

## Conceptual Design of a Separation Process for Higher Alcohols Made by Catalytic Condensation of Ethanol

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### Abstract

A downstream process for the separation of n-butanol from a product mixture containing unreacted ethanol, higher alcohols, aldehydes, water and traces of other chemical species was studied and therewith a conceptual design for the separation train has been devised. A novel approach and a newly developed catalyst were introduced to produce n-butanol (or iso-butanol) from ethanol as a raw material through an alternative path. The product stream from the reactor outlet consists of various chemical species ranging from saturated alcohol mixture, to aldehydes, to traces of aromatics and high boilers, and is ought to be separated into individual components based on their commercial/industrial applicability. Nine azeotropes of which one being ternary and the remaining eight binary azeotropes were identified between the various product components. Due to the chemical complexity, a multi-column downstream separation unit is needed therefore the schema containing several distillation units is likely to be energy intensive. The goal of this work was primarily to assess the technical and commercial feasibility of such separation technology; further process intensification however, is a subject for later studies.

**Keywords:** Ethanol; Butanol; Distillation; Higher alcohols; Biofuels; Chemicals

### Introduction

World demand for fuels, chemicals, energy, materials and feedstock are increasing exponentially day-by-day. Existing technologies and production methods are failing to keep abreast with the current consumption pattern in avoiding any turbulence to the demand-supply chain and simultaneously dealing with environmental issues. Moreover, the global impact on climate change has led to stringent environmental regulations, which makes the operating standards quiet arduous. High oil prices, market concerns regarding the subject of its availability and an increasing demand from fast growing economies like Brazil, Russia, India and China (BRICs) have propelled the global community to a new juncture to address the security of energy and material supplies and eventually decentralize our dependency on traditional resources. Therefore, there is a collective sense of urgency to deal with this challenge engulfing the 21<sup>st</sup> century in order to secure our energy and materials interests through sustainable means.

Today, biofuels account to 3.5% of the world's transportation and the investments into biofuels exceeded production capacity of 4.5 billion litres worldwide in 2012, and is steeply rising [1]. According to IEA, biofuels can provide up to 27% of world transportation fuel by 2050 [2]. Biofuels can also contribute to the improved development of the agro-industry and generate many new jobs [3]. In addition, many commodity materials like plastics, solvents and plasticizers are becoming greener at growth rather exceeding 10% per year. The trade association for European bioplastics predicted global bioplastics production capacity will reach 1.7 million tonnes by 2015, more than doubling 2010 capacity [4]. This trend has created a whole new market, the so called "green economy". Nevertheless, unfortunately, even after the huge subsidies, incentives and promotional schemes raised by the governments worldwide, bio-based materials and fuels still have some significant setbacks. The main issues are the cost-competitiveness to fossil-based products, the difficulties in policy making with regard to energy, transport, agriculture and environment, the *food vs. fuel* debate

and finally the social perception on the genetically modified crops for biomass production. Although the bio based fuels and materials have their own disadvantages and cannot totally replace fossil products, its contribution to the energy demand and their transitional role in cushioning the foreseeable oil driven supply and demand crisis is highly significant.

In order to fully realize the potential of bio-based products, a *sustainable business model* is required apart from low-carbon technologies. Such a model must comprise a mixture of value added products from ideally more than one independent value chain and supply chain respectively. Embarking on such a strategy helps rendering the economic and ecological balance sheet towards positive numbers, liberated from fluctuations of supply and demand in the crude oil market.

### Ethanol as Raw Material

In recent years, ethanol has become a commodity chemical, which will be being produced at a scale of about 90 million tonnes worldwide [5]. According to NOVOZYMES large scale production of second-generation "2G" bioethanol is only a few years away, clearly indicating that ethanol prices will stay moderate and its availability will strongly increase in the future. Application of heterogeneous catalysis for the exploitation of ethanol as raw material for producing value added products is of very high interest. Currently BRASKEM is in the planning phase of building large-scale ethylene units. The same holds

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true for the bulk chemical ethylene oxide according to constructing company Scientific Design [6].

It is also well established that ethanol and methanol can be converted to higher alcohols in a gas phase reaction. This pathway will be further elucidated in this contribution. Converting ethanol to higher alcohols, which sell for about double the price of ethanol is clearly attractive from a commercial point of view. In such a system, a multiple mixture of various alcohols, aldehydes and hydrocarbons are considered. In spite of the potential for catalytic condensation of ethanol to higher alcohols only very little is understood about the technology for achieving the product separation of such complex mixtures. The goal of this study consequently was to assess the technical and commercial feasibility of the separation technology.

### Higher Alcohols as 2G-Biofuels and Bio-based Chemicals

Second-generation biofuel production processes use biomass from a variety of non-food crops. These include waste biomass, hays stacks, wood chips, straw, miscanthus etc. Furthermore, the production of cellulosic ethanol from lignocelluloses as a feedstock has gained more attention in recent times. Historically the transformation of these raw materials is discussed under Biomass-to-Liquid (BTL) processes. Unlike first generation feedstock 2G feedstock does not compete with food production, are more environment friendly and preferably require less arable land. In the renewable fuel context, higher alcohols are seen as biofuels where one refers to butanol, ethers of n-hexanol and n-octanol, but potentially also other higher alcohols might be considered to be 2G-Biofuels and bio-based chemicals.

