

Comparison of Various Column Packing Materials' Efficiency for Hydrocarbons and Aqueous Mixtures



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<https://doi.org/10.15255/CABEQ.2018.1565>

Original scientific paper
Received: December 20, 2018
Accepted: June 6, 2019

The efficiency of industrial column packings is commonly tested by standard hydrocarbon mixtures. However, a reduced efficiency value is often observed, particularly during distillation of aqueous mixtures. In this paper, distillation experiments with various binary mixtures were carried out on different column packings to evaluate relative separation efficiencies of mixtures for each packing material. Each of the binary mixtures, which comprised heptane–methylcyclohexane, ethanol–water, morpholine–water, and acetic acid–water, was distilled under atmospheric pressure and total reflux ratio on column packings that were made of PTFE, ceramic, zirconium metal, and inox steel 316. According to the results, aqueous solutions of morpholine and acetic acid generally exhibited low relative separation efficiency (in comparison with standard mixture of heptane–methylcyclohexane), ranging between 40 % and 80 %. The highest relative efficiencies were observed with packings made of steel and ceramic. These observations will be useful for the future design of distillation columns, especially for aqueous solutions.

Keywords

hydrocarbons, acetic acid, distillation, column packing

Introduction

Distillation represents one of the most important separation processes in chemical production. Separation efficiency of a column packing is often quantified by the height of equivalent to a theoretical plate (HETP) value, which is usually quoted by column packing manufacturers. In order to reach high column separation efficiency (low HETP value), it is necessary to choose such column packing that ensures intensive mass transfer between phases, but at the same time does not limit column capacity too much.

Separation efficiency of distillation column packings is commonly tested by using standard mixtures of hydrocarbons, such as heptane–methylcyclohexane. These mixtures generally exhibit high wettability, therefore, high separation efficiency is observed. However, many other mixtures do not achieve the specified efficiency value – the separation is especially difficult for aqueous solutions, which generally have very low wettability, leading to a reduced interphase surface between liquid and vapor phases.

This observation can be explained by surface interactions between phases. A relevant quantity to

describe them is the surface tension (σ) – liquids with high σ value tend to cluster into drops and rivulets instead of spreading out into a thin film. No less important is the gradient of surface tension, which is defined in the direction of liquid phase flow – a system is defined as surface tension positive when the more volatile compound has a lower σ value. Analogically, systems are defined as surface tension neutral or negative according to the σ gradient. A positive σ gradient improves mass transfer due to the Marangoni effect¹, the influence of which on distillation efficiency is described in literature – surface tension positive systems generally exhibit higher separation efficiency, while surface tension negative systems show a lower efficiency^{1–4}.

Although the influence of σ on separation efficiency is well proven, this quantity only describes the vapor–liquid interaction without regard to the packing material, and therefore, it cannot be used for correlation of separation efficiency on different packing materials. A more suitable quantity is the contact angle, which has been studied many times as a parameter in distillation efficiency. For example, addition of a surfactant lowers surface tension and contact angle, which leads to enhanced separation efficiency^{5,6}. A chemical treatment of column packing surface can be used to achieve the same result^{7,8}. However, while experimental data for surface tension of binary mixture are plentiful in liter-

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ature, data for contact angle are scarce considering the wide range of possible materials, especially with development of new materials for column packings.

In order to find the most suitable packing material for industrial distillation columns, it is necessary to consider not only their HETP value, but also technological aspects, such as corrosion resistance in the specified environment and mechanical stability. Naturally, price and availability on market are also pivotal parameters.

The main part of this work is to compare separation efficiencies of different mixtures on different column packings, while acetic acid–water mixture will receive special attention, with the aim to study the influence of surface interactions on distillation of aqueous mixtures. These findings can then be used for design of industrial distillation columns.

Experimental

Chemical samples

Five standard mixtures were prepared using the chemicals listed in Table 1. Heptane–methylcyclohexane is a representative of hydrocarbon mixtures, and since it is a common standard for measurements of column packing HETP values, it has also been chosen as a reference mixture. Ethanol–water mixture was chosen as a representative of a surface tension positive system. Special attention has been given to surface tension negative systems, which are represented by a morpholine–water mixture and two acetic acid–water mixtures with different compositions. Details on the prepared mixtures are summarized in Table 2. Compositions of the mixtures were chosen with regard to expected compositions in reboiler and distillate – in order to ensure precise determination of the number of theoretical plates, molar fraction of the more volatile compound should not be too close to 0 in reboiler, or too close to 1 in distillate (or the azeotrope in case of ethanol–water mixture). In case of the acetic acid–water system, two mixtures were prepared with different compositions, so the effect of different wettability could be assessed.

