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# Adding Value to Bioethanol through a Purification Process Revamp

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## ABSTRACT

A comprehensive technical feasibility study was conducted of a bioethanol demonstration plant with the aim of converting parts of an existing fuel-grade bioethanol production into a more valuable solvent-grade ethanol. The study focuses on the separation unit, which consists of three consecutive distillation columns and a dehydration step using molecular sieves. This separation unit did not permit sufficient removal of crotonaldehyde and methanol for obtaining solvent-grade ethanol. Therefore, an additional distillation column after the dehydration step was investigated by simulation. It is operated at subatmospheric pressure, and (i) enables simultaneous removal of methanol, crotonaldehyde, and water in the distillate, (ii) the distillate meets the fuel-grade ethanol specifications while the bottom product meets the solvent-grade specifications, (iii) enables around 70% solvent-grade ethanol production, and (iv) employs a vacuum pump that is already used in the considered plant.

A stationary operating point is characterized by on-line operational data and experimental results of liquid samples. Particular emphasis during the characterization is put on trace compounds. Ethanol and the following 13 trace compounds were analyzed experimentally: Acetaldehyde, 1-propanal, 1-butanal, crotonaldehyde, benzaldehyde, ethyl acetate, methanol, 1-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-1-butanol, and 3-methyl-1-butanol. A simulation platform was established and evaluated with excellent agreement compared to the operational data. The beer composition (separation unit feed) and a complete stream summary for the separation unit are provided.

Keywords: Bioethanol, demonstration plant, trace component, distillation, simulation, data reconciliation

## 1 INTRODUCTION

The presence of trace impurities in industrial chemical processes is quite common but often neglected in simulation studies[1]. This also applies to the production of bioethanol[2]. During the fermentation of sugars into bioethanol, several carbonaceous impurities are formed, covering primarily low-carbon aldehydes, alcohols, and carboxylic acids (**Table 1**). These impurities are present in small amounts, which is why they are referred to as trace compounds (TCs).

While the ethanol content in the broth resulting from fermentation of lignocellulosic feedstock in conventional technologies rarely exceeds 5% (by mass)[3], the content of the TCs can be significant in the final anhydrous ethanol product if they are not removed.

The vapor-liquid equilibrium (VLE) behavior of TCs in aqueous ethanol systems cannot be determined by simple means, such as ranking of normal boiling points. Certain TCs exhibit different levels of volatilities throughout the composition range of ethanol[4] and thus reliable VLE models are required in order to describe the fate of the TCs during distillation.

**Table 1. List of relevant trace compounds in the purification of bioethanol considered in simulation studies by various sources. "Y" means that the compound is considered in simulation, while "*" is only considered for theoretical analysis.**

| Group | Compound | Is considered in simulation | | | |
|---|---|---|---|---|---|
| | | Decloux/Coustel[4] | Baeyens et al.[5] | Marriaga[2] | This work |
| Aldehydes and ketones | Formaldehyde | - | - | - | * |
| | Acetaldehyde | Y | Y | Y | Y |
| | 1-Propanal | - | - | - | Y |
| | 1-Butanal | - | - | - | Y |
| | Crotonaldehyde | - | - | - | Y |
| | Benzaldehyde | - | - | - | Y |
| | Furfural | - | - | - | * |
| | Acetone | - | - | - | * |
| Esters | Ethyl formate | - | Y | - | * |
| | Methyl acetate | - | Y | - | * |
| | Ethyl acetate | Y | Y | - | Y |
| | Ethyl isobutyrate | - | Y | - | * |
| Alcohols | Methanol | Y | Y | Y | Y |
| | 1-Propanol | Y | Y | Y | Y |
| | 2-Propanol | - | Y | - | * |
| | 1-Butanol | - | Y | - | Y |
| | 2-Butanol | - | - | - | Y |
| | 1-Pentanol | - | Y | - | * |
| | 2-Methyl-1-propanol | Y | Y | - | Y |
| | 2-Methyl-1-butanol | - | - | - | Y |
| | 3-Methyl-1-butanol | Y | Y | Y | Y |
| | Glycerol | - | Y | Y | - |
| Carboxylic acids | Diethyl acetal | - | - | - | * |
| | Formic acid | - | Y | - | * |
| | Acetic acid | - | Y | Y | * |
| | Propionic acid | - | Y | - | * |
| | Butyric acid | - | Y | - | * |
| | Lactic acid | - | Y | - | - |

Bioethanol is commonly purified by distillation until azeotropic composition, followed by dehydration through molecular sieves[5]. For the sole purpose of concentrating ethanol, two distillation columns are used: A crude column, which removes water and the nonvolatile compounds of the fermentation broth, and a polishing column, which produces azeotropic ethanol and fusel. Only a few researchers have considered the importance of the TC removal for obtaining high-grade bioethanol for other purposes than fuel, despite the

increasing significance of bioethanol[6]. Marriaga[2] demonstrated a complete removal of traces of acetic acid, acetaldehyde, propanol, 3-methyl-1-butanol, methanol, glycerol, and $CO_2$ by distillation using the NRTL activity coefficient model in AspenPlus. Decloux/Coustel[4] and Hoch/Espinosa[7] agree that trace amounts of methanol cannot be removed without a dedicated distillation column (a demethylizer). Alternatively, Hoch/Espinosa[7] proposed a "hybrid column", which combined the rectification column and a methanol separation column, thus reducing the total number of required distillation columns. Neither Marriaga[2] nor Hoch/Espinosa[7] considered light condensable impurities such as the aldehydes reported in **Table 1**, despite the importance of the removal of acetaldehyde in fuel-grade bioethanol production, as emphasized by Batista et al.[6]. During storage of bioethanol, acetaldehyde can be oxidized to acetic acid, which can lead to excessive fuel acidity. Acetaldehyde removal can be achieved by either a degassing system in the top of the rectification column or an additional distillation column before the rectification column[6]. A detailed simulation of a purification unit, producing neutral spirits, was conducted in ProSim Plus by Decloux/Coustel[4] who considered several relevant TCs (acetaldehyde, ethyl acetate, methanol, 2-methylpropan-1-ol, and 3-methyl-1-butanol). Their purification unit consisted of seven distillation columns, including a column to remove light TCs, a demethylizing column, and a column to recover ethanol from the TC rich waste streams.

A profound list of common TCs encountered in literature is summarized in **Table 1**. The table also reports the TCs considered in this study. Based on the above discussion, a minimum of the considered TCs in bioethanol production are acetaldehyde, methanol, and fusel constituents.

In this study, we analyze the phase behavior of all the 28 TCs qualitatively, while 13 TCs are selected for further analysis of a bioethanol demonstration plant. A potential upgrade of the ethanol product to a solvent-grade is investigated. We distinguish the two grades: Fuel-grade and solvent-grade, which are defined in Table S1 (Supporting Information). Thus, we investigate the technical feasibility of converting parts of the current fuel-grade bioethanol production of a bioethanol demonstration plant, into solvent-grade ethanol. Such a solution allows industrial symbiosis as it can extend the lifetime of the ethanol: The solvent-grade ethanol can be supplied to a nearby plant while spent solvent is fed and reprocessed. The fuel-grade ethanol leaving the cycle is still called bioethanol as long as the mass flow rate can be traced back to the straw feedstock.

The paper is structured as follows: A description of the purification unit of the Inbicon demonstration plant is provided in Section 2. The methods and tools are described in two sections: The experimental section (Section 3) outlines the experimental procedures for quantifying the TC concentrations in various process streams. The simulation section (Section 4) describes the distillation column model, the thermodynamic model, and data reconciliation problem. Finally, a presentation of the results is provided in Section 5, followed by a discussion (Section 6) and conclusions (Section 7).

## 2 PURIFICATION UNIT DESCRIPTION

The Inbicon[8] demonstration plant (Kalundborg, Denmark) has supplied lignocellulosic bioethanol as a fuel additive since 2009. While 12-times larger bio-waste-to-energy complexes are contemplated[9], the Inbicon biomass refinery continues to explore energy efficiency and new business concepts based on industrial symbiosis. The nominal capacity of the Inbicon demonstration plant is 4000 $kg \cdot h^{-1}$ dry biomass (wheat straw)[10], which per ton dry matter (DM) is converted into 231 kg bioethanol, 374 lignin, and 80 vinasse[11].

The processes for obtaining bioethanol are: Pretreatment, liquefaction (enzymatic hydrolysis), fermentation, and purification. More details on the Inbicon process is provided by Larsen et al.[10].

The purification unit is a distillation train of three columns (Vogelbusch Biocommodities GmbH, Vienna, Austria) followed by a molecular sieve configuration as shown in **Figure 1**:

- COL-1: This column is referred to as the beer stripper. It has 18 trays, so $N_T$ = 18; the feed tray is number 18, i.e. $N_F$ = 18; and a distillate pressure of $P_D$ = 24.18 kPa. Its purpose is to strip off the ethanol from the viscous fermentation broth using steam, thereby recovering the ethanol in the distillate. The beer stripper is operated at subatmospheric pressure such that the temperature is kept sufficiently low to avoid degradation of enzymes and other temperature sensitive compounds, which are recovered in the bottom. The ethanol is concentrated to roughly 20% (mass) in the distillate.
- COL-2: The aldehyde column ($N_T$ = 30; $N_F$ = 22; $P_D$ = 102.4 kPa). The light impurities are removed as the top product. These impurities consist mainly of smaller oxidized organic compounds including aldehydes.
- COL-3: The rectification column has a side draw from stage 16 ($N_S$ = 16), and ($N_T$ = 40; $N_F$ = 11; $P_D$ = 291.2 kPa), where the remaining water (stream 8) is removed in the bottom of the distillation column. Fusel oil (heavy alcohols) is removed in a side stream (stream 9) near the middle of the column. In the top, azeotropic ethanol is produced as the distillate.
- COL-4a/b: In order to produce anhydrous ethanol, water is removed by a molecular sieve. Continuous operation is maintained by operating two molecular sieves in shifted dehydration/regeneration cycles.