#### Butanol as a potential automotive fuel

Biobutanol seems to emerge as a potential motor fuel of the future and could partially replace ethanol. Bio-butanol refers to *n*- or iso-butanol. Both can be produced by microbial fermentation [7], alike the production of ethanol from very similar raw materials. Bio-butanol however displays several advantages over ethanol [8] as listed below:

(i) Lower vapour pressure compared to that of ethanol; (ii) Energy density of butanol is close to gasoline; (iii) Butanol has octane value closer to gasoline; (iv) Solubility of water to butanol is lower than that of ethanol; (v) Butanol can easily be transported through existing pipelines and (vi) Can be used in existing IC engines in higher concentrations than ethanol

The worldwide fuel market for butanol is about 1.3 billion litres per year. *n*-butanol (or iso-butanol) is widely produced via the so-called "Oxo-process" from propylene and syngas [9]. About 80% of the production costs are linked to the raw material price of propylene, which is usually manufactured in parallel to ethylene by steam cracking of naphtha. Hence, the butanol pricing is closely tied up with the oil market, and one can observe frequent cost fluctuations.

#### Ethers of n-hexanol and n-octanol as cetane number enhancer

Addition of ethers of hexanol and octanol to diesel fuel results in significantly increased cetane numbers. The addition of such ethers, at concentrations of 2 and 5 percent by weight, results in cetane number well above 100 [10]. Ethers could replace toxic, unstable and explosive alcohol nitrates like ethyl-hexyl-nitrate and in particular nitrates of n-hexanol and n-octanol.

### Higher alcohols as diesel fuel

Likewise neat alcohols can also serve as diesel fuel. Practically suitable cetane numbers in the 40s are displayed by *n*-octanol, whereas numbers around 80 are reported for *n*-tetradecanol [11]. However, in general relatively moderate cetane numbers and the high price make alcohols economically unattractive as fuels for now.

### Applications of higher alcohols as chemicals

Table 1 shows existing applications of higher alcohols for commodity and specialty products. Own estimations show that about 20 million tons of derivatives of higher alcohols are produced annually. The market and applications for *n*- and iso-butanol are already very diverse [12]. Without claiming completeness for all existing and potential applications, it becomes obvious that a large market can potentially be exploited by replacing the fossil based oxo-process with a green alternative, once costs are already competitive or at least could become competitive.

### Applications of higher aldehydes as chemicals

In case aldehydes as by products cannot be avoided, it is then important to consider potential commercial outlets for these compounds. Table 2 lists existing applications of higher aldehydes for commodity and specialty chemicals.

### Catalytic Technologies for Synthesis of Higher Alcohols

Several materials have already been investigated and tested as catalyst for butanol-synthesis. Yang *et al.* [13] reported that zeolites, aluminosilicates modified by ion exchange with alkaline earth metals such as Lithium or Potassium are suitable catalysts. In addition, aluminium oxides which have been doped with the transition metals nickel, iron and cobalt, were used by Yang and Meng [14] as catalysts for butanol-synthesis. Based on the experimental results they suggested that the synthesis of butanol occurs by a direct condensation of two molecules of ethanol. According to this, the carbon-hydrogen-bond of an activated basic molecule reacts with another molecule by elimination of water. Ndou analysed the catalytic production of butanol from ethanol and used pure alkali or transition metals modified magnesium or aluminium oxide [15].

The oxidation from ethanol to acetaldehyde, followed by aldol condensation to beta methyl acrolein with subsequent hydrogenation is described as a further mechanism. However, Ndou verified that the predominant part of the butanol is synthesised by the mechanism of direct condensation as postulated by Yang and Meng. That is, the main reaction path goes over direct condensation as illustrated in Figure 1.

Tsuchida *et al.* [16-18] investigated the butanol synthesis by the use of hydroxylapatites, a mineral of the category of anhydrous phosphates, with the stoichiometric formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . This mineral can also be synthesised non-stoichiometrically out of calcium nitrate and ammonium phosphate, whereas the relation of calcium to phosphorus defines the allocated acid and basic active sites. Following butanol, also higher linear and alpha-branched alcohols were produced in significant amounts.

Also Cosimo [19], who analysed the impact and the explanations for branching during the condensation reaction to higher alcohols, affirms that the butanol-synthesis could not only proceed by direct condensation but also by alcohol condensation and in the presence of

Chemical Composition	Alcohol	Branching	Applications
Phosphoric acid ester	C4, C6	Optional	Hydraulic fluid, solvent, plasticiser, lubricant
Citric acid ester	>C4	Optional	Environmentally benign plasticiser
Phthalic acid ester	>C4	Optional	Plasticizer (mostly banned, e.g. DEHP)
Trimellitate ester	>C6	Yes	TOTM/TEHTEM – alternative DEHP
Maleic acid ester	C4	Optional	Plasticiser
Adipic acid	>C8	Optional	Plasticiser
Acetic acid ester	≥C4	No	Solvent for coatings
Butyric acid ester	≥C4	No	Solvent
Fatty acid ester	≥C4	Optional	Lubricant, wax, herbicide additive
Ethoxylates	>C4	Optional	Cosmetics, drilling fluid additive
Neat alcohols	≥C4	Optional	Solvent, coal floatation frothing agent
Nitric acid ester	≥C6	Yes	Cetane enhancer
Sugar ethers	>C6	Optional	Low and high foaming surfactant
Dialkylether	≥C4	Optional	Cosmetics, solvent, heat storage material
Guerbet alcohols	>C6	Optional	Cosmetics, fatty alcohols, surfactant
Potential new applications in the pipeline			
Lactic acid ester	>C4	Optional	Solvent
Dialkylether	>C4	Optional	Cetane enhancer
Neat alcohols	>C4	Optional	Intermediate for alkenes

Table 1: Commodity and specialty products from higher alcohols.

