

## MINIPLANT IN MODELLING DISTILLATION FOR AN ISOCTENE PROCESS

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The paper presents the use of a miniplant scale distillation column for modelling a distillation process for isooctene production. The development of an accurate VLE model and the model for a miniplant scale distillation column are described.

The industrial importance of isooctene has been given a boost recently, when US legislation has banned the use of methyl-*tert*-butyl ether (2-methoxy-2-methyl propane, MTBE) as a gasoline component in certain states. Isooctane, the hydrogenation product of isooctene, is one of the most prominent alternatives for MTBE substitute, having octane number 100 by definition.

KEYWORDS: isooctane, isooctene, TBA, water, miniplant, simulation, distillation, VLE

### INTRODUCTION

Scale-up often relies essentially on construction of a series of plants of increasing size starting from the laboratory scale until the full production scale has been achieved. This approach is time consuming and costly.

The model-based approach is based on constructing a mathematical model of the process. Only experiments necessary for collecting physical and chemical data not available from other sources are performed. After gathering all necessary data, a model of the whole process is set up and the plant is designed and optimized as a model using a computer thus the costly and time consuming construction and operation of pilot plants is avoided.

The miniplant concept tries to combine the best properties of both these development routes. In the approach a substantial part of the process development is based on modelling. Then a pilot-plant as small as possible for achieving meaningful results is constructed and the validity of the models applied are tested against the achieved results [1]. Currently the size of miniplant is between laboratory scale and pilot scale equipment, typical feed being 0.2–3 kg/h. Miniplant hardware costs, as well as utility and chemical costs are usually moderate which makes the technology available for e.g. universities and small research institutes. Also safety issues are more easily handled with small-scale equipment [2].

The paper presents the use of a miniplant scale distillation column for modelling a distillation process for isooctene production. The development of VLE model process and the model for a miniplant scale distillation column are described.

The industrial importance of isooctene has been given a boost recently, when US legislation has banned the use of methyl-*tert*-butyl ether (2-methoxy-2-methyl propane, MTBE) as a gasoline component in certain states [3,4]. Isooctane, the hydrogenation product of isooctene, is one of the most prominent alternatives for MTBE substitute, having octane number 100 by definition [5]

### VAPOR-LIQUID EQUILIBRIUM MODEL

Isooctene is here produced by dimerising isobutylene. Tri- and tetraisobutylenes are formed as side products [6]. The feed to the reactors consists of ~40 % isobutylene, the rest being short (C3-C5) aliphatic or olefinic hydrocarbons. *Tert*-butyl alcohol (2-methyl-2-propanol, TBA) is used in the feed as selectivity controlling agent [7]. Without TBA, the reaction kinetics favor forming larger, C12 and C16 oligomers of isobutene [8].

The product stream from the reactor train, which in addition to the feed components has oligomers of isobutylene in it, is led to the distillation column [9]. The desired product(s), the oligomers, are separated from lighter hydrocarbons, TBA and water, that has formed as a product of TBA decomposition. TBA and unreacted isobutylene are recycled back to the reactor train, whereas the light C3-C4 hydrocarbons are purged out of the system from the top of the column. See Figure 1 for a schematic of the distillation column of the process. The need for accurate VLE model arises from the fact that the recycle stream composition must be precisely predicted.

### EXPERIMENTAL

Two types of apparatus were used in this work for the VLE measurements: circulation still [10] and an apparatus utilizing the static total pressure method [11].

The most important binary vapour liquid equilibrium data for accurate process simulation were determined as the TBA-systems: TBA + alkanes, + alkenes, + water. For most TBA + hydrocarbon systems, VLE-data were not available in the literature. Also the reliability of the measurements was in some cases questionable. From the measurements available and the UNIFAC [12] predictions it could be seen in advance that the TBA + water containing systems to be studied were highly non-ideal. For the ideal hydrocarbon + hydrocarbon systems UNIFAC was used. For the hydrocarbon + water systems, infinite dilution activity coefficient data found in the literature were used [13]. The data sources for the different binary TBA-systems are presented in Table 1.