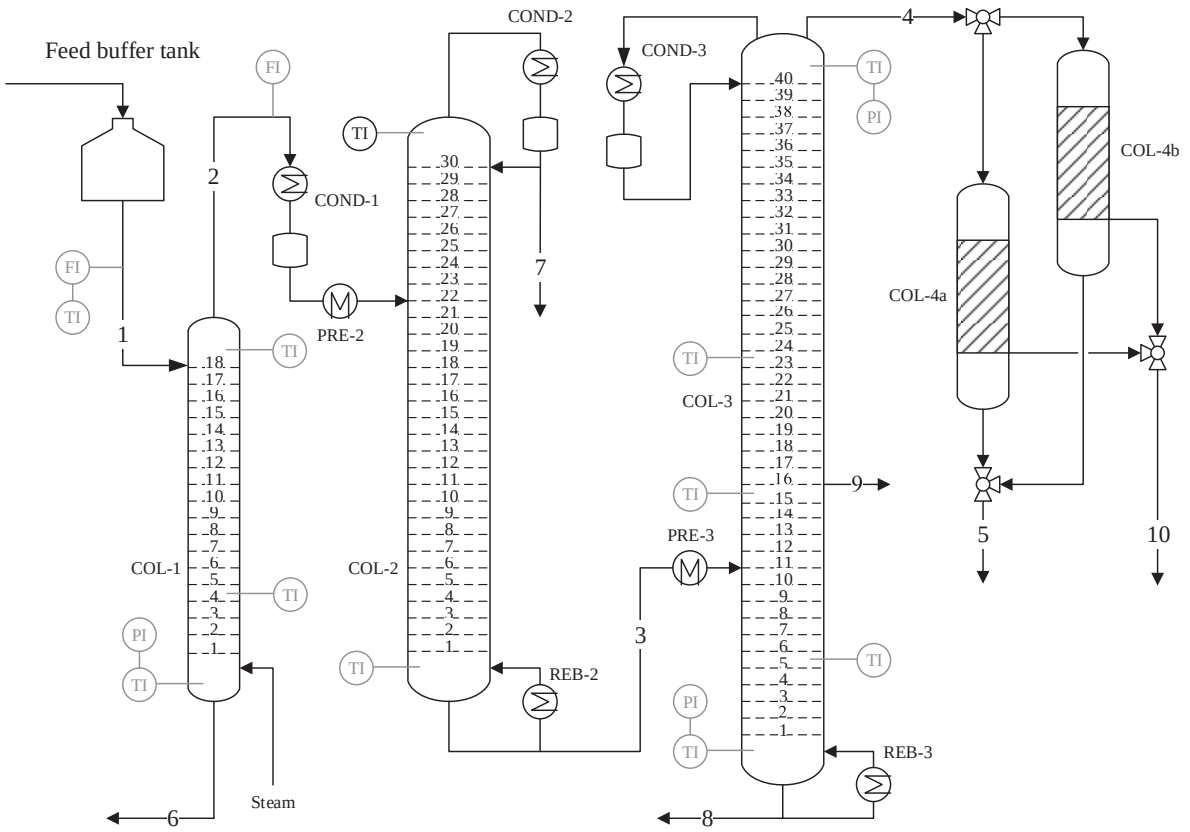


**Figure 1**. Simplified representation of the purification unit of the Inbicon demonstration plant. Stream names, equipment names, and measurement indicators are listed with the following abbreviations: TI is a temperature indicator, PI is a pressure indicator, FI is a flow rate indicator, COL is column, REB is reboiler, COND is condenser, and PRE is feed preheater.

## 3 EXPERIMENTAL WORK

The experimental work covers the sampling procedure and the experimental analysis of the demonstration plant samples.

### 3.1 Logged Operational Data

The Inbicon plant operational data is continuously measured and logged at a frequency of one sample per second. Keeping feed trays fixed as specified above, a reasonably satisfactory five-hour steady state was identified and chosen as a representative data set of the nominal operating point. The available flow rate measurements are restricted to the beer stripper feed, beer stripper distillate, and rectification column distillate, i.e. streams 1, 2, and 4 in **Figure 1**. Temperature and pressure measurements were available for all

top and bottom trays of the three columns, while tray #4 of the beer stripper and trays #5, #15, and #23 were available for the rectification column.

### 3.2 Sampling Procedure

Prior to the identification of the representative steady state, 55 samples were taken from streams 1, 2, and 4-8 (**Figure 1**) over a period of eight days. The corresponding data set of the identified steady state (seven samples) was selected for experimental analysis. The samples were stored in 100 mL glass vials with plastic caps at 5 °C until analyzed. The vials were completely filled with liquid to avoid vapor headspace. The procedure of the experimental analysis is described below.

### 3.3 Analytical Methods

All the analytical work is carried out in a standard Agilent Gas chromatography-mass spectrometry (GC-MS) single-quadrupole system using a Tenax adsorbent resin. Dynamic headspace sampling with total evaporation was used for compounds with rather high breakthrough volumes on Tenax: 1-Propanal, 1-butanal, crotonaldehyde, benzaldehyde, 1-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-1-butanol, and 3-methyl-1-butanol. Static headspace sampling was used for compounds with low breakthrough volumes on Tenax: Ethanol, acetaldehyde, ethyl acetate, 1-propanol, and 2-butanol. The dynamic headspace analyses were repeated twice for each sample while the static headspace analyses were repeated three times. The 1-propanol and 2-butanol concentrations were determined by both methods to ensure consistency.

#### *3.3.1 Dynamic Headspace Sampling and GC-MS*

100 µL of sample was pipetted to a gas washing bottle. A purge head with a Tenax trap was attached. The traps contained 250 mg of Tenax-TA with mesh size 60/80 and a density of 0.37 $g \cdot mL^{-1}$ (Buchem BV, Apeldoorn, The Netherlands). The sample was purged with nitrogen 100 $mL \cdot min^{-1}$ until it was completely evaporated (max. 20 min) to ensure complete transfer of components to the trap. The trapped volatiles were desorbed using an automatic thermal desorption unit (TurboMatrix 350, Perkin Elmer, Shelton, USA). Primary desorption was carried out by heating the trap to 250 °C with a flow 50 $mL \cdot min^{-1}$ of carrier gas $H_2$ for 15.0 min. The stripped volatiles were trapped in a Tenax TA cold trap (30 mg maintained at 5 °C), which was subsequently heated to and maintained at 300 °C for 4 min (secondary desorption, outlet split 1:10). This allowed for rapid transfer of volatiles to a gas chromatograph-mass spectrometer (GC-MS, 7890A GC-system interfaced with a 5975C VL MSD with Triple-Axis detector from Agilent Technologies, Palo Alto, California) through a heated 225 °C transfer line. Separation of volatiles was carried out on a DB-Wax capillary column 30 m long by 0.25 mm internal diameter, 0.50 µm film thickness. The column pressure was held constant at 15.9 kPa resulting in an initial flow rate of 1.4 $mL \cdot min^{-1}$ using hydrogen as carrier gas. The column temperature program was: 10 min at 30 °C, from 30 °C to 240 °C at 8 $°C \cdot min^{-1}$, and finally 5 min at 240 °C. The mass spectrometer was operating in the electron ionization mode at 70 eV. Mass-to-charge ratios between 15 and 300 were scanned.

### *3.3.2 Static Headspace Sampling and GC-MS*

Sampling was carried out on a Combi Pal autosampler (CTC Analytics, Switzerland). 1 mL of sample was pipetted into a 10 mL vial, which was closed with a lid with septum. The vial was equilibrated at 70 °C for 15 minutes and then 250 µm of headspace was taken by a gas tight syringe maintained at 80 °C. The headspace sample was injected into the injection port of the GC using a split ratio of 10:1. The GC-MS equipment was an Agilent (Palo Alto, CA) G1530A GC with a DB-Wax column (30 m by 0.25 mm by 0.25 µm) in combination with an Agilent 5973 mass spectrometer. The GC column flow rate was 1.5 $mL \cdot min^{-1}$ using hydrogen as carrier gas. The column temperature program was: 1 min at 20 °C, from 20 °C to 80 °C at 5 $°C \cdot min^{-1}$, and finally increased to 250 °C at 40 $°C \cdot min^{-1}$ with a final hold time of 6.75 min. The mass spectrometer was operating in the electron ionization mode at 70 eV. Mass-to-charge ratios between 10 and 105 were scanned. Volatile compounds were identified by probability based matching of their mass spectra with those of a commercial database (Wiley275.L, HP product no. G1035A). The software program, MSDChemstation (Version E.02.02.1431, Agilent Technologies, Palo Alto, California), was used for data analysis.

### *3.3.3 Quantification*

Standard solutions were prepared to calibrate the analysis. For dynamic headspace analyses with total evaporation, pure 99.9 wt-% ethanol was added 0, 5, 50, 100, or 1000 $mg \cdot L^{-1}$ of the components to be quantified. This series of dilutions were analyzed together with the real samples on a regular basis. For static headspace analyses, the effect of the matrix on the release of volatiles to the headspace has to be taken into account. Five series of standards (0, 5, 50, 100, and 1000 $mg \cdot L^{-1}$) were therefore prepared in different matrices (0.5, 4, 11, 35 and 90 wt-% of ethanol in water) and analyzed together with the real samples.

## 4 SIMULATION TOOLS

The following subsections describe a tool for qualitative evaluation of the distillation column performances, the simulation procedure, and finally a data reconciliation problem formulation to determine the feed composition.

### 4.1 Phase Behavior Modelling

Decloux/Coustel[4] describe the application of the relative volatility, $\alpha$, of TCs at infinite dilution to predict their fate in an ethanol/water purification process. In this work, a corresponding logarithmic relative volatility is found more suitable for graphical representation:

$$\ln \alpha_j = \ln \frac{K_j}{K_{\text{ethanol}}}, j = 1,2,\ldots,N_{TC} \tag{1}$$

Where $K_j$ is the volatility and $N_{TC}$ is the number of TCs. The TC $j$ is more volatile than ethanol when ln $\alpha_j \geq 0$, and less volatile when ln $\alpha_j \leq 0$. Thus, eq (1) can be used as a tool to conduct a preliminary feasibility analysis of the separation performance of any aqueous ethanol distillation column, when evaluated in the relevant ethanol and water composition ranges.

For such analysis, only the ethanol/water/TC interactions are relevant. Since the TC/TC interactions become negligibly small at mole fractions below 0.01, infinite dilution activity coefficients of the TCs in the binary ethanol/water system can be used for the estimation of $K_j$ in eq (1). These considerations apply to the majority of the equilibrium stages in the considered distillation columns. It should be stressed that measurements of infinite dilution activity coefficients are associated with large uncertainties, which may be reflected in the VLE models.

Due to the high amount of required model parameters for existing activity coefficient models to describe a mixture of 30 compounds (435 binary pairs), a predictive activity coefficient model (like UNIFAC[12]) appears to be the favorable choice.

An essential element in the development of a simulation platform is a proper description of the volatilities of the TCs, which are present in low concentrations. Decloux/Coustel[4] investigated the performance of UNIFAC compared to NRTL for the water/ethanol/TC system. They concluded that UNIFAC could sufficiently describe VLE data for a handful of TCs (propanol, 2-methylpropan-1-ol, 3-methyl-1-butanol, and methanol) and it was used in a purification plant simulator. In addition, Faúndez and Valderrama[13] compared the performance of NRTL, UNIFAC, and Predictive-SRK models to experimental data of nine ethanol/TC and nine water/TC binary systems. These nine TCs are included in this study (**Table 1**). The performance of the three activity models was similar, but substantial deviations from experimental data are seen for the following systems: Acetic acid/water, 3-methyl-1-butanol/water, furfural/water, acetic acid/ethanol, and furfural/ethanol. However, these systems are generally difficult to model due to dissociation or immiscibility. Based on the above considerations, it was decided to employ UNIFAC in this study. Pure component temperature dependent properties are described by the DIPPR correlations and database.

### 4.2 Simulation Procedure

A model summary and the numerical aspects are described below. The employed model is described by Mauricio-Iglesias et al.[14]. The following assumptions are made:

A1. Perfectly mixed stages at equilibrium

A2. Ideal mixture physical properties from temperature dependent pure component DIPPR correlations.

A3. Modified Raoult's law, implying

- Ideal gas vapor phases

- Activity coefficient model for liquid phases

A4. No liquid phase instability caused by VLLE (fusel oil and water are immiscible)

A5. The parallel molecular sieves functions as a simple stream splitter, which continuously removes 99.99% of the water.

As indicated in **Table 1**, 13 TCs are considered by simulation in this study. According to assumption A3, the VLE behavior is determined by the employed activity coefficient model and the DIPPR 101 vapor pressure correlation. The model was implemented in MATLAB. A two-step solution approach was employed in order to obtain a steady state solution for each distillation column: First, the Wang-Henke Boiling point method[15] was used to obtain an approximate steady state solution, followed by a simultaneous correction method to solve the MESH equations with the required numerical precision. For the simultaneous correction method, the "fsolve" command in MATLAB was employed using the "active-set" algorithm with a termination tolerance on the function value of $10^{-10}$ (TolFun) and a termination tolerance on the input of $10^{-10}$ (TolX). More details on the implementation and simulation method of the distillation column model is available in a previous paper[16].