Chemical Name	Applications
Acetal	Intermediate, acetic acid, 2-ethyl-1-butanol (solvent)
Butanal	Intermediate for n-butanol, 2-ethyl-hexanol, 2-ethyl-1-butanol
Hexanal	Intermediate for hexanol
Octanal	Intermediate for n-octanol, fatty alcohols, surfactants

Table 2: Commodity products from by-product aldehydes.

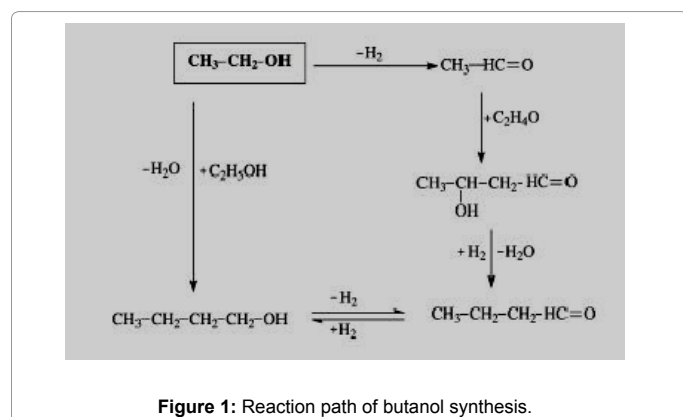


Figure 1: Reaction path of butanol synthesis.

acid and basic sites. Synthetic hydrotalcite, which are layered minerals out of magnesium and aluminium oxides that belong to the group of “Layered Double Hydroxides” and hold both acid and basic active sites, were employed as catalysts. Several patents have been filed by DuPont, using different types of hydrotalcite crystals [20].

The synthesis of higher alcohols out of a methanol-ethanol-mixture was analysed by Olson [21]. It turns out that activated carbon which is impregnated with magnesium oxide was active too. However, the manufactured impregnated carbons lost their catalytic activity within a very short time on the onset of the reaction.

As input for assessing the potential of catalytic condensation of higher alcohols and possibly also for the related aldehyde by-products with respect to downstream processing, the results from a continuously operated mini-plant have been used as an input for the calculation.

Details about the applied catalyst were published separately [22].

## Downstream Processing Strategy for Higher Alcohols

Separations are the core to any physical, chemical or biochemical processes that requires purification, recovery or the elimination of certain components from the product mixture. Separation technologies play a vital role in terms of engineering as well as process economics. Separation systems constitute roughly 40-70% of both fixed and working capital. Distillation is the most widely used industrial separation process despite its low thermodynamic efficiency. It is estimated that around 40,000 columns operate in the U.S., handling 90-95% of all separations for product recovery and purification. The capital investment in distillation alone is at least \$8 billion [23]. Despite this, distillation has a notable efficiency for large throughputs. Therefore, distillation has been chosen as the preferred method for product separation.

## Structure and process model of the downstream units

The conceptual design work [24] was carried out in a hierarchical manner, starting from collection of thermodynamic data, understanding the VLE, LLE and VLLE behaviour and then setting up of a column sequence for the separation train using Residue Curve Maps. These data were used to establish an initial base case design and the subsequent simulation studies were carried out using Aspen Plus<sup>®</sup>. The best possible design after careful evaluations and sensitivity studies has been proposed as an outcome of this investigation. However, this publication will mainly focus on conceptual modelling and not on technical details.

An overview of the process model for the separation process for the purification of Biobutanol is illustrated in Figure 2. The chosen separation strategy for this work was to separate any low boiling aldehydes, i.e. acetaldehyde and butyraldehyde, from butanol upfront. Furthermore, it is necessary to separate ethanol as well, as unreacted ethanol will be recycled back to the reactor. All other higher alcohols are collected together as one fraction (Figure 3) for input/output flow structure. The chosen plant capacity for this study is 260,000 t/a which

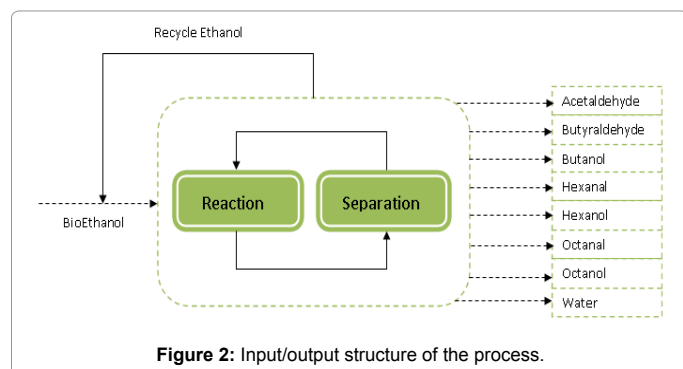


Figure 2: Input/output structure of the process.

breaks down to 129,000 t/a of bio-butanol and 131,000 t/a of other chemicals, mainly higher alcohols. Since the target products are future transportation fuels as well as chemicals, the specifications and purity of these fuels are not regulated so far. Therefore, the product purity for butanol was fixed to 95 mole percent in the present analysis. Aldehydes are considered to be technically pure.

The production unit is modelled to be operated for 8000 h per year. The reactor product stream which has been used as calculation basis for the following separation unit is shown in Table 3. A complex mixture of nine azeotropes, of which one being ternary and the remaining eight are binary azeotropes, are to be dealt with. Furthermore, the high water content of the product stream complicates the separation additionally.

The whole concept of distillation lingers around the boiling point of the chemical species. So, one need to be prudent while working with the vapor-liquid envelope which gives vital information regarding the feasibilities where a distillation column could probably operate. Complexities like azeotropes or regions of immiscibility act as a major hindrance for desired separation. i.e., an azeotrope creates a condition where equilibrium is reached in terms of separation with respect to boiling point. A detailed insight of the thermodynamics was necessary during the conceptual phase. One such graphical tool used was the *residue curve map*. These generated maps not only provide the separation possibilities and constraints of a ternary azeotropic system, but also help to validate the models used to predict equilibrium data.