Column packing materials

Distillation column packings are made of various materials. In this work, five types of materials were used – polytetrafluoroethylene (PTFE), zirconium metal, inox steel 316, and 2 ceramic materials. The shape and characteristics of the column packings are listed in Table 3, along with elemental compositions of selected materials, which were acquired using X-ray fluorescence spectrometry. Only elements with mass fraction above 0.1 % are listed.

Table 1 – *Chemical samples*

Compound	Source	Purity
Water	UCT Prague	Distilled
<i>n</i> -Heptane	Penta	p. a., min. 99.0 %
Methylcyclohexane	Merck	Reagent grade, min. 99 %
Acetic acid	Penta	p. a., 99.0 %
Ethanol	Penta	p. a., min. 99.8 %
Morpholine	Sigma-Aldrich	Reagent grade, min. 99 %

Table 2 – *Composition (molar fractions) of mixtures used to determine the relative efficiency of column packings*

Mixture	Molar fraction (1)
Heptane (1)–Methylcyclohexane (2)	0.161
Ethanol (1)–Water (2)	0.148
Water (1)–Morpholine (2)	0.302
Water (1)–Acetic acid (2) I.	0.599
Water (1)–Acetic acid (2) II.	0.300

Table 3 – *Characteristics of the materials used as column packings*

Material	Shape	Description
PTFE	Raschig rings	Inner diameter 4.0 mm, thickness 1.0 mm, length 6.0 mm
Ceramic ^a	Berl saddles	Characteristic length 4.4 mm
Zirconium metal	Raschig rings	Inner diameter 6.5 mm, thickness 1.4 mm, length 8.0 mm
Inox steel 316	Dixon rings	Diameter 6 mm, length 9 mm
"Flexeramic" ceramic ^b	Irregular fragments	Ground oriented packing Flexeramic (thickness 2.5 mm). Sieved to obtain fraction with characteristic length 3.15 – 8.0 mm.

Elemental compositions of materials (wt. % normalized to exclude oxygen):

^aSi 67.1 %, Al 20.3 %, K 6.9 %, Na 1.8 %, Fe 1.6 %, Ca 1.0 %, Ti 0.4 %, Mg 0.3 %, P 0.2 %

^bSi 56.8 %, Al 24.7 %, K 7.2 %, Fe 5.9 %, Ti 2.3 %, Ca 0.9 %, Mg 0.8 %, Na 0.4 %, Ba 0.2 % Sr 0.2 %

Apparatus and procedures

Distillation experiments were carried out for each column packing material with all the standard mixtures. The batch distillation column consisted of a directly heated round-bottom flask as a reboiler, a

total condenser at the top and a double-coated heated column 90 cm high and 30 mm in diameter. Reboiler heater power was measured by a wattmeter (EMOS FHT 9999) in order to set a specific power value. Heating of column surface was manually regulated to ensure that the temperature of column surface was between temperature of reboiler and condenser to minimize heat loss. Experiments were carried out under total reflux and atmospheric pressure. Pairs of samples from reboiler and distillate were acquired after an hour to ensure steady state. During collection of distillate samples, time and mass were measured in order to calculate the mass flow rate of the distillate. After the acquisition of samples, the procedure was repeated to check the data for reproducibility, and then a different reboiler power was set. Three power values were measured during each experiment. Maximal power value was set to prevent flooding of the column, while the minimal value was determined by need for sufficient distillate flow rate, which means sufficient flow to ensure reliable measurement of flow rate as well as sufficient power to cover the heat loss – given small enough flow rate, the temperature in condenser would drop far below the expected value, indicating premature condensation. Ranges of power differed greatly, mainly due to different enthalpy of vaporization for various mixtures, but also due to different flow properties of column packings.