Published TBA + hydrocarbon data were also utilized in the regression. Hydrocarbon + hydrocarbon interactions are almost ideal. For the water + TBA system, both VLE and excess enthalpy data published in the literature were used. For the regression of hydrocarbon + water activity coefficient model parameters, infinite dilution activity coefficient data from [13] were used. The literature study led to the conclusion that measurements were needed for 6 binary systems, TBA + 2,4,4-trimethyl-1-pentene [11,14], 2-methylpropene [15], *cis*-2-butene [16], *trans*-2-butene [17], 2-methylpropane [36] and *n*-butane

**Table 1.** Literature references for VLE data for selected TBA + hydrocarbon binaries

TBA+	2,4,4-trimethyl-1-pentene	11,14
	2-methylpropene	15
	2-methylpropane	36
	2-methylbutane	32
	Water	33–35

The circulation still was used for the measurements of TBA + 2,4,4-trimethyl-1-pentene system. For the TBA + C4 components a static total pressure method was utilized. The results from measurements for TBA + n-butane binaries are yet to be published.

#### PARAMETER FITTING

The Soave-Redlich-Kwong equation of state with quadratic mixing rule for the attractive parameter and a linear mixing rule for the covolume parameter for the evaluation of vapour phase fugacity coefficients was used [18]. The binary interaction parameter in the quadratic mixing rule was set to zero. The liquid phase was modelled with the temperature dependent Wilson equation [19]. For the use of Wilson method, linear temperature dependent binary parameters were fitted for each component binary in the component matrix.

Absolute or relative differences between measured and calculated pressures were used as objective function for Nelder-Mead – Simplex [20] and Davidon [21] optimization algorithms.

Critical temperatures, critical pressures, acentric factors and liquid molar volumes were acquired from the DIPPR database [22]. The vapor pressure equation parameters were chosen through comparing the measured values and the values calculated from different sources. The vapor pressure values calculated from the DIPPR correlation were closest to our measurements and were thus chosen to represent the vapour pressure behaviour, except for the 2,4,4-trimethyl-1-pentene, for which the Antoine equation was used.

#### RESULTS

One way of comparing VLE models is to look at predicted azeotropic compositions for component binaries at different temperatures and pressures. This is done here for the following binaries that are known to present azeotropic behavior: TBA – water and TBA – TMP-1. Both of these azeotropes are important for the operation of this particular distillation system.

The azeotropic composition for water and TMP-1 ranging from 50 °C to 200 °C were compared made with Wilson method and UNIFAC were compared to the measured azeotropic compositions found from literature [23,24,11].

For TMP-1 – TBA–binary, the prediction of Wilson method follows measured values closely. At moderate temperatures, UNIFAC prediction approaches the Wilson predictions. At higher temperatures the predictions differ significantly from each other.

For water – TBA, azeotropic curve determined by Wilson method follows quite closely the average of literature azeotropic data. The shape of the *azeotropic composition* (mol-%) vs. *T*-curve is similar for Wilson method and UNIFAC, but UNIFAC predicts 5–10 mole % higher compositions for water than Wilson.

TBA – isopentane (2-methylbutane, IP) binary is reported [25,32] to present azeotropic behaviour. However, this is not of great importance to our column simulations due to our process conditions.

### DISTILLATION COLUMN

The distillation column is part of the miniplant system constructed in the Helsinki University of Technology, at Laboratory of Chemical Engineering and Plant Design. The column ( $\varnothing_{ID} = 39.4$  mm) consists of compatible, 25 cm and 50 cm long packing units. The main packing are stainless steel springs (height = 4 mm,  $\varnothing = 4$  mm). A 2 cm layer of Intalox saddles (height = 10 mm, width = 11 mm,  $\varnothing = 6$  mm) was used in the ends of the packing units between wire mesh (6 mm) and springs to prevent the springs from penetrating through the mesh. There was also a 2 cm long, empty space at the ends of all packing units. All packing units have two pockets for temperature measurement probes.

The reboiler is heated using an electrical heater with freely adjustable power (0..1 kW). Temperature and pressure ranges are 1..2.5 MPa and 0..250 °C, respectively.

The condenser used is a cross flow condenser.

