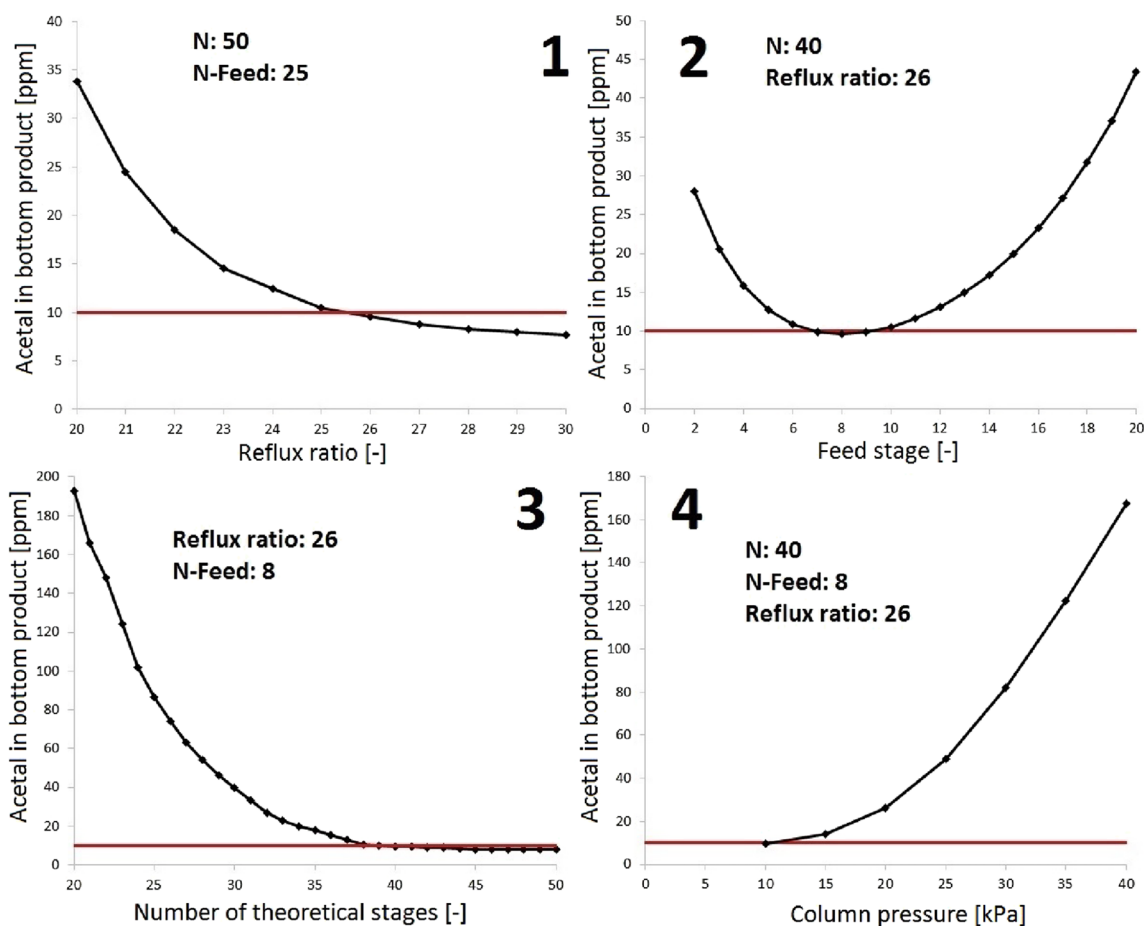

Figure 5. Optimization process of modeling of anhydrous ethanol purification.
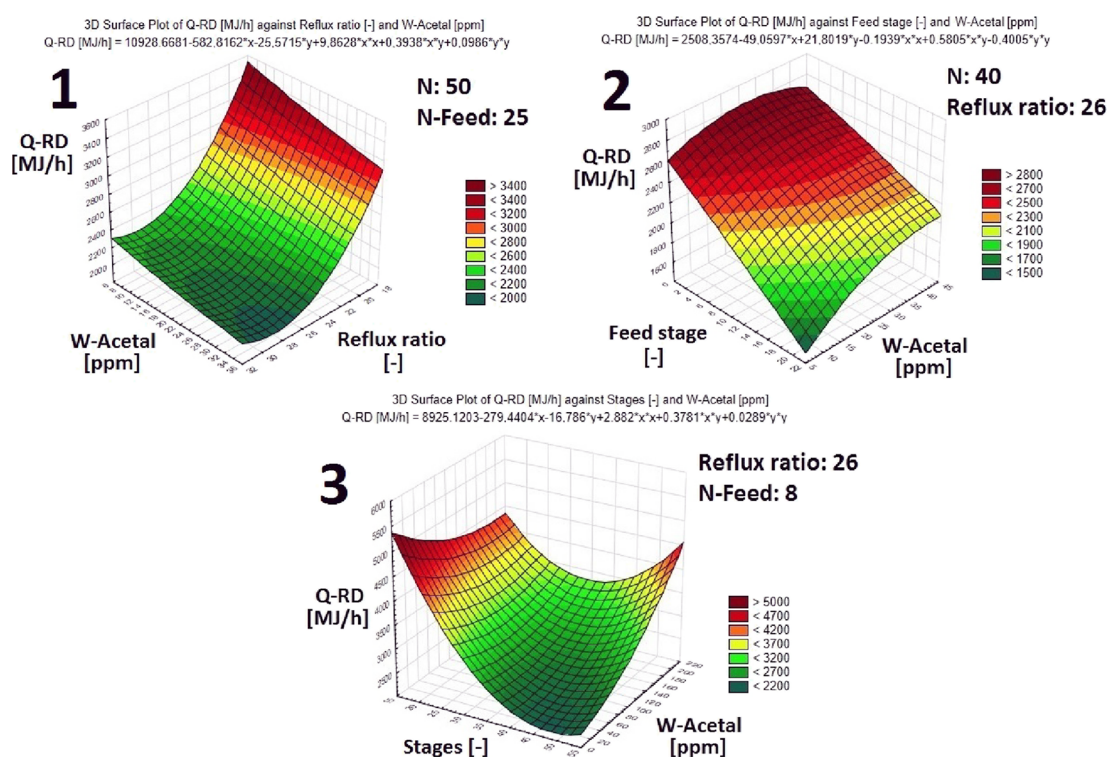
Figure 6. Influence of the reboiler duties [Q-RD (MJ/h)] and acetal concentration of the bottom product [W-Acetal (ppm)] on the reflux ratio [−] (1), feed stage [−] (2), and stages [−] (3)

Table 6. Comparison of Simulated and Measured Data of the Anhydrous Ethanol Purification Process

		modeling results		experimental results		OF-distillation	
	feed	distillate	bottom	distillate	bottom	distillate	bottom
ethanol [wt %]	99.79	98.22	99.97	98.21	99.97	3.25×10^{-9}	2.50×10^{-11}
methanol [ppm]	63.6	635.9	0.0	623.7	0.0	3.80×10^{-4}	0
acetal [ppm]	994.0	9853.7	9.6	9892.4	9.5	1.53×10^{-5}	8.40×10^{-5}
ethyl acetate [ppm]	41.1	410.5	0.0	402.6	0.0	3.84×10^{-4}	0
acetaldehyde [ppm]	278.3	2783.0	0.0	2794.8	0.0	1.80×10^{-5}	0
diethyl ether [ppm]	37.8	377.8	0.0	379.0	0.0	9.77×10^{-6}	0
isobutanol [ppm]	210.6	0.0	234.0	0.0	235.3	0	2.74×10^{-5}
stream [kg/h]	1000 and 3	100	900	0.3	2.7		
temperature [°C]	28.5	28.1	29.1	27.9	29.2	5.14×10^{-5}	1.17×10^{-5}
pressure [kPa]	10	10	10	10	9		