All constraint residuals were scaled by appropriate feed variables; the feed flow rate was used to scale the mass balances, while the change in enthalpy of increasing the feed temperature to the normal boiling point differences of ethanol and water was used to scale the energy balances. The unknown variables were scaled as described:

- Compound mole fractions: Since the correct simulation of TC fate in distillation is essential to this study, the TC mole fractions were scaled by a factor of $10^3$, since these are present in significantly lower concentrations than ethanol and water on all the distillation column stages
- Temperatures: The arithmetic mean of the boiling points of ethanol and water 360 K was used to scale all stage temperatures
- Flow rates: The feed flow rate was used to scale the unknown flow rates
- Duties: The latent heat of the feed stream was used to scale the unknown heat duties

This distillation column model has previously been benchmarked against an industrial case study[14] related to the distillation of isopropanol/water with acceptable performance.

A compound removal efficiency is used to validate the expected separation performance of the distillation columns based on eq (1). Hence, the component removal efficiency for each waste stream is defined below:

$$\xi_{COL-1,j} = (m_6 w_{6,j}) / (m_1 w_{1,j}) \tag{2}$$

$$\xi_{COL-2,j} = (m_7 w_{7,j}) / (m_2 w_{2,j}) \tag{3}$$

$$\xi_{COL-3a,j} = (m_8 w_{8,j}) / (m_3 w_{3,j}) \tag{4}$$

$$\xi_{COL-3b,j} = (m_9 w_{9,j}) / (m_3 w_{3,j}) \tag{5}$$

$$j = 1,2,\ldots,N_C$$

where $m_i$ is the mass flow rate of stream $i$ (see **Figure 1**) and $w_{ij}$ is the mass fraction of component $j$. A large value of $\xi_{ij}$ is preferred for undesired TCs, since the value indicates the amount of component $j$ that is removed in a waste stream. A value close to zero is preferred for ethanol.

### 4.3 Data Reconciliation

A precise determination of the feed composition is of particular importance for separation unit simulations. Therefore, a data reconciliation problem is formulated such that information of several streams is combined in order to produce a consistent data set. Due to scarcity of flow rate measurements in the separation unit, the data reconciliation problem is only formulated around the beer stripper (COL-1). In addition, dynamic operational effects (e.g. mass accumulation) are also minimized when only considering the first column, since the feed flow rate is controlled. This data reconciliation problem (eq (6)) represents a constrained, nonlinear optimization problem, defined below:

$$\min_{m_i, w_{i,j}} \phi = \sum_{i=1}^{N_S} \left[ \left( \frac{\bar{V}_i - V_i}{(\sigma_{\bar{V}})_i} \right)^2 + \sum_{j=1}^{N_C} \left( \frac{\bar{w}_{i,j} - w_{i,j}}{(\sigma_{\bar{w}})_{i,j}} \right)^2 \right] \tag{6}$$

$$s.t.$$

$$0 = m_F w_{F,j} - m_D w_{D,j} - m_B w_{B,j}, j = 1,2,\ldots,N_C \tag{7}$$

$$0 = 1 - \sum_{j=1}^{N_C} w_{i,j}, i = F, D, B \tag{8}$$

$$0 = \frac{2970 \cdot 10^{-6}}{0.994} w_{D,\text{ethanol}} - w_{D,\text{methanol}} \tag{9}$$

$$0 = w_{B,\text{methanol}} \tag{10}$$

$$0 = V_i \rho_i - m_i, i = F, D, B \tag{11}$$

$$0 = \rho_i - \left( \sum_{j=1}^{N_C} \frac{w_{i,j}}{\rho_j} \right)^{-1}, i = F, D, B \tag{12}$$

$$0 \le m_i, i = 1,2,\ldots,N_S \tag{13}$$

$$0 \le w_{i,j} \le 1,\ j = 1,2,\ldots,N_C, i = 1,2,\ldots,N_S \tag{14}$$

where $V_i$ is the reconciled volumetric flow rate of stream $i$, $w_{i,j}$ is the reconciled weight fraction of compound $j$ in stream $i$. The overbars represent experimentally obtained values, while $(\sigma_{\bar{w}})_{i,j}$ and $(\sigma_{\bar{V}})_{i,j}$ are their experimental standard deviations. In addition, $\rho_i$ is the density, and the subscripts $F$, $D$, and $B$ refer to the feed, the distillate, and the bottoms, respectively.

Eq (7) represents the component mass balance of the beer stripper. It is assumed that all the present compounds are known, and hence a summation balance is imposed (eq (8)). No measurements were conducted for methanol for any of the relevant streams. Therefore, it was assumed that the methanol is conserved throughout the separation unit using a methanol measurement of the dehydrated product, leading to eq (9) - (10). This assumption is a consequence of the previously discussed difficulty of removal of trace amounts of methanol. Eq (11) - (12) are used to convert volumetric flow rate measurements into mass flow rates. In total, 15 compounds are considered ($N_C$ = 15), including ethanol, water, and the 13 TCs reported in **Table 1**. The data reconciliation problem contained 170 variables with linear and nonlinear equations. It was solved by a local build-in solver function "fmincon" (with the "active-set" algorithm) in Matlab.

## 5 RESULTS

The results are presented below in the following order: First, an overview of the experimental results (stream compositions of the purification unit in **Figure 1**), second the feed composition based on the data reconciliation problem solution, third the thermodynamic analysis, fourth the simulation platform design and evaluation, and fifth the separation unit performance is evaluated. Finally, a revamp proposal for obtaining solvent-grade bioethanol is presented.

### 5.1 Experimental Results

The logged operational data in the nominal steady state operating point are listed in Table S2 in the Supporting Information. Furthermore, the GC-MS results are listed in Table S3. The data reconciliation

problem in eq (6) – (14) is solved in order to obtain the feed composition. A local minimum was achieved with a minimal objective function value of 14.8. The resulting feed stream composition is given in **Table 2**. The ethanol concentration in the feed is relatively low (3.49 wt-%). Acetaldehyde, 1-propanal and ethyl acetate are the dominating low-boiling TCs while methanol, 1-propanol, 2-methyl-1-propanol, 2-methyl-1-butanol, and 3-methyl-1-butanol are the dominating alcohols.

In general, the standard deviations of the determined concentrations of the TCs are relatively large (in most cases around 20% in relative terms). A significant difference between the measured and the reconciled concentrations of 1-propanol, 2-butanol, and ethyl acetate in the feed (stream 1) are observed when Table 2 is compared to Table S3. These differences could be due to the complexity of the experimental determinations of the feed stream composition due its inhomogeneous composition. Therefore, the data reconciliation serves as a means to incorporate the more reliable distillate (clear liquid) and the bottoms (nearly pure water that contains solids).

**Table 2. Feed stream (beer) composition obtained by data reconciliation. 1 ppm = 1 mg·kg$^{-1}$.**

| Compound | Unit | Content |
|---|---|---|
| Water | wt-% | 96.5 |
| Ethanol | wt-% | 3.49 |
| Acetaldehyde | ppm | 6.13 |
| 1-Propanal | ppm | 12.3 |
| 1-Butanal | ppm | 0.0966 |
| Crotonaldehyde | ppm | 0.0351 |
| Benzaldehyde | ppm | 0.0237 |
| Ethyl acetate | ppm | 41.6 |
| Methanol | ppm | 102 |
| 1-Propanol | ppm | 63.3 |
| 1-Butanol | ppm | 0.301 |
| 2-Butanol | ppm | 0.68 |
| 2-Methyl-1-propanol | ppm | 70.6 |
| 2-Methyl-1-butanol | ppm | 15.8 |
| 3-Methyl-1-butanol | ppm | 25.5 |

## 5.2 Thermodynamic Analysis

The thermodynamic behavior of the complete list of TCs (**Table 1**) in an ethanol/water system was analyzed using the logarithmic relative volatilities (eq (1)). The calculated curves at atmospheric pressure are shown in **Figure 2**.

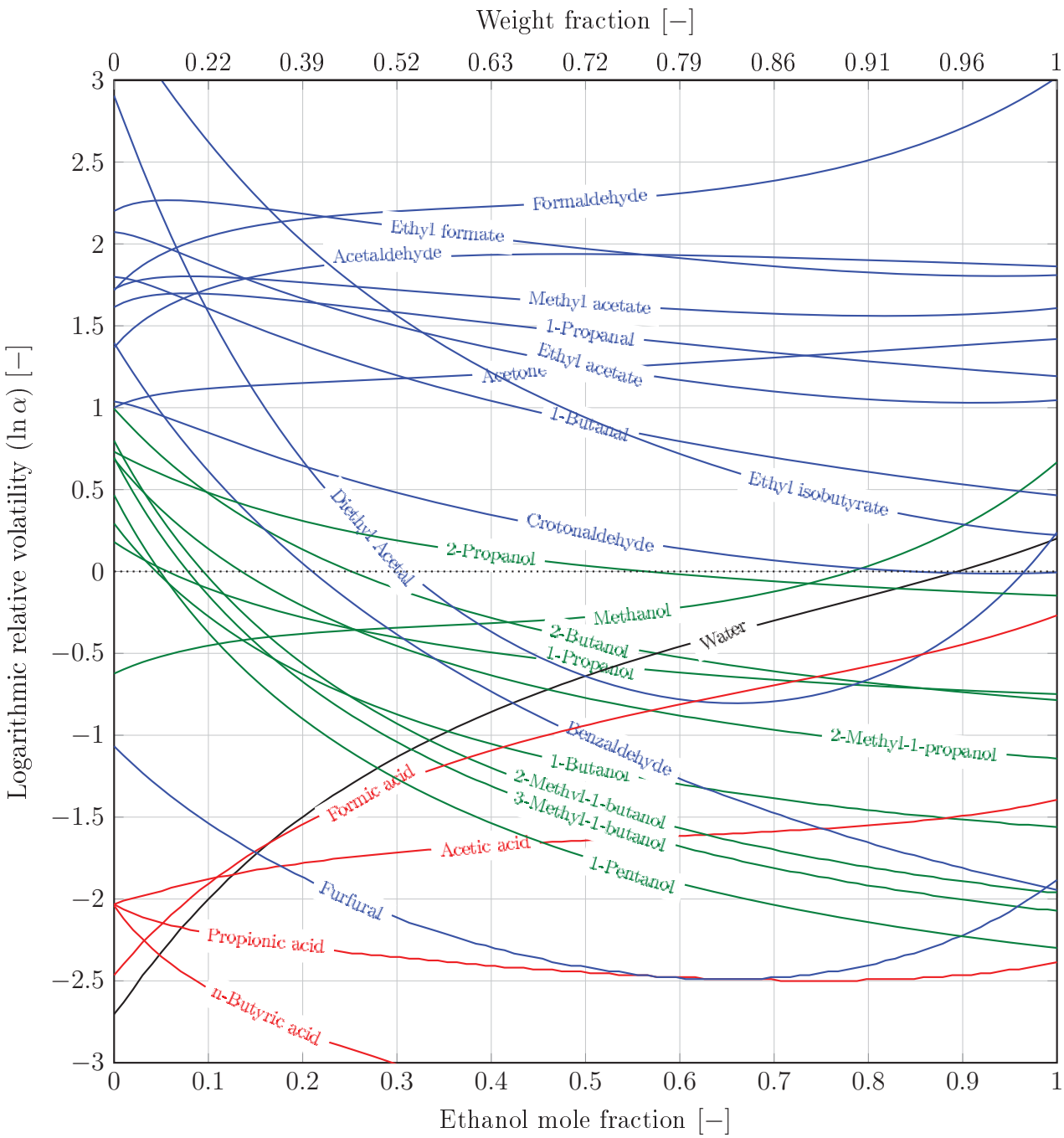


**Figure 2.** The logarithmic relative volatilities of various trace compounds at 101.325 kPa. The position of a curve of a TC relative to zero determines its behavior during distillation: If ln ln $\alpha_j \geq 0$, component $j$ will concentrate in the distillate, and if ln $\alpha_j \leq 0$, component $j$ will concentrate in the bottom. In practice, a limit of 0.5 for ln $\alpha_j$ is reasonable. Colors: Aldehydes + other (blue), alcohols (green), and carboxylic acids (red).