There is a possibility to use 14 temperature and two online pressure measurements inside the column. Flow rates in and out of the system are measured using scales. All data can be stored. Liquid level in reboiler is monitored visually.

### COLUMN MODEL (HETP, HEAT LOSSES, PRESSURE DROP)

We did not find adequate correlations for the mass transfer coefficients or NTUs for our packing (small springs) thus the modern simulation models to calculate real plates of the columns could not be used. By these methods is meant the rate based model [28,29] or methods based on calculation of binary NTUs (number of transfer units) along with calculation of Murphree point efficiency from these NTUs using the two-film theory and the Maxwell-Stefan equations [26,27,30]. In both approaches the quality of the simulations relies on the correlated mass transfer coefficients and mass transfer areas.

Instead we decided to use an equilibrium model and make a set of test runs to estimate the HETP of the packing. The column operated in total reflux with a mixture of n-hexane and cyclohexane. The variables were pressure (ranging from 0.4 to 1.0 MPa), composition (25% to 75% for both n-hexane and cyclohexane mass percentages) and heating (150..500 W). The steady state was specified following 15 temperature profiles, reflux pump settings and pressure and rotameter values. When steady state was achieved

samples were taken from reboiler, condenser and packings simultaneously and analyzed using a gas chromatograph.

Surface temperatures were measured from the surface of the insulation using a surface temperature meter.

Simulation of total reflux is not straightforward with our distillation model since it is designed to simulate distillation columns in usual operation modes. For simulation of the total reflux operation we chose the approach where the total reflux is simulated by feeding a large stream on the column reboiler and taking in practice only one product stream out of the column (from reboiler). The composition of the feed stream is the same as the measured reboiler composition; this way the simulated bottom composition matches with the measured one. The reboiler duty is also matched with the measured one to set the inner flows in the column equal to the real column. The top product of the column is set as small as numerically possible.

The HETP was determined by trial and error by altering the number of ideal stages to match the simulated condenser composition to the measured one. We included one ideal stage for the empty part of the column. HETP was calculated and plotted as a function of *f*-factor. *F*-factor (vapor kinetic energy term). The HETP value for the feasible operating range of the column was 0.055 m.

When operating such a small column special attention need to be paid in calculating the heat losses. These calculated rigorously and were included in the simulations.

In such small equipment the reflux from the condenser was somewhat smaller than the measured liquid flow due to the heat losses. This has to be kept in mind when interpreting the HETP values of the packing.

Pressure losses were neglected in the calculations, since neither previous test runs nor this one has shown any measurable pressure losses in the column.