Table 7. Description of Chemicals Applied in This Work (MW: Molecular Weight)

chemical name	formula	MW [g/mol]	source	initial mole fraction purity	purification method	final mole fraction purity	analysis method
ethanol (1)	C_2H_6O	46.07	molar chemicals	0.9999			GC−MS
acetal (2)	$C_6H_{14}O_2$	118.17	sigma-aldrich	0.9800	distillation	0.9995	GC−MS
acetaldehyde	C_2H_4O	44.05	sigma-aldrich	0.9950	distillation	0.9999	GC−MS

correlated with Wilson, NRTL, and UNIQUAC models. It was demonstrated that acetal forms a minimal boiling azeotropic mixture with ethanol. The data were applied for the design of an ethanol purification unit. Pharmacopeial quality anhydrous alcohol can be produced with the vacuum distillation method. The pollutant content of the bottom product can be reduced below 300 ppm and for the most important compound, acetal, a value under 10 ppm can be reached. Evaluating the simulated and the experimentally measured data, it can be stated that almost perfect isolation can be guaranteed with the application of the best available laboratory devices. The other conclusion to be drawn is that close to 0% or to 100% we land in a dangerous

region where modeling becomes more important and special attention needs to be paid to the experimental work and analytics. It must be mentioned that there is consistency between the results of flowsheet simulations, distillation and VLE experiments, respectively.

4. MATERIALS AND METHODS

Before the examination of anhydrous ethanol purification, vapor−liquid measurements were performed. The VLE data of acetaldehyde−ethanol is already well known in the literature.[29] Therefore, this mixture was examined for the correct operation of the VLE still.

Table 8. Experimental and Literature Refractive Indexes (n_D) at 293.2 K of Pure Compounds Used and Antoine Constants

property	ethanol	acetal	acetaldehyde
n_D present work	1.3611	1.3805	1.3308
n_D literature	1.3613	1.3819	1.3316
n_D reference	37	38	39
Antoine constants[a]			
A	5.24677	4.7498	3.68639
B	1598.673	1573.964	822.894
C	−46.424	−43.681	−69.899
T-min [K]	292.77	250	293.4
T-max [K]	366.63	375.3	377.5
reference	40	41	42,43

[a]Antoine constants (bar, K) of ethanol, acetal, and acetaldehyde were calculated by NIST from literature data.

Table 9. Components of the Anhydrous Ethanol Sample with the Boiling Point of Pure Component at 101 kPa

substance	ppm-v/v	wt %	pure component boiling point [°C]
ethanol	-	99.79	78.4
methanol	64	8.05×10^{-3}	64.7
acetal	994	1.26×10^{-1}	102.5
ethyl acetate	41	5.20×10^{-3}	77.1
acetaldehyde	278	3.53×10^{-2}	20.2
diethyl ether	38	4.79×10^{-3}	34.6
isobutanol	211	2.67×10^{-2}	108.0
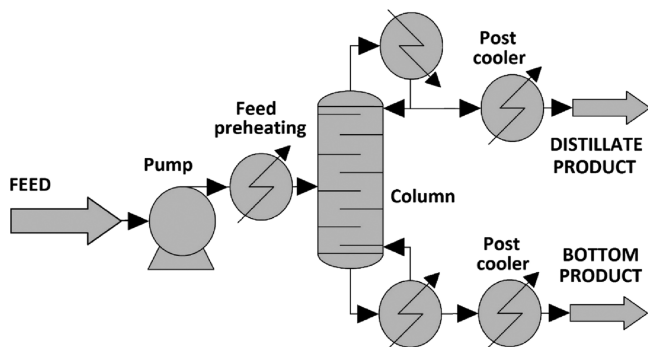
Figure 7. Flowsheet of anhydrous alcohol purification.

The properties of the commercially available chemicals used in VLE examination are introduced in Table 7. Ethanol was applied without further purification. Acetal and acetaldehyde were purified by vacuum distillation at a pressure of 27 kPa.