A simple interpretation of **Figure 2** is that all compounds with curves above zero are more volatile than ethanol and all compounds with curves below zero are less volatile than ethanol. Furthermore, the magnitude of the logarithmic relative volatility provides information on the difficulty of the separation of a given TC from ethanol; the further from zero, the easier the separation. The logarithmic relative volatility of water becomes zero at the azeotropic point at a mole fraction of around 0.89 (95 wt-%).

A reasonable logarithmic relative volatility that can be used to predict a complete removal of a TC is around 0.5 (relative volatility of around 1.6). As a result, the following classes of compounds can be distinguished:

- Beer stripper bottoms (Stream 6, **Figure 1**): At 3.5 wt-% (1.4 mol-%) ethanol, the carbonic acids (formic acid, acetic acid, propionic acid, and n-butyric acid) and furfural are expected to be removed with this stream.
- Aldehyde column top (Stream 7, **Figure 1**): At 21.5 wt-% (10 mol-%) ethanol, the majority of the aldehydes (formaldehyde, acetaldehyde, 1-propanal, 1-butanal), ethyl formate, methyl acetate, ethyl acetate, ethyl isobutyrate, and diethyl acetal are expected to be removed in this stream along with a fraction of crotonaldehyde.
- Rectification column side stream (Stream 9, **Figure 1**): A significant amount of higher alcohols (1-propanol, 2-butanol, 1-butanol, 2-methyl-1-propanol, 2-methyl-1-butanol, 3-methyl-1-butanol) along with benzaldehyde show a noteworthy intermediate behavior of volatility, as they turn less volatile than ethanol from more volatile than ethanol over the composition range of the rectification column (from pure water to azeotropic composition). This leads to a local accumulation of those compounds, which enables their removal through a side stream.
- Rectification column bottoms (Stream 7, **Figure 1**): Mainly water along with the components, not removed in the beer stripper bottoms.

Crotonaldehyde, 2-propanol, and methanol appear to be particularly challenging to remove in the current purification unit. These conclusions are consistent with the observations on crotonaldehyde by Ikari et al.[17] and on methanol by Decloux/Coustel[4].

### 5.3 Simulation Platform Design and Evaluation

The developed simulation platform covers the beer stripper (COL-1), the aldehyde column (COL-2), the rectification column (COL-3), and the molecular sieves (COL-4a/b). The distillation column degrees of freedom (top key compound removal efficiency, bottom key compound removal efficiency, and side draw flow rate) and the Murphree efficiencies were adjusted manually in simulation in order to obtain agreement with the experimental data (**Table 3**). A constant Murphree efficiency was assumed throughout a column and for all components. The feed composition reported in **Table 2** was employed.

COL-1 is operated without reflux, and thus the distillate flow rate is adjusted until the top tray temperature matches the measured value. The Murphree efficiency is adjusted to match the measured bottom temperatures. In COL-2, the reflux ratio was fixed to meet the top temperature and the Murphree efficiency was fixed at a default value of 0.80 since the bottom temperature was considered incorrect. Finally, the reflux ratio and the boilup ratios of COL-3 were adjusted to meet the column temperature profile. The side draw flow rate was fixed to achieve more than 90% recovery of 1-propanol, and the Murphree efficiency was adjusted such that the required reflux flow rate matched the measured flow rate. A comparison of the measured data and the simulation results is given in **Table 3**. Excellent agreement is seen. The simulation platform only slightly overestimates the temperature of tray #4 in COL-1 and the temperature of tray #15 in COL-3. Furthermore, the simulated bottom tray temperature of COL-2, $T_1$, does not seem to agree with the measured temperature. However, due to the similarity of the top and bottom temperature measurements, we believe that the bottom temperature sensor is not properly calibrated and/or positioned.

**Table 3. Comparison of the operational steady state data and simulation data.**

| Variable | Unit | Operational data | Simulation data |
|---|---|---|---|
| Beer stripper (COL-1) | | | |
| $T_{18}$ | K | 334.5 | 334.5 |
| $T_4$ | K | 339 | 341.2 |
| $T_1$ | K | 341 | 341.9 |
| Aldehyde column (COL-2) | | | |
| $T_{30}$ | K | 351.6 | 351.2 |
| $T_1$ | K | (352.9) | 358.9 |
| Rectification column (COL-3) | | | |
| $T_{40}$ | K | 380.3 | 380.5 |
| $T_{23}$ | K | 381.8 | 382 |
| $T_{15}$ | K | 389.3 | 391 |
| $T_5$ | K | 407.3 | 407.6 |
| $T_1$ | K | 407.5 | 407.8 |
| $L$ | $m^3 \cdot h^{-1}$ | 5.3 | 4.68 |

The Murphree efficiencies ($E$) and the distillation column operational degrees of freedom are reported in **Table 4**. As seen, the rectification column (COL-3) operates at a high reflux ratio. This ensures stability in operation, as it reduces disturbances from feed variations, which is important for ensuring high recovery of heavy alcohols in the fusel stream (stream 9). The complete stream summary of the separation unit is available in Table S4.

**Table 4. Distillation column operating conditions that were treated as adjustable variables to fit the experimental data.**

| Variable | Unit | Value | | |
|---|---|---|---|---|
| | | COL-1 | COL-2 | COL-3 |
| $E$ | - | 0.5 | 0.8 | 0.55 |
| $Q_F$ | kW | 0 | 47.8 | 45.0 |
| $Q_R$ | kW | 1036 | 55.8 | 909.3 |
| $Q_C$ | kW | -732.9 | -54.8 | -822.1 |
| $L/D$ | - | 0 | 12.9 | 12.3 |
| $V/B$ | - | 0.241 | 0.080 | 1.56 |

## 5.4 Inbicon Separation Unit Performance

Next, we investigate the separation performance of the Inbicon demonstration plant in relation to the thermodynamic analysis from Section 5.2.

### *5.4.1 Beer Stripper (COL-1)*

**Figure 3** shows the ethanol and TC tray composition profiles. The main purpose of COL-1 is to remove heavy compounds, while maximizing the recovery of ethanol in the distillate. Unfortunately, the compositions of the low-volatility TCs (mainly carboxylic acids and furfural in **Figure 2**) were not determined experimentally and are thus not included in the simulation. Furthermore, solids (non-volatiles) are concentrated towards the bottom. Consistent with the thermodynamic analysis, methanol displays a less volatile behavior than the remaining TCs. In fact, the figure suggests that it is possible to remove small amounts of methanol in a side stream at trays #10-15 without a considerable ethanol loss. The ethanol composition is almost constant in the lower part of COL-1.

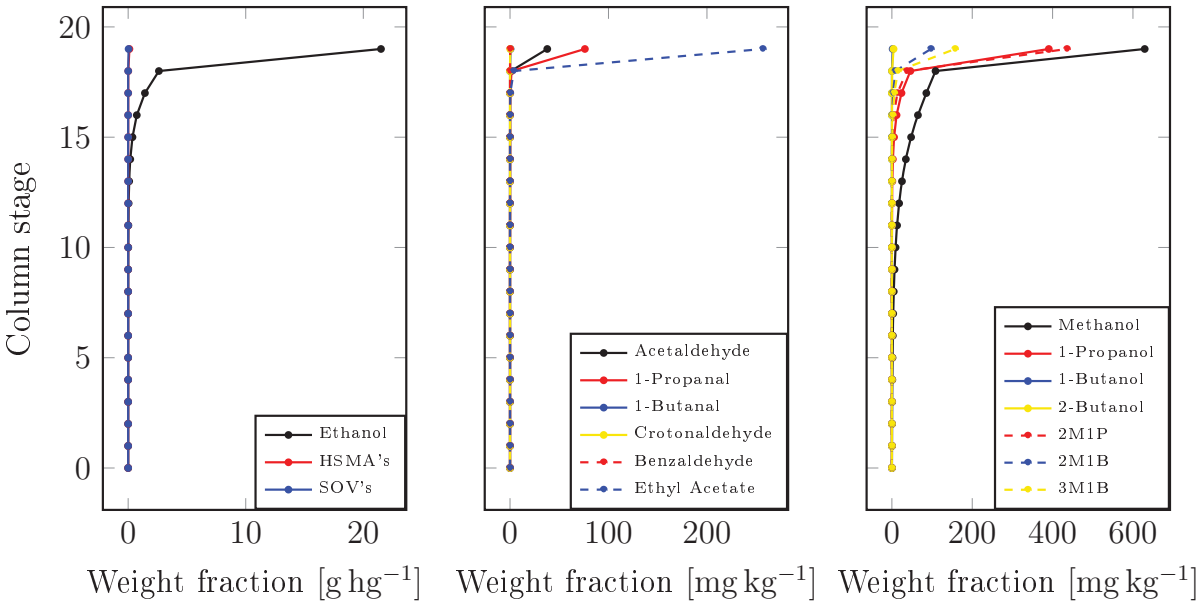


**Figure 3.** Beer stripper (COL-1) tray composition profiles. Abbreviations: Sum of volatiles (SOV), higher saturated mono alcohols (HSMA), 2-Methyl-1-propanol (2M1P), 2-Methyl-1-butanol (2M1B), and 3-Methyl-1-butanol (3M1B).

### *5.4.2 Aldehyde Column (COL-2)*

In COL-2 (aldehyde column), the volatile TCs are concentrated in the top. This is illustrated in the tray composition profiles in **Figure 4**. Similar to COL-1, the lower part of COL-2 has little impact on the separation. This is a result of the relatively small reflux flow rates compared to the feed flow rate. A similar observation was reported by Decloux/Coustel[4] in the column they refer to as the extractive distillation column. Pronounced concentration spikes are observed for the heavier alcohols and benzaldehyde. These exhibited intermediate volatility behavior. This is in agreement with the thermodynamic analysis, since ethanol is concentrated from around 21.5 wt-% to 89.8 wt-% (9.7 mol-% to 77 mol-%). A similar trend is observed in COL-3 as described below.