Sample analyses

Various analytical methods were used to measure compositions of different mixtures. Samples of hydrocarbon mixtures (heptane–methylcyclohexane) were analyzed using gas chromatography with a flame-ionization detector (GC-FID). Samples of aqueous mixtures were analyzed using gas chromatography with a thermal-conductivity detector (GC-TCD). Parameters of the analytical procedures are summarized in Table 4. The results acquired from chromatograms were then converted from peak area percentages to molar fractions using calculated calibration coefficients. Those were obtained by analyses of standard mixtures of known compositions, that had been prepared beforehand using a HR-200-EC (A&D Instruments Ltd.) analytical balance.

Karl-Fischer titration was also applied to all aqueous mixtures to determine water content. These analyses were performed using TitroLine Alpha (Schott Instruments) automatic titrator with “Hydranal composite 5 K” mixture (Honeywell) as a titrant. Additionally, samples of acetic acid mixtures were analyzed by alkalimetric titration using sodium hydroxide as a titrant and phenolphthalein as the equivalence point indicator. Several experiments were performed before with both the indicator and

Table 4 – Parameters of GC procedure

	GC – FID	GC – TCD
Chromatography system	Shimadzu GC-2010	Shimadzu GC-17A
Operating software	Clarity (DataApex)	Clarity (DataApex)
Column	DB-5 (J&W Scientific)	DB-WAX (J&W Scientific)
Column length	60 m	30 m
Column inner diameter	0.32 mm	0.32 mm
Film thickness	1 μm	0.25 μm
Column temperature	100 °C	60 °C ^a , 90 °C ^{b,c}

^aethanol – water system, ^bmorpholine – water system, ^cacetic acid – water system

potentiometric measurement to confirm accuracy of the phenolphthalein indication. All of the three analytical methods were found to be in good agreement. All analyses results were then processed to pairs of molar fractions in reboiler and distillate, defined for the more volatile compound.

Calculations

Using the data from analyses, the number of theoretical plates (NTP) was calculated for each reboiler-distillate pair. For that purpose, McCabe-Thiele method⁹ was implemented in MATLAB computing environment.

Such calculation requires a function $y = f(x)$ that describes vapor-liquid equilibrium (VLE) for the specific binary system at standard pressure (atmospheric pressure). To acquire such functions, binary interaction parameters (BIPs) had to be calculated based on experimental data published in the literature. For the calculation of BIPs, the Aspen Plus simulation program was used. The VLE can be expressed by various equations that describe non-ideal behavior of substances in liquid phase, which is quantified by activity coefficient values. In this study, activity coefficients were calculated using the NRTL equation¹⁰, which calculates activity coefficients based on the excess Gibbs free energy, and the model is specified in this paper as follows:

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right) \quad (1)$$

$$\text{where } \tau_{ij} = a_{ij} + \frac{b_{ij}}{T}; G_{ij} = \exp(-\alpha_{ij} \tau_{ij}),$$

where T represents thermodynamic temperature, τ_{ij} represents the dimensionless interaction parameters that are calculated from BIPs a_{ij} and b_{ij} for compo-

nents i and j , γ_i represents the activity coefficient of the i component, x is the molar fraction in the liquid phase, and G represents a coefficient dependent on an adjustable parameter α_{ij} and τ_{ij} .

Non-ideal behavior of the substances in the liquid phase is common due to formation of clathrates by the H-bonds. Moreover, systems such as aqueous solutions of carboxylic acids behave non-ideally even in vapor phase, mostly due to the formation of carboxylic acid dimers as well as combined dimers of water and carboxylic acid. The vapor phase non-ideality is quantified using the fugacity coefficient. In order to describe the VLE for the acetic acid–water system, Hayden-O'Connell theory¹¹ was used in this work to calculate the values of fugacity coefficients. In case of the remaining systems, vapor phase was described as an ideal gas.

To describe the column load, F -factor was calculated for each sample pair via the following equation:

$$F = u_v \sqrt{\rho_g} \quad (2)$$

where u_v is vapor velocity calculated using the measured mass flow rate, and ρ_g is vapor density (estimated using distillate temperature and its composition throughout the experiment)¹².