The VLE still is a modified Gillespie apparatus. An amount of about 100 mL of the appropriate mixture was added to the liquid container at the site of the top valve. For the heating of the mixture, an electric resistance wire was used, folded around the boiler tube. Through the Cottrell-pump, the vapor−liquid mixture was lifted into the thermometer well. Subsequently, the phases were directed into the equilibrium chamber, where their separation could occur, at an equilibrium state. The condensation of the vapor phase took place on the surface of the chamber and in the condenser, then the resulting condensate was transferred to the vapor sampler. The sample originating from the liquid phase was obtained at the site of the liquid sampler. For temperature measurement, a VWR Traceable Digital Thermometer (China) was used (223−573 K), presenting an uncertainty of 0.1 K. As for atmospheric pressure,
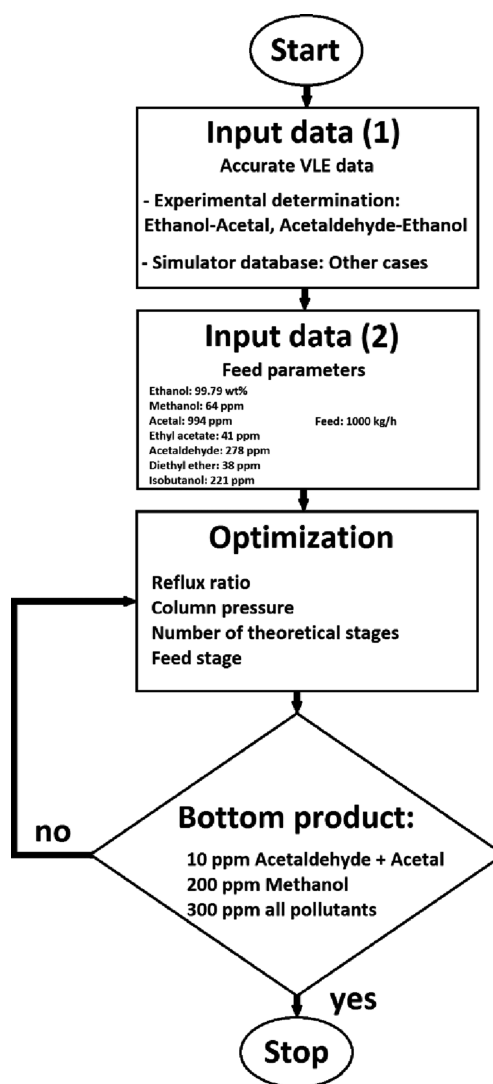
Figure 8. Flowchart of the optimization process of anhydrous alcohol purification.

the accuracy of the measurement was 1 kPa.[36] The atmospheric pressure was measured by a VACUUBRAND PC2003 VARIO (China) vacuum pump.

Refractive indexes were determined for the analysis of the equilibrium samples, three replications were applied. In addition, gas chromatography analysis was performed for certain equilibrium and calibration samples as a validation for the refractometric method.[36] A Carl Zeiss Abbe Refractometer (Type G) was applied for the analysis of refractive indexes. The accuracy of the refractometer was 0.0001 at 293.2 K, according to the manufacturer. Literature and experimental refractive indexes and Antoine constants of the used chemicals are listed in Table 8. As it can be seen, the experimental refractive indexes show good agreement with the literature data.

Table 9 contains the main compounds of the raw anhydrous ethanol sample.