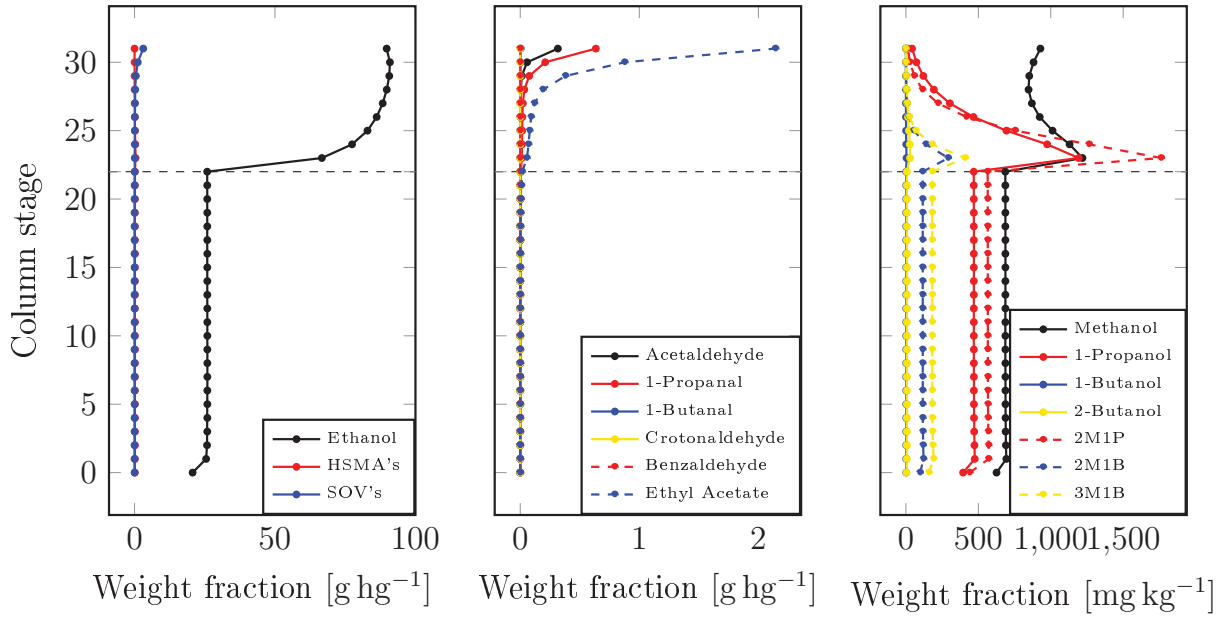


**Figure 4.** Aldehyde column (COL-2) tray composition profiles. Abbreviations: Sum of volatiles (SOV), higher saturated mono alcohols (HSMA), 2-Methyl-1-propanol (2M1P), 2-Methyl-1-butanol (2M1B), and 3-Methyl-1-butanol (3M1B).

### *5.4.3 Rectification Column (COL-3)*

In the last distillation column (COL-3), ethanol is concentrated to azeotropic composition in the distillate (**Figure 5**). According to the thermodynamic analysis, the alcohols that are heavier than ethanol and benzaldehyde have intermediate volatility behavior and are expected to accumulate in the middle of the column. As illustrated in the figure, the heavy alcohols and benzaldehyde do in fact accumulate within the column, which makes their removal possible by a liquid side stream draw at tray #16. The total concentration of the higher saturated mono alcohols (HSMA's) peaks at almost 9.4 wt-% around the liquid side draw tray. The slowly decreasing stage holdup of crotonaldehyde at high ethanol concentrations is consistent with its volatility approaching that of the mixture.

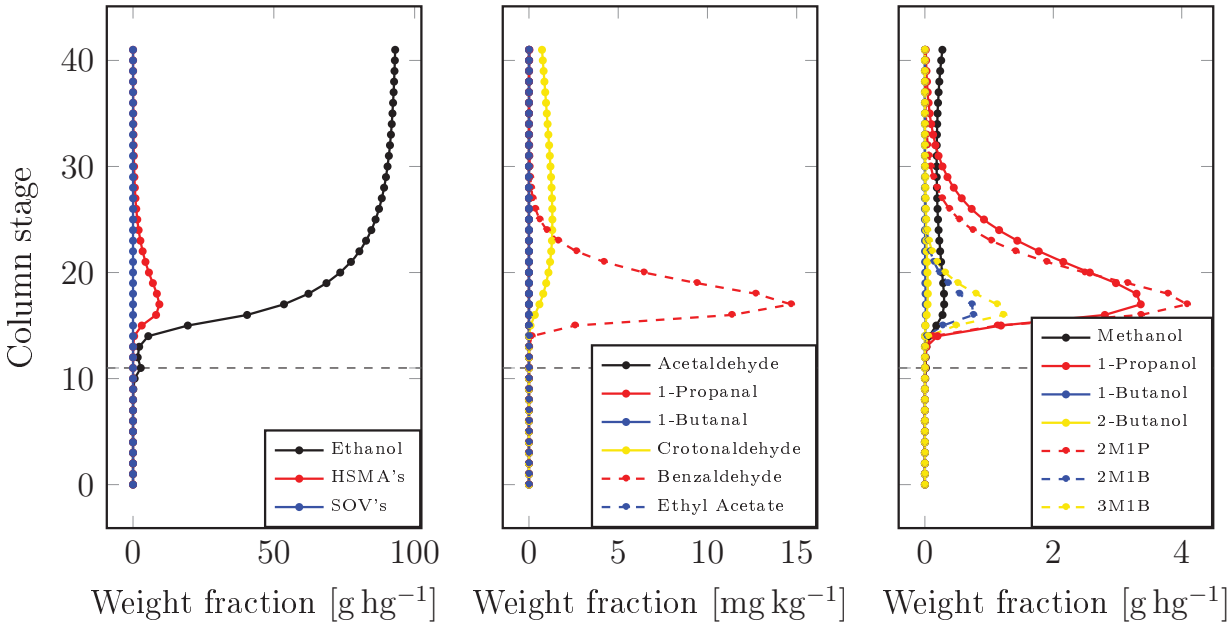


**Figure 5.** Rectification column (COL-3) tray composition profiles. Abbreviations: Sum of volatiles (SOV), higher saturated mono alcohols (HSMA), 2-Methyl-1-propanol (2M1P), 2-Methyl-1-butanol (2M1B), and 3-Methyl-1-butanol (3M1B).

### *5.4.4 Summary*

The component removal efficiencies (eq (2) - (5)) of the four waste streams are illustrated in **Figure 6**.

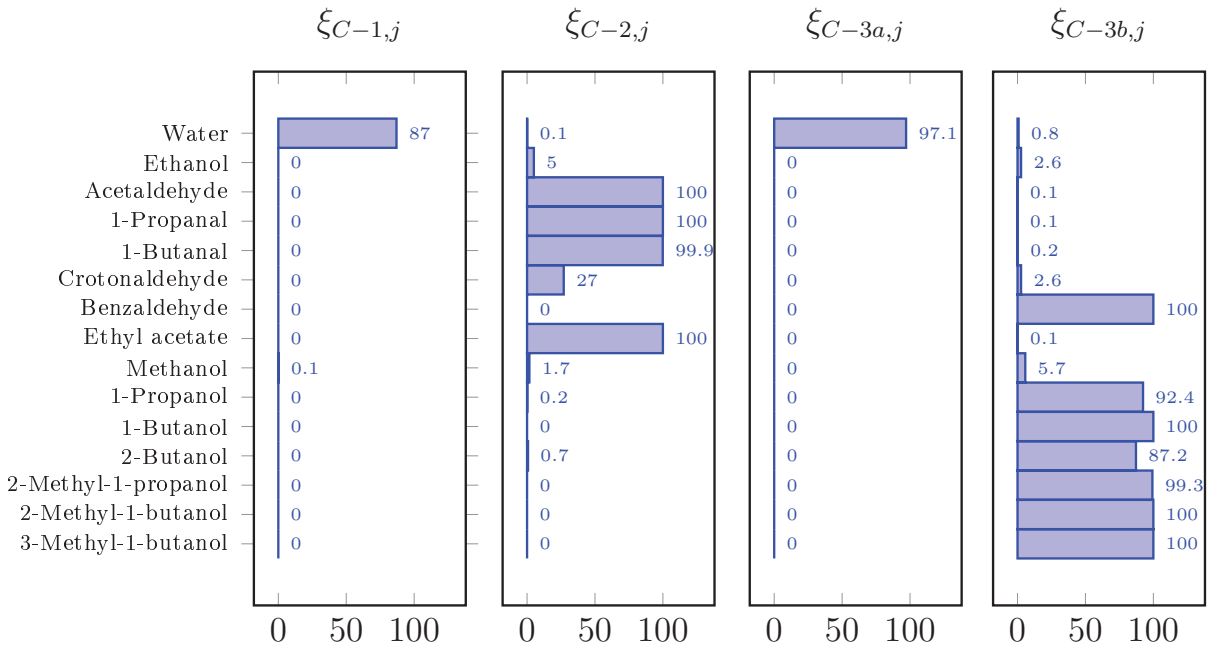


**Figure 6.** Removal efficiency of the various waste streams. The definitions of the removal efficiencies are provided in eq (2)-(5).

Excellent agreement between the expectations derived from the thermodynamic analysis and the rigorous simulation is found. Hence, near complete removal of the light TCs (acetaldehyde, 1-propanal, 1-butanal, and ethyl acetate) is obtained in the distillate COL-2 at a cost of losing 5% ethanol (mass-based). This is a relatively high ethanol loss, which potentially can be reduced at a cost of possibly lower removal efficiencies of the TCs. The bottoms of both COL-1 and COL-3 remove mainly water. The side stream of COL-3 enables near complete removal of benzaldehyde, 1-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-1-butanol, and 3-methyl-1-butanol. This is also consistent with thermodynamic analysis.

The resulting composition of the dehydrated product (**Table 5**) verifies that the Inbicon demonstration plant is capable of meeting the requirements for fuel-grade ethanol. However, the ethanol recovery in the simulation is 93% (mass-based). The simulation results reveal that the operating conditions can be relaxed in order to improve the ethanol recovery, since the product is over-purified.

**Table 5. Dehydrated product composition (stream 5) from simulation and experimental results compared to the solvent-grade and fuel-grade limits. 1 ppm = 1 mg·kg$^{-1}$.**

| Compound(s) | Unit | Limits for ethanol grades | | Results | |
|---|---|---|---|---|---|
| | | Solvent | Fuel | Simulation | Experimental |
| Water | | - | 3000 | 0.7092 | - |
| Ethanol | wt-% | >99.9 | >98.7 | >99.69 | (111) |
| Acetaldehyde | ppm | 2 | - | 0.0039 | 67 |
| 1-Propanal | ppm | - | - | 0.031 | 44.3 |
| 1-Butanal | ppm | - | - | 0.003 | 0.219 |
| Crotonaldehyde | ppm | 0.2 | - | 0.78 | 2.45 |
| Benzaldehyde | ppm | 7 | - | 0 | 0.0748 |
| Ethyl acetate | ppm | 7 | - | 0.0075 | 1177 |
| Methanol | ppm | 7 | 10,000 | 2900 | - |
| 1-Propanol | ppm | - | - | 150 | 1080 |
| 1-Butanol | ppm | - | - | 0.0023 | 0.0468 |
| 2-Butanol | ppm | - | - | 2.7 | 46.7 |
| 2-Methyl-1-propanol | ppm | - | - | 15 | 430 |
| 2-Methyl-1-butanol | ppm | - | - | 0.024 | 0.197 |
| 3-Methyl-1-butanol | ppm | - | - | 0.021 | 1.03 |
| SOV* | ppm | 300 | - | 0.045 | - |
| HSMA† | ppm | - | 20,000 | 168 | - |

*Sum of acetaldehyde, 1-propanal, 1-butanal, and ethyl acetate

†Sum of 1-propanol, 2-butanol, 2-methyl-1-propanol, 1-butanol, 2-methyl-1- butanol, and 3-methyl-1-butanol

The thermodynamic analysis identifies crotonaldehyde, methanol, and 2-butanol, as challenging TCs when it comes to efficiency of removal by distillation. When considering the achieved product composition in **Table 5**, we note that the 2-butanol content is insignificant. However, the crotonaldehyde and in particular the methanol contents must be reduced in order to obtain solvent-grade bioethanol. This observation is consistent with the removal efficiencies of methanol and crotonaldehyde in **Figure 6**. A process revamp proposal for removing these two TCs is investigated in the following section.