Results and discussion

Correlation of VLE data

The experimental VLE data were exported from literature for following systems – heptane–methylcyclohexane^{13–15}, ethanol–water^{16–22}, morpholine–water^{23–25}, and acetic acid–water^{26–31}, and fitted afterwards by NRTL model to reach a good conformity between the data and the model. The α parameter was manually set to the value of 0.3, which can be done for mixtures with small deviations from ideality in liquid phase while maintaining a good fit¹⁰. However, in order to fit the data accurately for ethanol–water system, all parameters were calculated, including α . The BIPs of the NRTL model for all the systems are listed in Table 5, while Table 6 contains calculated parameters of the Hayden-O'Connell model only for the acetic acid–water system. The original data as well as the calculated functions are shown in Figs. 1–4.

Table 5 – Binary interaction parameters of NRTL correlation model for all measured systems

Mixture	a_{12}	a_{21}	b_{12} (K)	b_{21} (K)	α_{12}
Heptane (1)–Methylcyclohexane (2)	20.45	–0.658	–7304.05	–9.58	0.30
Water (1)–Ethanol (2)	11.06	–7.780	–3243.04	2707.98	0.32
Water (1)–Morpholine (2)			–251.34	552.83	0.30
Water (1)–Acetic acid (2)			422.48	–115.33	0.30

Table 6 – Parameters of Hayden-O'Connell correlation model for the acetic acid–water system

Mixture	1-1	1-2	2-2
Water (1)–Acetic acid (2)	1.7	2.5	4.5

Relative efficiencies of column packings

A series of distillation experiments were performed with five binary mixtures on five column packings. Each experiment provided two samples gathered for three given values of reboiler power, which were analyzed using various methods. For each sample pair, the number of theoretical plates (NTP) was calculated using the McCabe-Thiele method⁹. A graphical illustration of the algorithm is shown in Fig. 5.

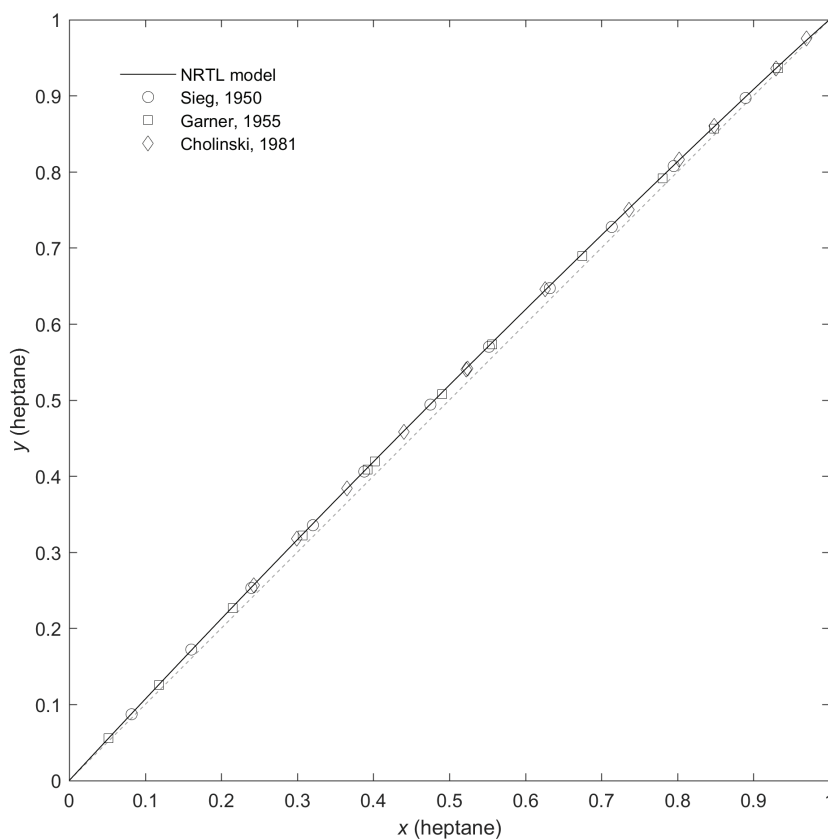


Fig. 1 – VLE data and NRTL model for the heptane–methylcyclohexane system^{13–15}