The main purification requirements for the composition of pharmacopeial quality anhydrous alcohol are the following: 200 ppm in methanol, 10 ppm in acetaldehyde + acetal, 2 ppm in benzene, and 300 ppm in all pollutants.[13] It can be seen that more types of substances are above the prescribed composition.
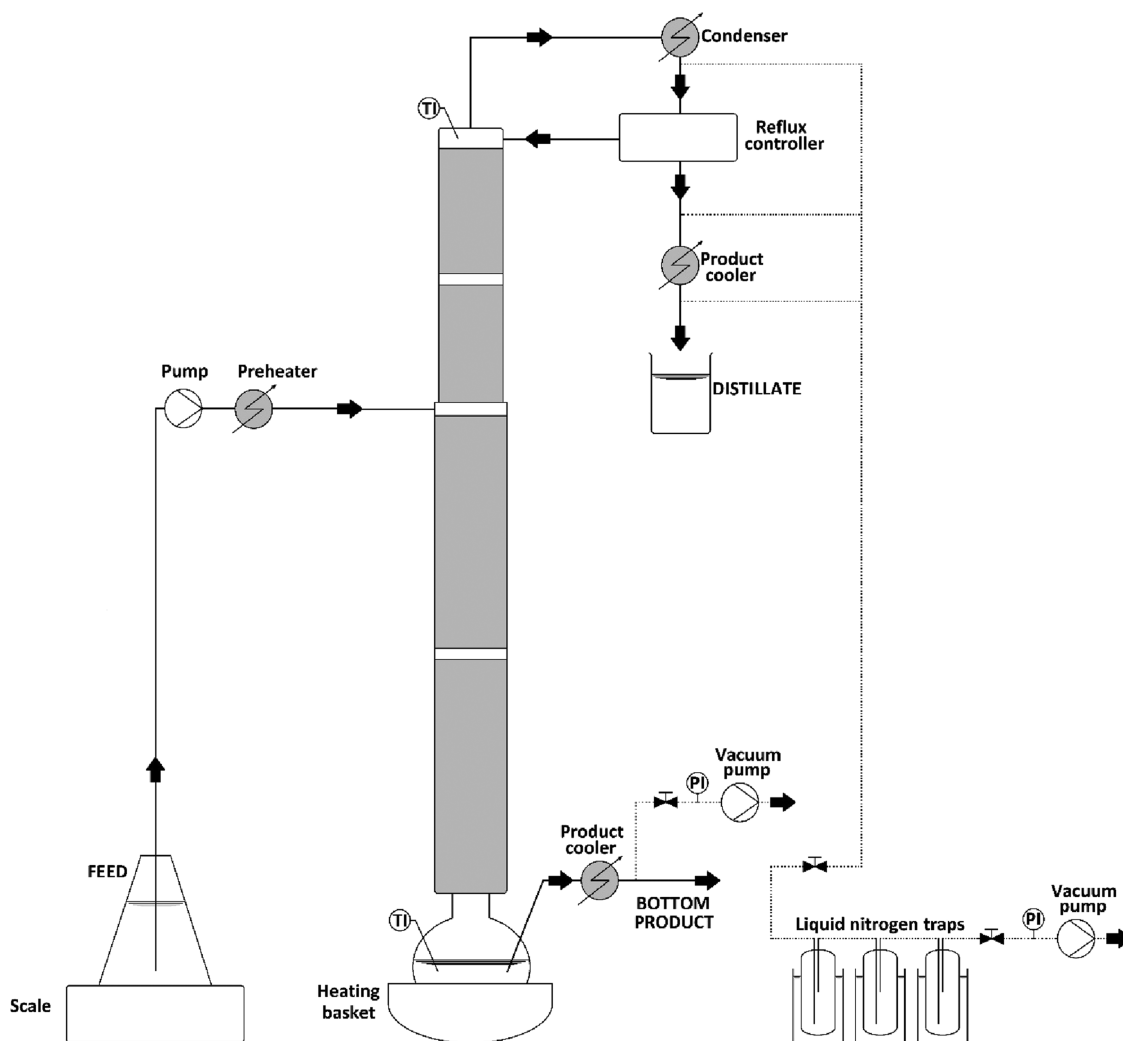
Figure 9. Laboratory demonstrative column for alcohol purification.