## MODEL VALIDATION

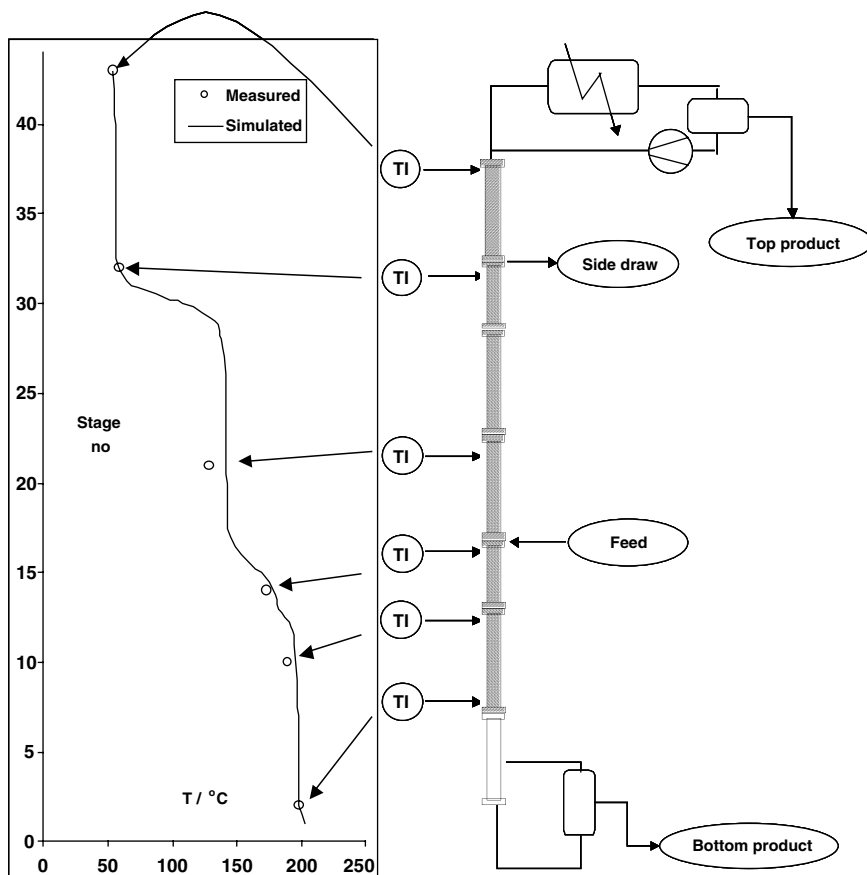
### EXPERIMENTAL

The experimental set-up was made using a 2.5-meter high column with three product stream take-outs. Schematic of the column is shown in Figure 1.

There were seven temperature indicators in the column and a voltage indicator in the reboiler. Frequent GC analyses were made for feed and output streams of the column. The pressure in the column was 0.9 MPa and the temperature range was 50...200 °C.

The feed consists mainly of isobutane, dimerisation products and unreacted isobutene. *Tert*-butyl alcohol (TBA) is present only in small amounts, yet its presence affects the column behaviour markedly due to its non-ideal nature.

The column bottom product consists of diisobutene and heavier oligomers. A recycle stream back to the reactors is taken from the top part of the column in the whole process. The recycle should contain as much of TBA and unreacted isobutylene as feasible. Other light hydrocarbons fractionate between the top product and the recycle stream according to the separation efficiency of the top part of the column.



**Figure 1.** Column temperature profile against the schematic column. Circles present the measured temperatures and solid line the simulated profile. Temperature probe locations are connected to corresponding measured values with arrows

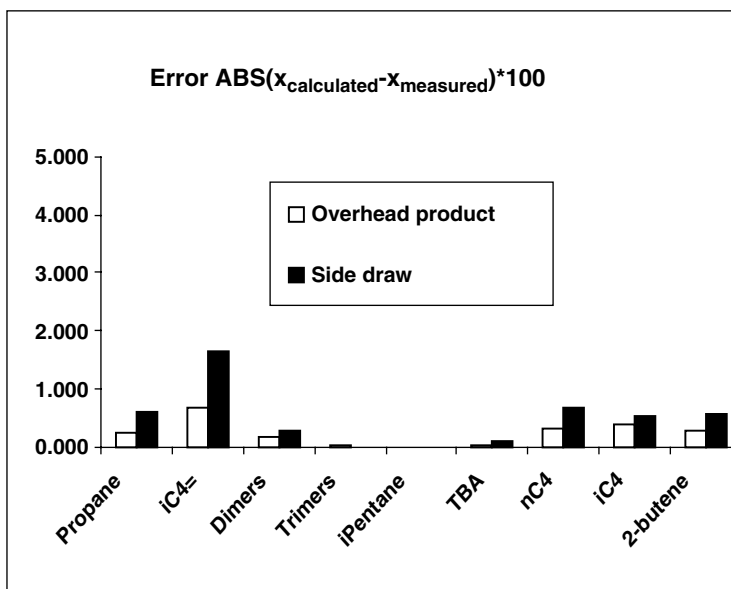
## RESULTS

The main objective of the VLE model for the process is to predict the behavior of tert-butyl alcohol in a mixture of hydrocarbons. Hydrocarbon-hydrocarbon interactions are usually close-to-ideal, and their separation characteristics are defined by vapour pressures. Furthermore, sophisticated predictive methods, such as UNIFAC or ASOG [31], can predict the slight deviations from ideality in hydrocarbon mixtures accurately. Therefore accurate and consistent vapour pressure correlations were needed for the hydrocarbons in

question. DIPPR database provided parameters for vapour pressure correlations that were chosen to best match our results.