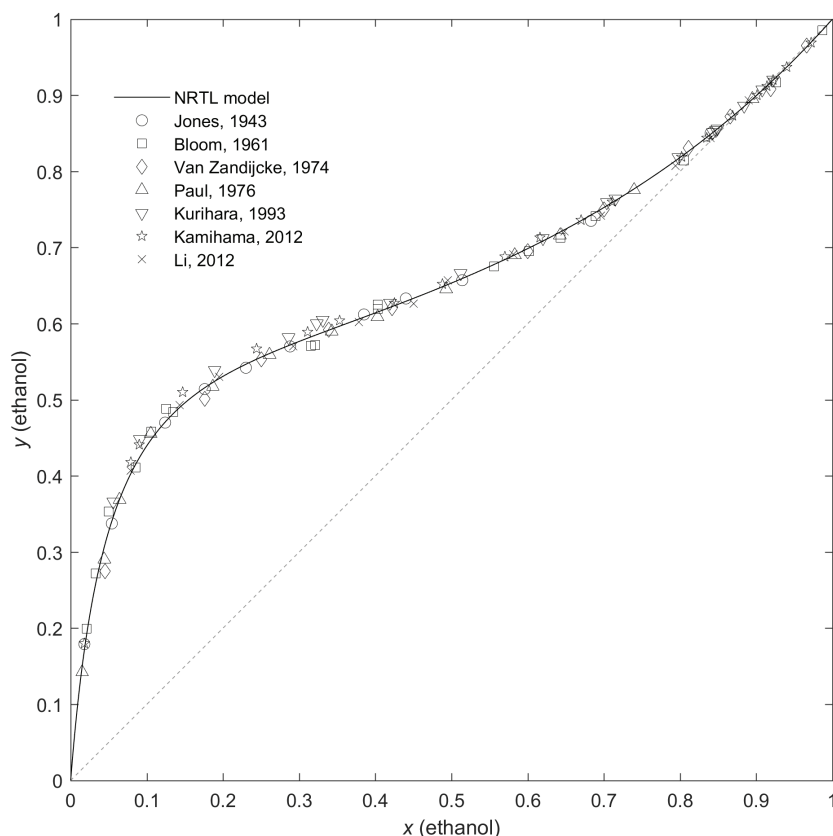


Fig. 2 – VLE data and NRTL model for the ethanol–water system^{16–22}

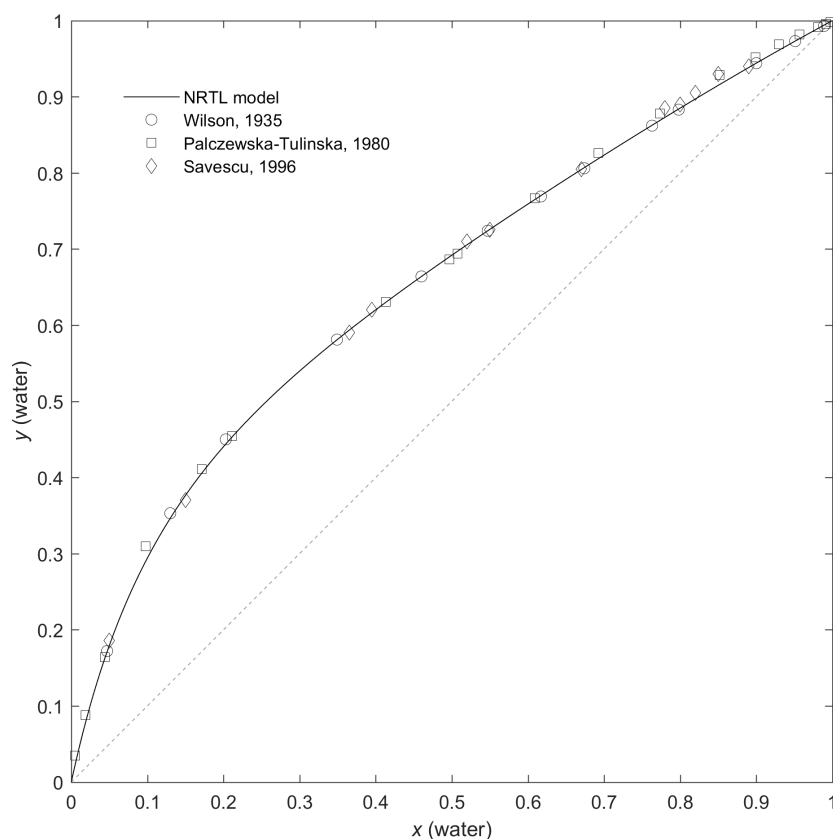


Fig. 3 – VLE data and NRTL model for the morpholine–water system^{23–25}

When multiple analytical methods were used, NTP value was calculated for each molar fraction pair, and the average value was considered to be the final result. As expected, the NTP value has been found to slightly decrease with increasing F-factor on all of the measured column packings. This is a common behavior due to the fact that F-factor is proportional to vapor velocity.