### Selection of a suitable thermodynamic model

In this work the thermodynamic data were primarily collected for physical properties and phase equilibria in terms of VLE, LLE and VLLE data, azeotropic points, distillation boundaries and finally residue curve maps (RCMs) for ternary systems. The gathered information has paved a generalised means to understand the underlying thermodynamics and also to visualise both the constraints as well as the feasibility for the separation train in a qualitative manner. Accurate phase equilibrium data of the component system to be separated is most important for the design, simulation and optimization of the separation process. Accuracy of a process simulation strongly depends on the chosen thermodynamic model. Therefore, a heuristic approach was employed to choose the appropriate property method [25] in order to establish a good base case scenario. Several factors like the nature of the components, the composition of the mixture, temperature and pressure range, availability of the binary interaction parameters etc., were carefully examined before setting up the simulation.

In this simulation UNIQUAC [UNiversal QUasi Chemical] activity

coefficient model with binary parameters built-in Aspen Plus databank was used for the simulation after careful consideration of the available data and the literature. This choice was made due to the polar and non-electrolytic nature of the reaction products.

### Column sequencing and composition profile mapping

A residue curve [26] represents the liquid composition against time as the result of a single stage batch distillation. The results, when plotted on the triangular graph are known as residue curves because the plot follows the liquid residue composition in the still. As shown in Figure 3 an example of an RCM, the ternary systems involving azeotropes contain different split regions and these regions are separated by distillation boundaries. These boundaries cannot be crossed by conventional distillation hence making certain splits extremely difficult if not impossible. However, various techniques have been devised for overcoming these distillation boundaries using pressure shifting, exploiting boundary curvature or volatility or kinetics using liquid-liquid decantation, membrane separation etc. respectively. Here, RCMs have been used extensively for composition profile mapping which in turn contributed a vital role in column sequencing. As an example the RCM for butanol, ethanol and water is depicted in Figure 3.

### Connecting downstream units

Figure 4 presents the process flow sheet of the separation unit. The downstream processing unit consists of the distillation columns D101, D102 and D103 for the recovery of acetaldehyde and gaseous mixture, recovery of ethanol and the recovery of butanol respectively. A stripper S101, fed to a decanter, acts as an extraction unit for the recovery of butyraldehyde. All the columns were operated at atmospheric pressure.

The routine RADFRAC model was used to simulate the process conditions of the distillation columns it is a rigorous model for multistage vapour-liquid operations. The stage convention is numbered from top down in the simulation, reflux drum being the stage one. The operating variables such as reflux ratio, number of trays, distillate rate, feed tray location etc. were user specified. The design and operating variables were defined and eventually varied to observe its influence on energy requirement and product purity.

### Design methodology for simulation

For a multicomponent mixture with single feed and two product outlets, there are  $n+6$  degrees of freedom,  $n$  being the number of components for which the following variables are specified: (a) Feed flow rate,  $F$ ; (b) Feed composition,  $Z_i$ ; (c) Distillation composition,  $X_{D,i}$ ; (d) Bottom composition,  $X_{B,i}$ ; (e) Nature of the feed,  $q$ ; (f) Temperature/Enthalpy,  $T_f/h_p$ ; Reflux ratio,  $L/D$ ; Boil-up ratio,  $V/B$

Consequently, the following equations are solved for:

Overall material balance

$$F=B+D$$

Component balance

$$Z_i F = X_{i,dist} D + X_{i,bot} B$$

Energy Balance

$$Q_R + Q_C + h_F F = h_D D + h_B B$$

$Q_R/Q_C$ : Heat duty of the reboiler and of the condenser

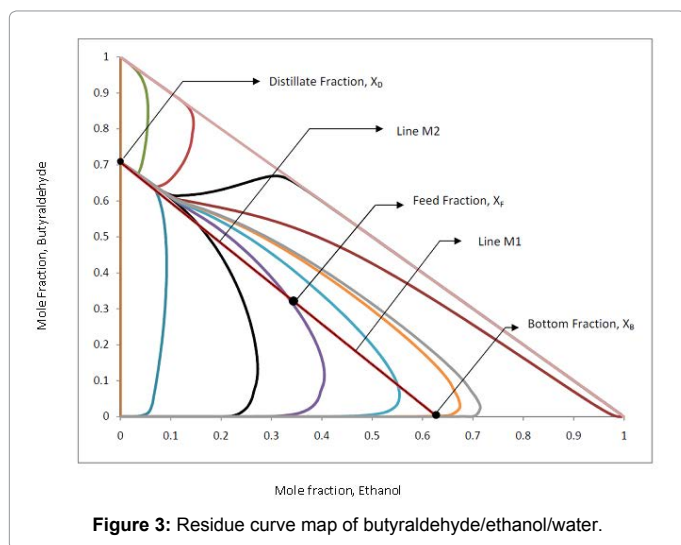


Figure 3: Residue curve map of butyraldehyde/ethanol/water.

With the increase in number of components the number of independent equations also increases, and so does the number of unknown variables. To solve this kind of problem a trial and error technique is employed, starting with an initial guess of the number of moles or mole fraction of one unknown component in the distillate or bottom fraction. The equations are then solved to convergence, and finally the solution is checked for conservation of mass and energy.