Distillation can be performed in discontinuous (batch) and continuous mode.[44−46] In the present study, the amount to be processed was relatively large (1000 kg/h) so continuous operation was recommended. The actual task was to remove polluting compounds and therefore to achieve a high-quality product. According to basic unit operation knowledge, a distillation column with a stripping section should be applied.[47] Therefore, considering the data in Table 9, it can be estimated in advance that the polluting compounds' removal results mainly in the distillate product and the bottom product contains the pharmacopeial anhydrous alcohol.

At first, flowsheeting simulations were carried out with the ChemCAD 7.1.5 program to get a comprehensive overview about the system and find promising alternatives. The optimal reflux ratio (thereby the distillate and bottom flow rates), column pressure, number of theoretical stages, feed stage, and heating and cooling requirements were also determined with the dynamic programming optimization method.[48−50] The investigated ethanol sample is considered highly nonideal, because it has more azeotropic binary pairs. As an equilibrium model for the calculation of highly nonideal vapor−liquid equilibria, the UNIQUAC method was applied.[51−54] Considering the vapor−liquid equilibria, that is, our modeling results obtained with ChemCAD, the separation of the ethanol sample can be

performed significantly better if vacuum distillation is applied. Figure 7 shows the flowsheet used for modeling the distillation.

Figure 8 summarizes the optimization process of anhydrous alcohol purification.

The modeling results were tested in a laboratory, under experimental conditions. The main parameters of the experimental column were the following: 1.5 m high and internal diameters of 25 mm (rectifying section) and 20 mm (stripping section) with Sulzer EX structured packing (see Figure 9). The column had 40 theoretical stages, according to the measurement carried out with an ethanol−water binary mixture. The feed was preheated and it was pumped into the eighth stage of the column. The column heating was controlled with a heating basket (300 W). The vacuum was maintained with a VACUUBRAND PC2003 VARIO vacuum pump and kept at 10 kPa. Another vacuum pump was also used for bottom product removal and kept at 9 kPa. The distillation apparatus was collected in three traps connected in series and cooled with liquid nitrogen to prevent the evaporation and loss of the distillate product. The reflux ratio was maintained with a Bertolt reflux controller.

As a startup procedure of the experiments, batch distillation was first carried out to obtain a relatively pure liquid satisfying the purity prescriptions in the reboiler.[13] Afterward, continuous

mode was used until a steady-state (constant output flows and temperatures) operation was achieved.

The content of the feed (F), distillate (D), bottom product (W), and traps were measured with a Shimadzu GC2010Plus + AOC-20 autosampler gas chromatograph with a ID-BP1 (60 m × 0.32 mm, 1.0 μm) column using helium as the carrier gas. The column temperature was kept at constant 60 °C while the injector was thermostated to 250 °C and MS ion source temperature was set to 250 °C. Pressure of the helium carrier gas (with 5.0 purity) was kept at 90 kPa. The results were the average of three analyses in the analytical method.[55]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04750.

Experimental equilibrium data and $y-x$ diagram and $T-y-x$ diagram for the acetaldehyde (1)−ethanol (2) system (PDF)

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Notes

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■ ABBREVIATION

Nomenclature

B_{ij}, B_{ji}	Dimensionless interaction parameters (NRTL model)
D	Distillate product
D_H	Parameter for Herington consistency test
F	Feed
J_H	Parameter for Herington consistency test
MW	Molecular weight
N	Number of theoretical stages
n_D	Refractive index
OF	Objective function
p	Pressure [kPa]
p_i^*	Partial pressure of component i [Pa]
Q	Area parameter (UNIQUAC model)
Q-RD	Reboiler duty [MJ/h]
R	Volume parameter (UNIQUAC model)
T	Temperature [°C; K]
ΔU_{ij}, ΔU_{ji}	Binary interaction parameter (UNIQUAC model)
VLE	Vapor−Liquid Equilibrium
W	Bottom product
wt %	Weight percent
x	Liquid mole fraction
y	Vapor mole fraction

Greek letters

α	Constant characteristic of the nonrandomness of the mixture (NRTL model)
γ_i	Activity coefficient
λ_{12}, λ_{21}	Adjustable parameters (Wilson model)

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