Because separation efficiency not only depends on column packing material, but also on the geometry of the packing (such as specific surface area), relative efficiencies were calculated, and are listed in Table 7. For each experiment, the average NTP value was calculated. Relative efficiency for each experiment was then obtained by dividing the average NTP by the average NTP of the reference mixture (heptane–methylcyclohexane) on the same column packing. The relative efficiency is expected to be independent of packing geometry, and describes the affinity of the mixture to the packing material. Even though the same mixture exhibits different NTP values on different column packings due to their specific geometrical parameters, ratios of NTP between different mixtures on the same column packing are expected to be the result of different wettability, and therefore, characteristic for the material and mixture.

According to the results from Table 7, the last three mixtures generally exhibit low separation efficiency. Those are the systems with water as the more volatile compound, and are all surface tension negative^{32,33}. Steel appears to have the highest separation efficiency for distillation of those mixtures, followed by ceramic, as both ceramic packings achieved similar, very high relative efficiency values. Although slightly lower values were observed for PTFE, it could still be considered for use due to its relatively low price. Zirconium metal was evaluated as the least suitable packing material not only due to the very low separation efficiency, but also because it is very expensive. Inclusion of zirconium in the experiments was motivated by its very high corrosion resistance, which is crucial for distillation of highly corrosive aqueous mixtures. This also means that steel is