According to the thermodynamic analysis (Section 5.2), it is expected to be possible to remove all the remaining TCs included in the figure, but not included in the simulation (**Table 1**). The good agreement between the thermodynamic analysis and the rigorous simulation of the considered TCs support this claim.

### 5.5 Revamp Proposal

As opposed to conventional high-grade ethanol, where methanol is removed in a demethylizing column before the dehydration step, we examine the use of a similar column after the dehydration step, while keeping the former distillation train (COL-1, COL-2 and COL-3) fixed as specified above. This column is referred to as the trace column and it separates dehydrated ethanol into fuel-grade ethanol (distillate) and solvent-grade ethanol (bottoms). This solution has the following advantages:

- Methanol can be removed with ethanol as the top product, while this product still satisfies the methanol specifications of fuel-grade ethanol.
- Crotonaldehyde can be removed as the top product by operating the column at sub-atmospheric pressure. It has been experimentally verified that the equilibrium ratio of crotonaldehyde in ethanol increases when lowering the pressure[18], i.e. crotonaldehyde becomes more volatile and therefore easier to separate.
- The ethanol/water binary system forms a low-boiling azeotrope, thereby making trace amounts of water more volatile. This ensures that a low water content is maintained in the bottom product (solvent-grade).
- Since the ethanol/water azeotrope is slightly pressure-sensitive, the column operating pressure can potentially be utilized to control the water content in the solvent-grade ethanol (bottoms).
- A vacuum pump is commonly used for distillation of fermentation beer[5]. This is also the case in the Inbicon demonstration plant.

When fuel-grade ethanol is to be obtained in the distillate and solvent-grade ethanol is to be obtained in the bottom product, a feasible operating point has been identified, which converts 70% of the incoming dehydrated ethanol into solvent-grade and the remaining ethanol into 30% fuel-grade. The column design and the operating conditions are shown in **Table 6**. No economic considerations are included in this work and thus the design is not optimized. The dehydrated product (stream 5) is condensed and the temperature is

fixed, such that it is saturated at the column operating conditions, before it is fed to the trace column. The latent heat in this stream may be partially recovered in the reboiler of the trace column, as it is operated at a lower temperature.

**Table 6. Trace column (C-4) design and operating conditions.**

| Variable | Unit | Value |
|---|---|---|
| $N_T$ | - | 37 |
| $N_F$ | - | 8 |
| $P_D$ | kPa | 0.2413 |
| $P_B$ | kPa | 0.4128 |
| $E$ | - | 0.80 |
| $Q_F$ | kW | -747 |
| $Q_R$ | kW | 2250 |
| $Q_C$ | kW | -1569 |
| $L/D$ | - | 81.0 |
| $L/B$ | - | 52.1 |

The resulting stream compositions are listed in **Table 7**. The heavy alcohols are the dominating TCs in the solvent-grade ethanol. However, operational changes in the rectification column (COL-3) can be made in order to improve their removal efficiencies through the side stream. Note that the crotonaldehyde content of the solvent-grade ethanol and its limit are equal. Furthermore, note that the methanol limit of fuel-grade ethanol is almost equal to the actual methanol content.

**Table 7. Solvent-grade (bottoms) and fuel-grade (distillate) compositions and limit requirements. The ratio of solvent-grade to fuel-grade ethanol is 70:30. 1 ppm = 1 mg·kg$^{-1}$.**

| Compound | Unit | Solvent-grade ethanol | | Fuel-grade ethanol | |
|---|---|---|---|---|---|
| | | Limits | Simulation | Limits | Simulation |
| Water | ppm | - | 0.82 | 3000 | 22 |
| Ethanol | wt-% | >99.9 | 99.98 | >98.7 | 99 |
| Acetaldehyde | ppm | 2 | 0 | - | 0.013 |
| 1-Propanal | ppm | - | 0 | - | 0.1 |
| 1-Butanal | ppm | - | 0 | - | 0.0098 |
| Crotonaldehyde | ppm | 0.2 | 0.2 | - | 2.1 |
| Benzaldehyde | ppm | 7 | 0.00013 | - | 0 |
| Ethyl acetate | ppm | 7 | 0 | - | 0.025 |
| Methanol | ppm | 7 | 0.7 | 10,000 | 9700 |
| 1-Propanol | ppm | - | 210 | - | 0 |
| 1-Butanol | ppm | - | 0.0034 | - | 0 |
| 2-Butanol | ppm | - | 3.8 | - | 0 |
| 2-Methyl-1-propanol | ppm | - | 21 | - | 0 |
| 2-Methyl-1-butanol | ppm | - | 0.034 | - | 0 |
| 3-Methyl-1-butanol | ppm | - | 0.031 | - | 0.15 |
| SOV* | ppm | 300 | 0 | - | 0.15 |
| HSMA† | ppm | - | 230 | 20,000 | 0 |

*Sum of acetaldehyde, 1-propanal, 1-butanal, and ethyl acetate

†Sum of 1-propanol, 2-butanol, 2-methyl-1-propanol, 1-butanol, 2-methyl-1- butanol, and 3-methyl-1-butanol

## 6 DISCUSSION

A brief discussion on the most relevant aspects of this work is provided in this section.

### 6.1 Process Simplifications

Due to issues with classified information on the process, certain process integrations were omitted in the developed flow sheet. This applies in particular to heat integration and to the reuse of the water waste stream, which is generated in the bottom of the rectification column (stream 8). In particular, heat integration plays a significant role in ensuring economic feasibility of bioethanol production. The Inbicon demonstration plant employs the IBUS concept[10] (Integrated Biomass Utilization System), which is a symbiosis concept that ensures cheap steam from a nearby power production plant. Here we do not provide simulation results for the fully integrated plant.

### 6.2 Purification Unit Feed Composition

Since the majority of the feed stream consists of water, the water-free compositions are significant when evaluating the requirements of the separation unit. This water-free basis gives an indication of the required

efforts of separation. The water-free concentrations are shown in **Table 8**, which also includes reported values from the open literature. Ethyl acetate, methanol, and 2-methyl-1-propanol are present at higher concentrations than the reported literature concentrations. However, the TC concentrations depend on the operating conditions of the upstream processes, i.e. the type of microorganisms, feedstock and more.

When comparing the water-free concentrations of the requirements for both fuel-grade ethanol and solvent-grade ethanol (**Table 7**), it is clear that separation of TCs is essential.

**Table 8. Obtained feed stream (beer) composition compared to literature compositions. The category "Other" covers mainly solid residues. The unit mg·kgPA$^{-1}$ refers to mg TC per kg pure alcohol (PA), meaning ethanol. Note that Baeyens et al.[5] only report the complete alcohol TC content.**

| Variable | Unit | Composition and feedstock by reference | | | |
|---|---|---|---|---|---|
| | | This work | Decloux/Coustel[4] | Baeyens et al.[5] | Marriaga[2] |
| | | Wheat straw | n.s. | Cassava | n.s. |
| Flow rate | kg·h$^{-1}$ | 7861 | 228,750 | - | 48,800 |
| Water | wt-% | 96.5 | 91.9 | 81.4 | 92.6 |
| Ethanol | wt-% | 3.49 | 8.02 | 11.6 | 6.99 |
| Acetaldehyde | mg·kgPA$^{-1}$ | 176 | 611 | 431 | - |
| 1-Propanal | mg·kgPA$^{-1}$ | 352 | - | - | - |
| 1-Butanal | mg·kgPA$^{-1}$ | 3 | - | - | - |
| Crotonaldehyde | mg·kgPA$^{-1}$ | 1 | - | - | - |
| Benzaldehyde | mg·kgPA$^{-1}$ | 1 | - | - | - |
| Ethyl acetate | mg·kgPA$^{-1}$ | 1192 | 150 | 474 | - |
| Methanol | mg·kgPA$^{-1}$ | 2923 | 411 | - | 141 |
| 1-Propanol | mg·kgPA$^{-1}$ | 1814 | 1259 | - | 687 |
| 1-Butanol | mg·kgPA$^{-1}$ | 9 | - | - | - |
| 2-Butanol | mg·kgPA$^{-1}$ | 19 | - | 10,767 | - |
| 2-Methyl-1-propanol | mg·kgPA$^{-1}$ | 2023 | 1272 | - | - |
| 2-Methyl-1-butanol | mg·kgPA$^{-1}$ | 453 | - | - | - |
| 3-Methyl-1-butanol | mg·kgPA$^{-1}$ | 731 | 3080 | - | 1402 |
| Other | mg·kgPA$^{-1}$ | - | - | 600,000 | - |

### 6.3 Operational Aspects

To examine the robustness of the results, some sensitivity studies comprising slightly different feed mixtures have been made. In these cases, which involved lower ethanol feed stream concentrations, it was also possible to achieve a roughly 70:30 solvent:fuel grade mixture, although the reboiler duty (first converging solution, i.e. not optimized) was higher. Presumably this is due to the need for separating more water plus TCs from a smaller amount of ethanol. In order to complete the technical feasibility analysis, the trace columns (COL-4a/b) should be investigated in terms of the operational aspects. According to the simulation results of the achievable product compositions (**Table 7**), we note that both the distillate and the bottoms have TC contents, which are close to the respective grade limits (**Table 7**). This applies to methanol for the fuel-grade (distillate) and crotonaldehyde for the solvent-grade ethanol (bottoms). This observation indicates that these compositions should be controlled indirectly or directly in a dual composition control scheme. In addition, pressure control should be investigated carefully since (i) the ethanol/water azeotrope is slightly pressure-sensitive and (ii) since the pressure sensor location typically has an impact on the dynamic economic performance in distillation columns with large internal flow rates[19].

### 6.4 Economic Aspects

The market for fuel-grade ethanol is volatile and the demand in Europe is currently (2016) low. According to ICIS, many fuel-grade ethanol producing plants were not believed to be operating with profits in 2014. Hence, increasing the product portfolio of such plants might give economic advantages in a volatile ethanol market. Based on ICIS pricing of September 2015, the ethanol prices were around $\$820\cdot ton^{-1}$ for fuel-grade and $\$1025\cdot ton^{-1}$ for 99% industrial-grade ethanol. Adopting these prices and assuming a 70:30 solvent:fuel split, the value of the ethanol can be increased from $\$820\cdot ton^{-1}$ to $\$960\cdot ton^{-1}$. Without heat-integration or optimization, 2250 kW of steam is required per $0.07\ kg\cdot s^{-1}$, which corresponds to roughly 15 kg steam per kg ethanol. Thus, the revamp proposal decreases the net product value by $\$140\cdot ton^{-1}$ (accounting for steam at a price of $\$19\cdot ton^{-1}$). This example illustrates the importance of heat-integration. Since the trace column (COL-4) is operated at low pressure, the quality of the required steam is low, which leaves several options for heat integration. If for example 50% of the steam is fresh makeup, the 70:30 mixture has a value, which is equal to that of fuel grade-ethanol. **Figure 7** shows the historical development of the prices of the different ethanol grades. Assuming that heat-integration is possible, the figure illustrates that the revamp proposal has a potential for an economical gain as the value of the product becomes higher than that of fuel-grade ethanol. At the same time, it offers the possibility to even out some price fluctuation of the fuel-grade ethanol.