For a base case of 10 trays, the effect of feed tray location on the fractional recovery of the desired product was studied. The minimum reflux ratio,  $R_{min}$  for the separation and the minimum reboiler duty were thereby calculated. Now having known the minimum reflux ratio and reboiler duty, the effect of stripping stages, effect of rectifying stages and the effect of increase in reboiler duty were further calculated and optimized.

The design methodology can be explained by the following step-by-step algorithm:

- a) Definition of a base case and fixing the product purity or distillate rate
- b) Determination of the minimum reflux ratio
- c) Studying the effect of feed tray location
- d) Studying the effect of increase in rectifying stages
- e) Studying the effect of increase in stripping stages
- f) Studying the effect of increase in reboiler duty

### Process simulation of the downstream separation unit

**Distillation unit D 1001:** The first step in separation process is the separation of the gaseous components and acetaldehydes from the reactor exit stream (Figure 5). The feed component mixture, stream  $S01$ , enters the distillation column  $D-101$  at a feed inlet temperature of  $40^{\circ}\text{C}$ . The reason for entering the column at very low temperature is merely to condense any gases present and ease the separation; moreover, since the boiling point of acetaldehyde is  $21.06^{\circ}\text{C}$ , the column is operated at these conditions. Since there are no azeotropes in the distillate, all the acetaldehyde and the trace gases are completely recovered as the top product, stream  $S02$ . Therefore, the distillate rate of this column is 39

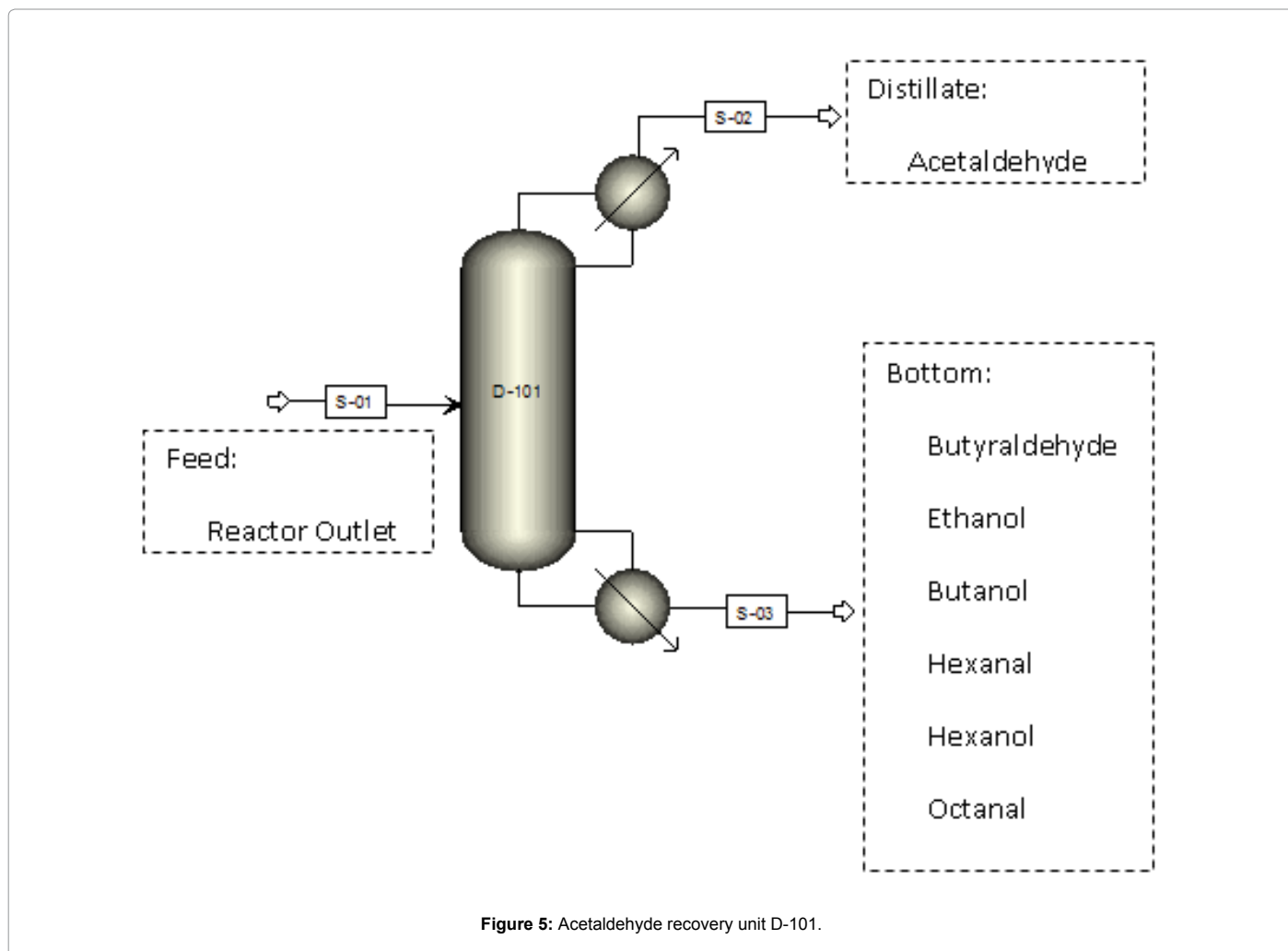
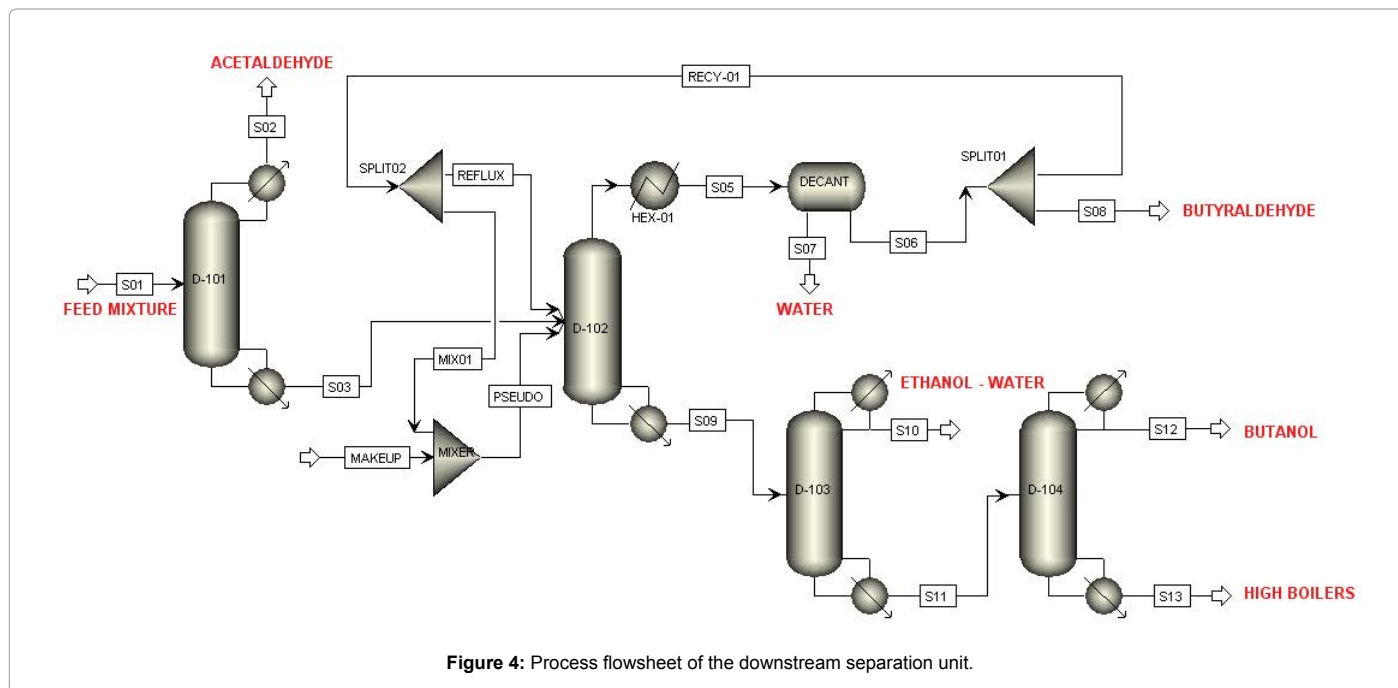
kmol/hr (Table 4), for further specifications.