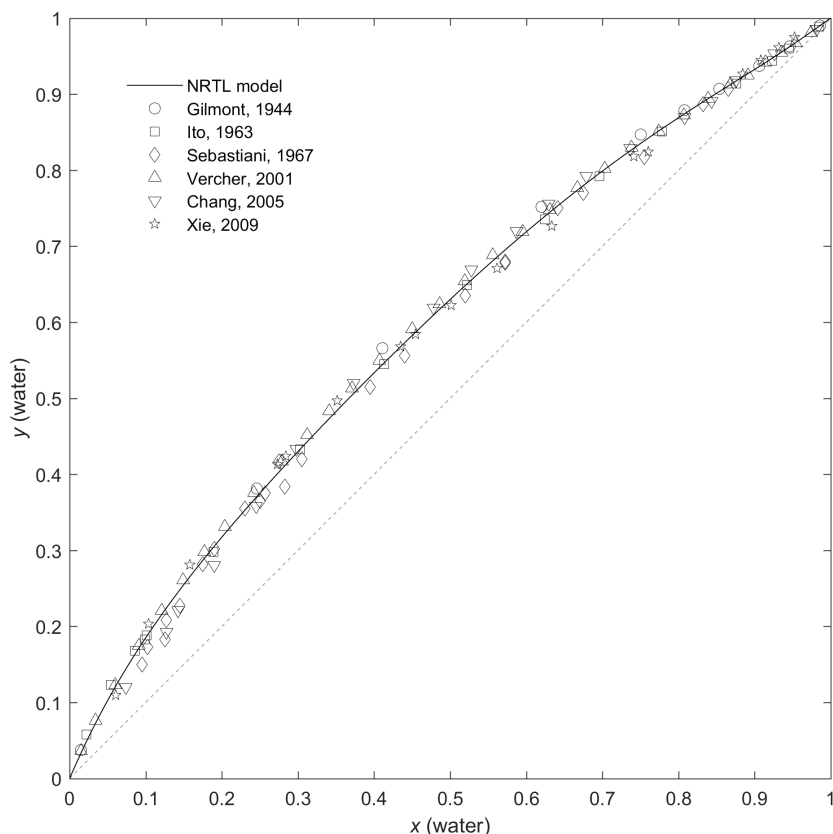


Fig. 4 – VLE data and NRTL model for the acetic acid–water system^{26–31}

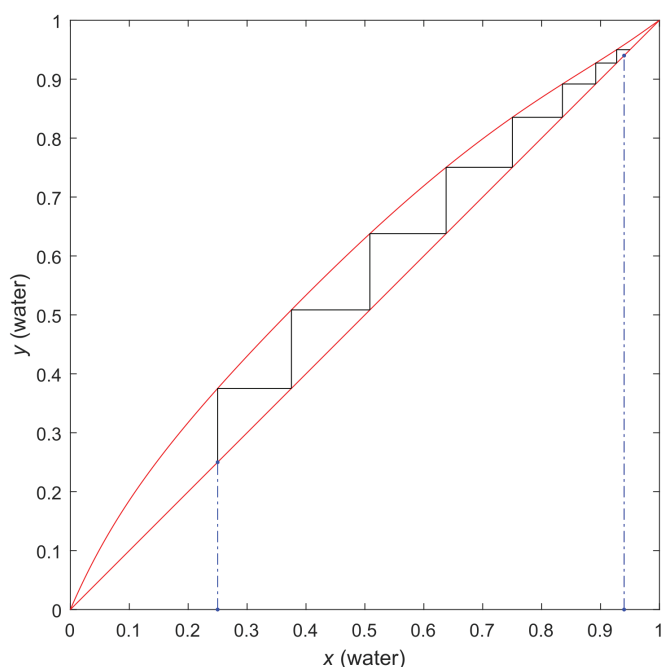


Fig. 5 – Illustration of the algorithm for NTP calculation using example data (acetic acid–water mixture). In this case, the NTP value is 7.6.

ruled out as a viable packing material for distillation of carboxylic acids.

The zirconium packing has been found to be the most efficient packing for ethanol–water distil-

lation. This mixture is a surface tension positive system³⁴, and is therefore easier to separate via distillation. However, determination of NTP for ethanol–water samples was typically quite inaccurate due to strong non-ideal behavior – although the experimental VLE data from literature are consistent and the NRTL model fits them well, the distillate samples were typically very close to the azeotropic point. Therefore, even a small deviation in analysis result would cause a major difference in calculated NTP.

Heptane–methylcyclohexane, the reference mixture, is expected to have perfect wettability, but its separation efficiency is consistently lower than that of ethanol–water mixture. This observation could be explained by the surface tension gradient – heptane–methylcyclohexane is a surface tension neutral system³⁵, while ethanol–water system is strongly surface tension positive.

Conclusions

Distillation experiments with different mixtures on various column packings were conducted to investigate relative separation efficiencies, specifically to determine the most suitable column packing for distillation of aqueous mixtures with water as the more volatile compound. Those mixtures are usually surface tension negative systems, and have generally shown very low relative efficiencies, while steel and ceramic were determined as the best packing materials for distillation of such mixtures. Ethanol–water mixture, a surface tension positive system, generally exhibited high separation efficiency, which agrees with theory. The experimental VLE data were extracted from literature and subsequently fitted by NRTL model, which describes the non-ideal behavior in liquid phase. The binary interaction parameters of NRTL model

Table 7 – Relative efficiency percentage values of studied column packing materials for various mixtures

Mixture	PTFE rings	Ceramic saddles	Zr rings	Flexe-ramic	Steel rings
Heptane–Methylcyclohexane	100	100	100	100	100
Ethanol–Water	102	137	206	151	140
Morpholine–Water	61	57	62	67	76
Acetic acid–Water I.	36	65	43	48	55
Acetic acid–Water II.	64	64	60	69	82

obtained in this work can be used for further measurements of column packing efficiencies. The assumption of lower separation efficiency for aqueous mixtures has been confirmed and quantified using relative efficiency values. These findings are very important for the design of industrial distillation columns.

Abbreviations

HETP	– height equivalent to a theoretical plate
PTFE	– polytetrafluorethylene
y	– molar fraction of the more volatile compound in vapor phase
x	– molar fraction of the more volatile compound in liquid phase
NTP	– number of theoretical plates
NRTL	– non-random two-liquid (model of activity coefficients)
BIPs	– binary interaction parameters
VLE	– vapor-liquid equilibrium
GC-TCD	– gas chromatography with a thermal-conductivity detector
GC-FID	– gas chromatography with a flame-ionization detector

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