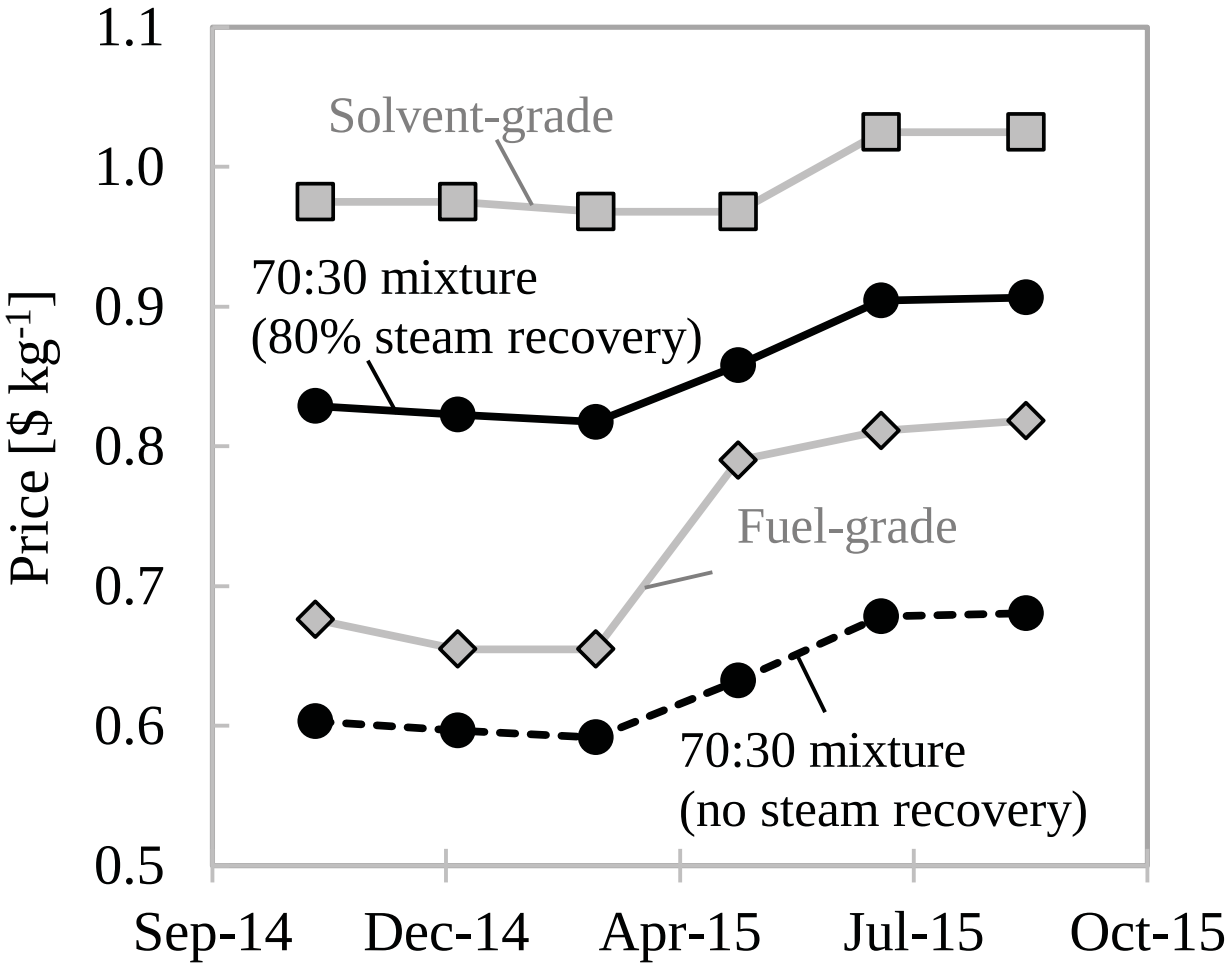


**Figure 7.** Historical development of prices of different ethanol grades (grey) and Inbicon revamp product values for the 70:30 solvent:fuel-grade mixture. The "no steam recovery" scenario means that fresh steam is used ($19·ton$^{-1}$), and the "80% steam recovery" means that 20% is fresh steam makeup.

## 7 CONCLUSION

The separation unit of a second generation bioethanol plant was investigated in this study. A second-generation bioethanol demonstration plant (Inbicon A/S) was used to support a simulation model with experimental results in the form of composition analyses of liquid samples and logged operational data. The contribution of this paper is twofold: First, we show that adding one additional distillation column to a conventional three-column bioethanol plant can diversify the product portfolio of a conventional bioethanol plant, which can represent an economic advantage. Second, we identify 13 significant trace impurities in such bioethanol plant, report their compositions of the streams in the purification unit as experimental and simulation results, and characterize the overall separation performance in terms of stream summaries and utility consumption.

The 13 identified trace compounds are acetaldehyde, 1-propanal, 1-butanal, crotonaldehyde, ethyl acetate, methanol, 1-propanol, 1-butanol, 2-butanol, 2-methyl-propanol, 3-methyl-1-butanol, and 3-methyl-1-butanol. These are present in the fermentation broth resulting from lignocellulosic feedstock. The feed composition was determined by reconciling the experimental data with the first distillation column in the separation unit. Then, a simulation platform was established, which could represent a steady state operating point of the separation unit with reasonable accuracy. The roles of the three distillation columns were identified by simulation with respect to the removal of the trace compounds:

- The beer stripper: Removes water and nonvolatile compounds (solids) in the bottom. Thermodynamic analysis suggests that less volatile trace compounds such as carboxylic acids and furfural also can be removed in the beer stripper bottoms, however this result was not confirmed by simulation.
- The aldehyde column: Removes acetaldehyde, 1-propanal, 1-butanal, and ethyl acetate in the distillate.
- The rectification column: Removes water in the bottoms, and benzaldehyde, 1-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-1-butanol, and 3-methyl-1-butanol.

Methanol and crotonaldehyde cannot be removed in the described three-column sequence of the demonstration plant. Hence, a fourth column was examined to effectively remove both methanol and crotonaldehyde simultaneously. By using such a column after the dehydration step (where anhydrous ethanol is obtained), the simulation results suggest that around 70% solvent-grade ethanol can be obtained as bottom product and 30% fuel-grade ethanol can be obtained as distillate.

## ACKNOWLEDGEMENT

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## SUPPORTING INFORMATION

Table S1. Definitions of fuel-grade (European Standard DS/EN 15376) and solvent-grade ethanol in terms of purity specifications. The ethanol specifications are given in lower limits while the impurities are listed in terms of upper limits. 1 ppm=1 $mg \cdot kg^{-1}$.

Table S2. Operational data of the purification unit in Inbicon demonstration plant.

Table S3. Gas chromatography-mass spectrometry results of liquid plant samples results. No liquid samples were taken from stream 3 (aldehyde column bottoms), stream 9 (rectification column side stream), and stream 10 (water from molecular sieve).

Table S4. Stream summary of the separation unit of Inbicon demonstration plant. All concentrations below $10^{-3}$ $mg \cdot kg^{-1}$ were set to zero.

This information is available free of charge via the Internet at http://pubs.acs.org/

## NOMENCLATURE

| | |
|---|---|
| $E$ | Murphree efficiency, - |
| $K$ | Volatility/equilibrium constant, - |
| $L$ | Reflux flow rate, $m^3 \cdot h^{-1}$ |
| $L/D$ | Reflux ratio, $kg \cdot kg^{-1}$ |
| $m$ | Mass flow rate, $kg \cdot h^{-1}$ |
| $N_C$ | Number of compounds, - |
| $N_F$ | Feed stage, - |
| $N_S$ | Side draw stage, - |
| $N_T$ | Number of trays, - |
| $N_{TC}$ | Number of trace compounds, - |
| $P_D$ | Pressure of distillate, kPa |
| $P_B$ | Pressure of bottoms, kPa |
| $Q_C$ | Condenser duty, kW |
| $Q_F$ | Feed pre-heater duty, kW |
| $Q_R$ | Reboiler duty, kW |
| $T$ | Temperature, K |
| $V$ | Volumetric flow rate, $m^3 \cdot h^{-1}$ |

| | |
|---|---|
| *V/B* | Boilup ratio, $kg \cdot kg^{-1}$ |
| *w* | Weight fraction, $kg \cdot kg^{-1}$ |

*Greek symbols*

| | |
|---|---|
| $\alpha$ | Relative volatility, - |
| $\xi$ | Removal efficiency, $kg \cdot kg^{-1}$ |
| $\rho$ | Density, $kg \cdot m^{-3}$ |
| $\sigma$ | Standard deviation |
| $\varphi$ | Objective function |

*Abbreviations*

| | |
|---|---|
| *TC* | Trace compound |
| *VLE* | Vapor-liquid equilibrium |
| *VLLE* | Vapor-liquid-liquid equilibrium |
| *HSMA* | Higher saturated mono-alcohols |
| *SOV* | Sum of volatiles |

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# List of Figure Captions

**Figure 1.** Simplified representation of the purification unit of the Inbicon demonstration plant. Stream names, equipment names, and measurement indicators are listed with the following abbreviations: TI is a temperature indicator, PI is a pressure indicator, FI is a flow rate indicator, COL is column, REB is reboiler, COND is condenser, and PRE is feed preheater.

**Figure 2.** The logarithmic relative volatilities of various trace compounds at 101.325 kPa. The position of a curve of a TC relative to zero determines its behavior during distillation: If ln ln $\alpha j \geq 0$, component *j* will concentrate in the distillate, and if ln $\alpha j \leq 0$, component *j* will concentrate in the bottom. In practice, a limit of 0.5 for ln $\alpha j$ is reasonable. Colors: Aldehydes + other (blue), alcohols (green), and carboxylic acids (red).

**Figure 3.** Beer stripper (COL-1) tray composition profiles. Abbreviations: Sum of volatiles (SOV), higher saturated mono alcohols (HSMA), 2-Methyl-1-propanol (2M1P), 2-Methyl-1-butanol (2M1B), and 3-Methyl-1-butanol (3M1B).

**Figure 4.** Aldehyde column (COL-2) tray composition profiles. Abbreviations: Sum of volatiles (SOV), higher saturated mono alcohols (HSMA), 2-Methyl-1-propanol (2M1P), 2-Methyl-1-butanol (2M1B), and 3-Methyl-1-butanol (3M1B).

**Figure 5.** Rectification column (COL-3) tray composition profiles. Abbreviations: Sum of volatiles (SOV), higher saturated mono alcohols (HSMA), 2-Methyl-1-propanol (2M1P), 2-Methyl-1-butanol (2M1B), and 3-Methyl-1-butanol (3M1B).

**Figure 6.** Removal efficiency of the various waste streams. The definitions of the removal efficiencies are provided in eq (2)-(5).

**Figure 7.** Historical development of prices of different ethanol grades (grey) and Inbicon revamp product values for the 70:30 solvent:fuel-grade mixture. The "no steam recovery" scenario means that fresh steam is used ($19·ton-1), and the "80% steam recovery" means that 20% is fresh steam makeup.