**Distillation unit D102:** The liquid stream from the bottom product of column 1 enters into the stripping column  $D-102$ , with a flow rate of 961 kmol/hr. The main function of this column is to separate butyraldehyde from the resulting mixture (Figure 6). Butyraldehyde forms binary low boiling heterogeneous azeotrope with water at  $69^{\circ}\text{C}$  and with ethanol at  $73.27^{\circ}\text{C}$ . At the same time, Ethanol forms an azeotrope with water at  $78.17^{\circ}\text{C}$ . This complex mixture makes the separation extremely difficult. The stream  $S03$  is therefore fed into the column at a temperature of  $82.5^{\circ}\text{C}$ , which is the exit temperature of stream  $S03$  from  $D-101$  and the distillate rate of the column, is set quite high to recover maximum water along with all the butyraldehyde as the top product. This explains the reason to limit the flow of water into other columns, which not only dilutes the stream but also complicates the separation process by the formation of azeotropes. The overhead product of the stream  $S05$  should now contain no or only marginal traces of ethanol. All the remaining components are driven down the column to be collected as a bottom product through stream  $S09$  (Table 5) for feed flows and product composition.

As seen from the RCM analysis, the butyraldehyde-water heterogeneous azeotrope consists on a molar basis of 0.71 butyraldehyde and 0.29 water. The mixture's heterogeneity it can be taken to one's advantage by using a simple decanter, *DECANT*. The distillate rate is initially set for 28.16 kmol/hr which is the azeotropic composition required to recover all the butyraldehyde. This top product is cooled down to a temperature of  $30^{\circ}\text{C}$  and sent into the decantation unit to be separated into organic and the aqueous phases. The organic phase which is completely rich in butanal is further sent into a feed splitter where a part of butanal is fed back as recycle into the column along with a make-up stream containing additional butyraldehyde to recover additional water.

**Distillation unit D-103:** The bottom product from the column  $D-102$  enters as a feed to column  $D-103$ . The feed stream  $S09$  is at a temperature of  $86.4^{\circ}\text{C}$ . The task of this column is to completely recover all the ethanol along with traces of butanal (if any) from the remaining stream (Figure 7). The idea here was to ideally recover only ethanol and water, which could directly be fed back to the reaction unit as the unreacted stream. However, since ethanol also forms a ternary azeotrope with water and hexanal at  $82.16^{\circ}\text{C}$ . If a mixture of ethanol-water alone is desired to be separated without any hexanal as distillate, unavoidably high water content has to be tolerated in the bottom product. This complicates the process and increases the operation costs. The reason to this is, that hexanal also forms a binary azeotrope with water at  $79.13^{\circ}\text{C}$  which necessitates the requirement of two more columns for separation, one where hexanal-ethanol azeotrope is obtained as the distillate and another for separating butanol from the remaining stream. In order to avoid more complex separations at further downstream, high operating costs have to be tolerated in this unit. Refer to Table 6 for feed flows and product composition.