Of the components in the present mixture, TBA has azeotropes with water, trimethyl pentene and isopentane. The temperature in the column varies roughly between 50 °C and 200 °C. The azeotropic composition in this temperature range predicted by Wilson's model was shown to be good.

The column was simulated using all miniplant data available. The bottom product was set to contain only dimers and trimers, with the composition of other components not exceeding 0.01 w-%. The outtake from 32nd stage, counted from reboiler up, was set to 100 g/h, which was the time-average of the real column outtake. Below the outtake the column stage number was calculated using the HETP values given earlier. Above the outtake, the separation efficiency of the packing was greatly reduced by the fact that the condenser of the column did not operate as a total condenser, but also cooled down the temperature of the reflux flow below dew point. This was simulated by both reducing the number of theoretical stages and assigning large heat losses to the stages above the outtake. According to the comparisons between simulations and miniplant data, this assumption was justified.



**Figure 2.** Errors in the overhead product and the side draw compositions of the main components for the simulations with Wilson method for the diisobutylene test run

The column temperature profile is shown in Figure 1 along with temperature probe locations. The column can be divided in three sections; at the bottom, the column is rich in diisobutene, in the middle section, TBA and C<sub>4</sub> hydrocarbons dominate and at the top part of the column the mixture consists almost entirely of light C<sub>3</sub> to C<sub>4</sub> hydrocarbons. With Wilson method, the dimer rich section reaches up to the 15th – 17th stage. Dimer has high boiling temperature, and thus the temperature at dimer rich stages is close to 200 °C. In the middle section of the column, the effect of time-averaging the measured values produces some error. The horizontal fluctuation of the bell-shaped, TBA-rich composition profile causes the temperature to shift up and down. This also makes the dynamic column control difficult, and detailed knowledge about the column behaviour is vital for successful operation. The top section of the column, rich in C<sub>3</sub> to C<sub>4</sub> hydrocarbons, remains in rather steady temperature. The differences in the boiling points of short hydrocarbons are quite moderate, and therefore the changes in composition cannot be straightforwardly detected from the temperature profile.

Figure 2 shows the errors between measured and calculated product stream mass fractions. TBA content is well predicted in both top product and side-draw. As a whole, the VLE-method, complemented with the column model, predicted the column behaviour successfully. Both feed and product stream locations were placed strictly following the HETP calculations. Sub cooled reflux and heat losses cause the separation efficiency above the side-draw to be weak. This causes bad separation of C<sub>3</sub>-C<sub>4</sub> hydrocarbons.

## CONCLUSIONS AND DISCUSSION

The experience shows that miniplant concept can be successfully applied in process development. This study illustrates well what is possible with the present modelling and analysis methods in distillation design. The column model was constructed piecewise, compiling individual sub-models to an overall model. Sub-models included a model for multicomponent vapour-liquid equilibrium and a detailed column model taking heat losses and column packing characteristics into account.

Nevertheless, miniplant concept can be further improved. Perhaps the most significant single improvement would be to build the miniplant equipment so that it can be operated unmanned at least overnight. If the purpose of the test is to verify the VLE model as in this case, it is enough to operate the column sufficiently long to certainly achieve the steady state and then perform the measurements. With a single distillation column this can usually be achieved in one or a couple of days. However, when the goal is e.g. to check that there are no components accumulating to the system, longer runs are often necessary.

Unmanned operation has been reality with continuous reactors already a long time, but distillation columns have been too complicated devices to operate unattended. Nevertheless, the small scale of a miniplant makes the unmanned operation thinkable. If the feed rate of the whole process is e.g. 0.2 dm<sup>3</sup>/h, and product flow rates are of the same order, a feed tank of 20 dm<sup>3</sup> and product receivers of the same size are more than enough for operating the process over a weekend and the whole equipment may be sufficiently small to be



built into a reactor bunker. When the diameters of the equipment are small, it can be designed to withstand high pressures giving a high safety margin. Online analyzers connected so that only the amount strictly necessary is drawn from the process are to be preferred. Finally as an additional problem, controllers suitable for small-scale equipment are often difficult to find.

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