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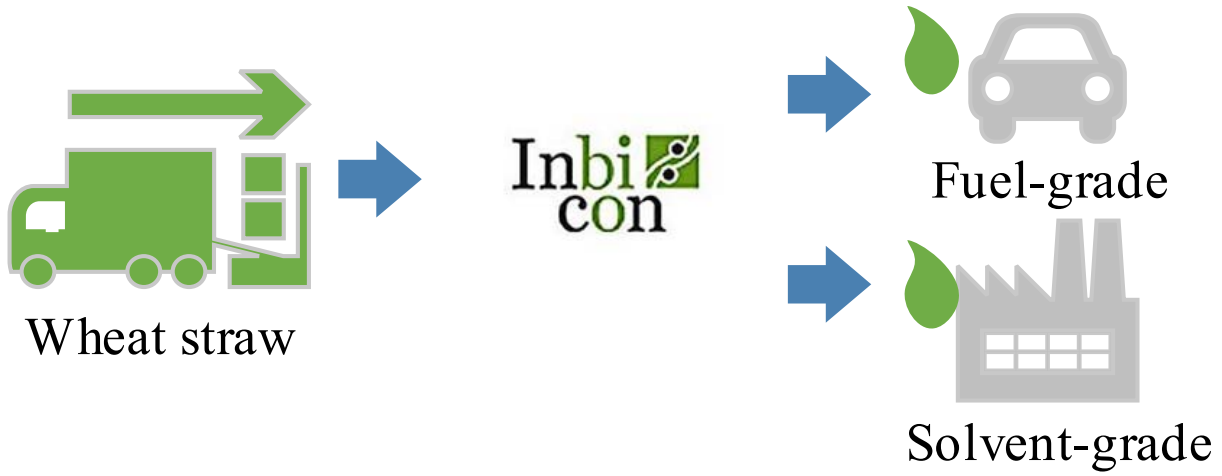

# Adding Value to Bioethanol through a Purification Process Revamp

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## SUPPORTING INFORMATION

**Table S1. Definitions of fuel-grade (European Standard DS/EN 15376) and solvent-grade ethanol in terms of purity specifications. The ethanol specifications are given in lower limits while the impurities are listed in terms of upper limits. 1 ppm = 1 mg·kg$^{-1}$.**

| Compound | Unit | Grade limits | |
|---|---|---|---|
| | | Fuel | Solvent |
| Ethanol | wt-% | >98.7* | >99.9 |
| Water | wt-% | 0.3 | 0.1 |
| Methanol | ppm | 10,000 | 7 |
| Total acidity | ppm | 70 | 70 |
| Crotonaldehyde | ppm | - | 0.2 |
| Acetaldehyde | ppm | - | 2 |
| Diethyl acetal | ppm | - | 7 |
| Benzaldehyde | ppm | - | 7 |
| Acetone | ppm | - | 7 |
| Ethyl formate | ppm | - | 7 |
| Ethyl acetate | ppm | - | 7 |
| Sum of other volatiles (Pr. Eur.) | ppm | - | 300 |

*May also include up to 2.0 wt-% higher saturated mono-alcohols.

**Table S2. Operational data of the purification unit of Inbicon demonstration plant.**

| | Unit | Column ID | | |
|---|---|---|---|---|
| | | COL-1 | COL-2 | COL-3 |
| $N_T$ | - | 18 | 30 | 40 |
| $N_F$ | - | 18 | 22 | 11 |
| $N_S$ | - | - | - | 16 |
| $P_D$ | kPa | 24.18±0.06 | 102.4±0.1 | 291.2±0.9 |
| $P_B$ | kPa | 29.22±0.16 | 104.2±0.1 | 308.8±1.0 |
| $T_F$ | K | 304.8±0.1 | - | - |
| $T_D$ | K | 334.5±0.1 | 351.6±0.3 | 380.3±0.1 |
| $T_B$ | K | 341.0±0.2 | (352.9±0.4) | 407.5±0.1 |
| $T_4$ | K | 339.00.1 | - | - |
| $T_5$ | K | - | - | 407.3±0.1 |
| $T_{15}$ | K | - | - | 389.3±0.5 |
| $T_{23}$ | K | - | - | 381.8±0.1 |
| $V_{cw}$ | m$^3$·h$^{-1}$ | - | 10.26±0.15 | 5.488±0.345 |
| $V_R$ | m$^3$·h$^{-1}$ | - | - | |

**Table S3. Gas chromatography-mass spectrometry results of liquid plant samples results. No liquid samples were taken from stream 3 (aldehyde column bottoms), stream 9 (rectification column side stream), and stream 10 (water from molecular sieve). "n.d." is "not detected". 1 ppm = 1 mg·kg$^{-1}$.**

| | | Stream ID | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 1 Feed | 2 Beer stripper distillate | 4 Rectification column distillate | 5 Dehydrated product | 6 Beer stripper bottoms | 7 Aldehyde column distillate | 8 Rectification column bottoms |
| Ethanol | wt-% | 3.5 | 21.5±0.2 | 86.1±14.9 | 111±21 | 0.0500±0.0500 | 81.2±17.0 | n.d. |
| Acetaldehyde | ppm | 10.9±0.6 | 8.99±1.19 | 35.2±1.8 | 67.0±7.7 | 4.96±0.08 | 575±68 | n.d. |
| 1-Propanal | ppm | - | 16.6±1.8 | 10.9±0.7 | 44.3±3.3 | 11.5±2.9 | 51.2±18.1 | 11.2±3.5 |
| 1-Butanal | ppm | - | 0.0833±0.0288 | 0.198±0.027 | 0.219±0.021 | 0.0991±0.0029 | 0.418±0.116 | 0.114±0.014 |
| Crotonaldehyde | ppm | - | 0.108±0.001 | 0.322±0.027 | 2.45±0.13 | 0.0214±0.0114 | 0.461±0.028 | n.d. |
| Benzaldehyde | ppm | - | 0.0194±0.0011 | 0.0119±0.0018 | 0.0748±0.0182 | 0.0245±0.0022 | 0.0526±0.0031 | 0.0208±0.0036 |
| Ethyl Acetate | ppm | 275±52 | 201±64 | 953±288 | 1177±210 | 1.98±0.10 | 1606±275 | 0.475±0.101 |
| Methanol | ppm | - | - | - | - | - | - | - |
| 1-Propanol | ppm | 201±48 | 290±121 | 26.3±15.9 | 1080±586 | 0.381±0.496 | 84.2±38.1 | 0.240±0.305 |
| 1-Butanol | ppm | - | 1.69±0.19 | 0.0894±0.0024 | 0.0468±0.0087 | 0.0395±0.0167 | 0.512±0.020 | 0.0110±0.0044 |
| 2-Butanol | ppm | 32.1±12.9 | 3.32±2.01 | 0.646±0.792 | 46.7±27.8 | n.d. | 8.79±6.38 | n.d. |
| 2-Methyl-1-propanol | ppm | - | 444±19 | 5.57±0.30 | 430±15 | 0.430±0.020 | 86.1±3.1 | 0.429±0.056 |
| 2-Methyl-1-butanol | ppm | - | 99.3±7.8 | 0.192±0.005 | 0.197±0.019 | 0.0331±0.0043 | 1.85±0.09 | 0.00790±0.00250 |
| 3-Methyl-1-butanol | ppm | - | 160±10 | 0.875±0.018 | 1.03±0.11 | 0.211±0.025 | 7.12±0.40 | 0.0489±0.0125 |

**Table S4. Stream summary of the separation unit of Inbicon demonstration plant. All concentrations below $10^{-3}$ mg·kg$^{-1}$ were set to zero.**

| Stream ID | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Phase | - | Liquid | Liquid | Liquid | Vapor | Vapor | Liquid | Liquid | Liquid | Liquid | Vapour |
| Flow rate | kg·h$^{-1}$ | 7867 | 1275 | 1260 | 272.7 | 254.6 | 6592 | 15.27 | 970.7 | 16.39 | 18.06 |
| | m$^3$·h$^{-1}$ | 7.997 | 1.374 | 1.381 | 70.91 | 170.1 | 6.707 | 0.02036 | 1.009 | 0.0201 | 30.8 |
| Pressure | kPa | 24.18 | 24.18 | 104.3 | 291.7 | 105 | 29.81 | 102.5 | 309.7 | 302.5 | 105 |
| Temperature | K | 304.8 | 325.5 | 359 | 380.6 | 388.2 | 342.1 | 351.2 | 407.8 | 386.6 | 388.2 |
| Molecular weight | g·mol$^{-1}$ | 18.41 | 20.76 | 20.64 | 41.72 | 46.01 | 18.02 | 41.95 | 18.02 | 26.07 | 18.02 |
| Density | kg·m$^{-3}$ | 983.8 | 927.6 | 912.3 | 3.845 | 1.497 | 982.9 | 749.8 | 961.8 | 815.5 | 0.5862 |
| Composition | | | | | | | | | | | |
| Water | wt-% | 96.48 | 78.29 | 79.15 | 6.623 | 0.0007092 | 100 | 7.015 | 100 | 51.02 | 100 |
| Ethanol | wt-% | 3.485 | 21.5 | 20.68 | 93.09 | 99.69 | 0 | 89.79 | 0 | 40.51 | 0 |
| Acetaldehyde | mg·kg$^{-1}$ | 6.1 | 38 | 0 | 0.0037 | 0.0039 | 0 | 3200 | 0 | 0 | 0 |
| 1-Propanal | mg·kg$^{-1}$ | 12 | 76 | 0.0063 | 0.029 | 0.031 | 0 | 6300 | 0 | 0 | 0 |
| 1-Butanal | mg·kg$^{-1}$ | 0.097 | 0.6 | 0 | 0.0028 | 0.003 | 0 | 50 | 0 | 0 | 0 |
| Crotonaldehyde | mg·kg$^{-1}$ | 0.035 | 0.22 | 0.16 | 0.73 | 0.78 | 0 | 4.7 | 0 | 0.33 | 0 |
| Benzaldehyde | mg·kg$^{-1}$ | 0.024 | 0.15 | 0.15 | 0 | 0 | 0 | 0 | 0 | 11 | 0 |
| Ethyl acetate | mg·kg$^{-1}$ | 42 | 260 | 0.0015 | 0.007 | 0.0075 | 0 | 21000 | 0 | 0 | 0 |
| Methanol | mg·kg$^{-1}$ | 100 | 630 | 630 | 2700 | 2900 | 0.13 | 930 | 0.0012 | 2700 | 0 |
| 1-Propanol | mg·kg$^{-1}$ | 63 | 390 | 390 | 140 | 150 | 0 | 42 | 0 | 28000 | 0 |
| 1-Butanol | mg·kg$^{-1}$ | 0.3 | 1.9 | 1.9 | 0.0022 | 0.0023 | 0 | 0.0045 | 0 | 140 | 0 |
| 2-Butanol | mg·kg$^{-1}$ | 0.68 | 4.2 | 4.2 | 2.5 | 2.7 | 0 | 1.4 | 0 | 280 | 0 |
| 2-Methyl-1-propanol | mg·kg$^{-1}$ | 71 | 440 | 440 | 14 | 15 | 0 | 13 | 0 | 34000 | 0 |
| 2-Methyl-1-butanol | mg·kg$^{-1}$ | 16 | 97 | 98 | 0.022 | 0.024 | 0 | 0.09 | 0 | 7600 | 0 |
| 3-Methyl-1-butanol | mg·kg$^{-1}$ | 26 | 160 | 160 | 0.02 | 0.021 | 0 | 0.084 | 0 | 12000 | 0 |