**Distillation unit D-104:** The bottom product from the column  $D-103$  enters as a feed to final column  $D-104$ . The feed stream  $S11$  is at a temperature of  $112.4^{\circ}\text{C}$ . The column is used for the recovery of the desired commercial product butanol (Figure 8). Butanol forms a heterogeneous azeotrope with water at  $92.5^{\circ}\text{C}$  at a composition of 0.25 moles. Since the distillate composition in this column is azeotropic, in order to recover pure butanol one may invest in techniques such



Component	Mole flow, kmol/hr
Acetaldehyde	39
Ethanol	421
Butyraldehyde	20
Butanol	114
Hexanal	5
Hexanal	19
Octanal	1
Octanol	4
Water	377

Table 3: Product stream from reactor outlet.

Unit: D-101	
Number of trays	40
Feed tray location	19
Feed temperature, °C	40
Distillate rate, kmol/hr	39
Product recovery, kmol/hr	39
Heat duty, MW	5
Reboiler type	Kettle
Condenser type	Partial condenser

Table 4: Specifications: unit D-101.

Unit: D-102	
Number of trays	60
Feed tray location	30
Feed temperature, °C	82.1
Distillate rate, kmol/hr	290
Product recovery, kmol/hr	184.5
Heat duty, MW	20
Reboiler type	Kettle
Condenser type	None

Table 5: Specifications: unit D-102.

Unit: D-103	
Number of trays	55
Feed tray location	27
Feed temperature, °C	82.7
Distillate rate, kmol/hr	620
Product recovery, kmol/hr	420.9
Heat duty, MW	13
Reboiler type	Kettle
Condenser type	Total condenser

Table 6: Specifications: unit D-103.

Unit: D-104	
Number of trays	40
Feed tray location	20
Feed temperature, °C	98
Distillate rate, kmol/hr	184
Product recovery, kmol/hr	113.97
Heat duty, MW	13
Reboiler type	Kettle
Condenser type	Total condenser

Table 7: Specifications: unit D-104.

as pervaporation. Refer to Table 7 for feed flow rates and product composition.

## Conclusion

This study describes a preliminary feasibility study of a conceptual downstream processing plant manufacturing alcohols and aldehydes. Based on the experimental data conducted by Fraunhofer UMSICHT, the results with high compositions of alcohols, water and aldehydes were taken as a basis for this study. A generic design to handle complex multicomponent separation was developed. Therefore, the proposed design makes it highly flexible to produce both fuels and high value chemicals like.

It was found that the separation scheme is energy intensive involving four distillation columns. The main complexity in designing the separation unit was with the amount of water present in the feed entering in to the downstream section. The reason to this is that the units are all operated at atmospheric pressure and the top product compositions in the columns D102 and D103 equals their azeotropic composition, thereby carrying a large amount of water as a bottom product into the next successive column. Moreover, this necessitates the increase in the number of columns. In order to deal with this, a stripper followed by a condenser and a decanter has been designed to extract the maximum amount of water by recycling a split fraction of recovered butyraldehyde back into the column. The decanter was used to phase separate butyraldehyde-water azeotrope, which is heterogeneous in nature. In the Column D103, the design to recover ethanol-water, at its azeotropic compositions was found to be the best option, as it eliminates the requirement of an additional column. This distillate obtained will to be recycled back into the reactor as unreacted ethanol.

In order to make higher alcohols according to the proposed processing route feasible, further R&D is required. The following list outlines some important topics to be addressed in the future:

- Alternative technologies for separation of water in terms of energy consumption, in particular evaporation should be investigated. This is already the state-of-the-art for separation of ethanol and water.
- Alternative technologies for water separation could include esterification or etherification of the crude products mix with acids, since up-front water separation would not be required or strongly reduced. Significant energy savings can be expected, and the number of overall unit operations would be reduced.
- The commercial value of aldehydes versus alcohols should be evaluated. In particular the economics of hydrogenating aldehydes into alcohols versus separation of aldehydes, either stand-alone or coupled to an existing oxo-process, should be scrutinized.
- If acetaldehyde cannot be avoided, its conversion to acetic acid via known technology, ideally coupled with esterification with the higher alcohols, should be considered.
- The optimal product mix of chemicals versus fuel, if any, should be carefully evaluated to maximize economic returns and to minimize economical risks.
- Life-cycle analysis tools would provide helpful to sort out the greenest processing window.

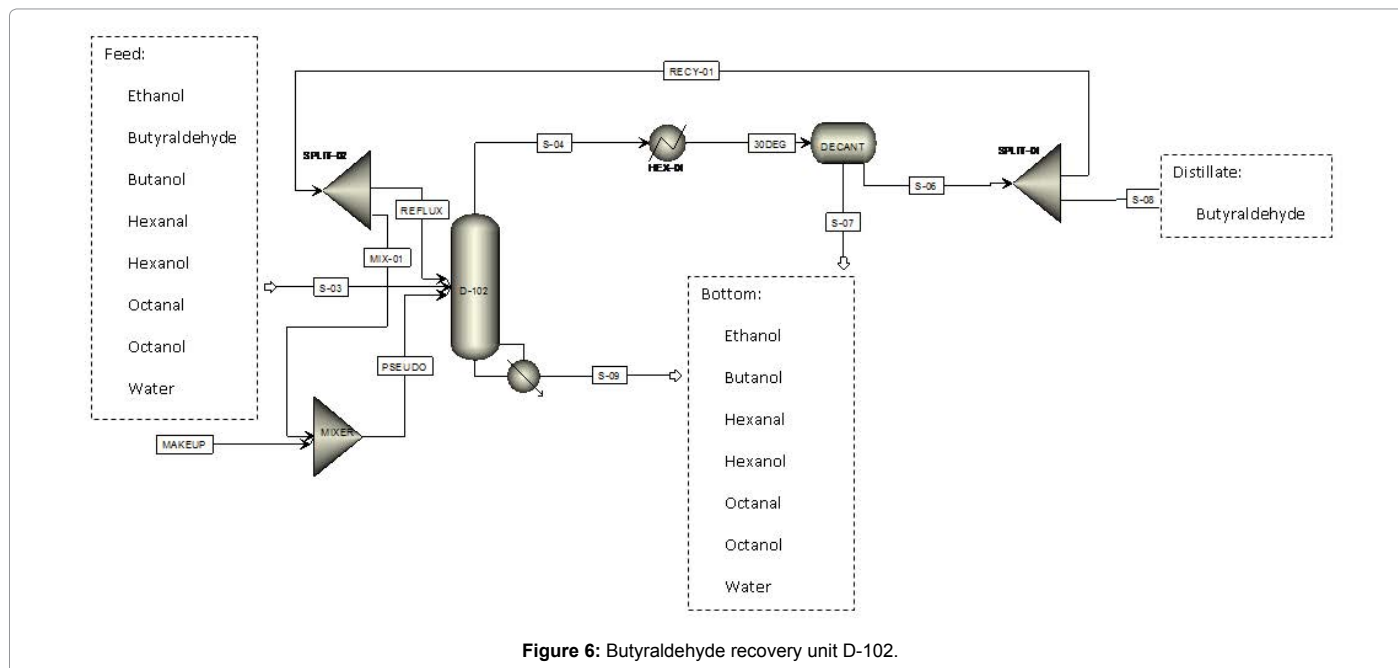


Figure 6: Butyraldehyde recovery unit D-102.

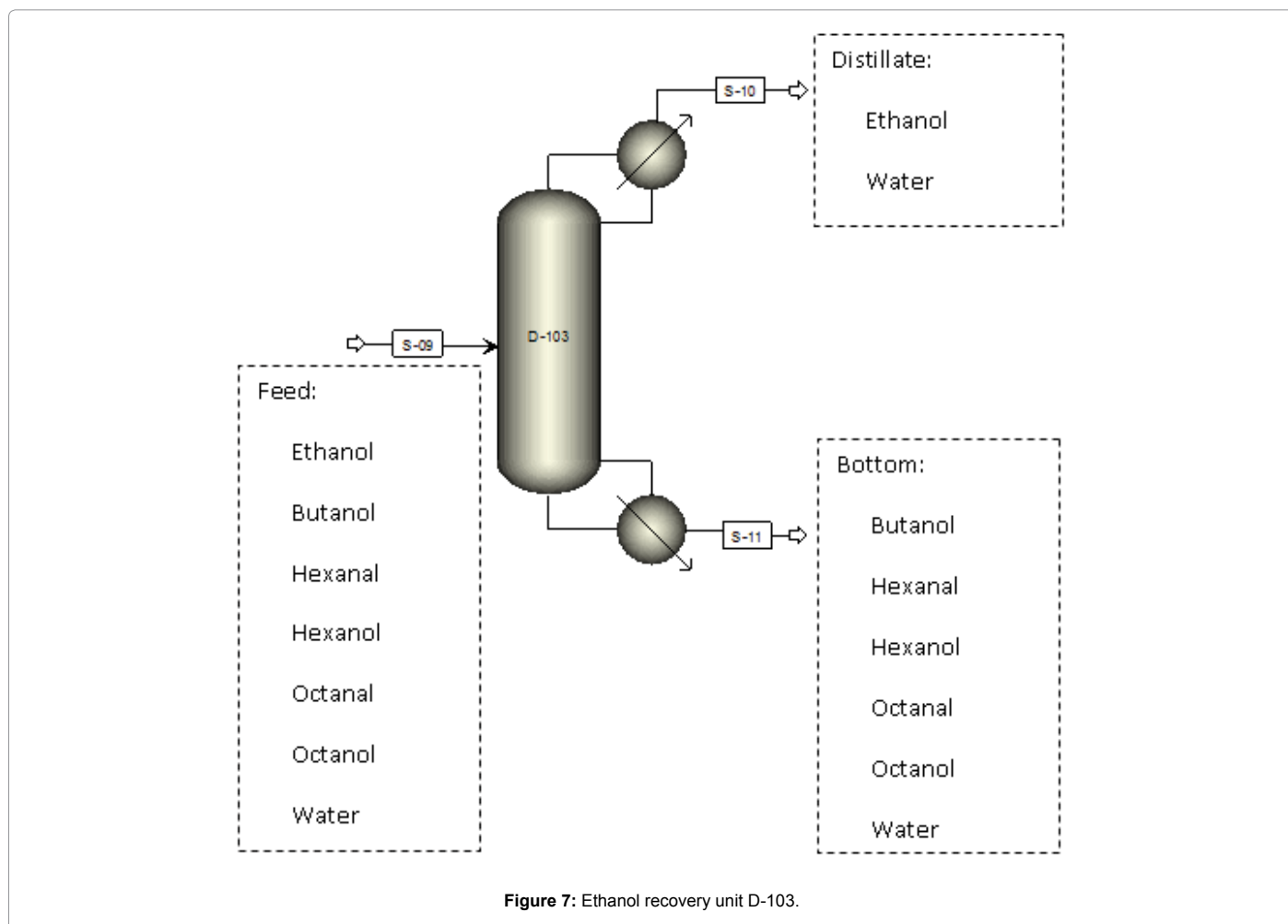


Figure 7: Ethanol recovery unit D-103.



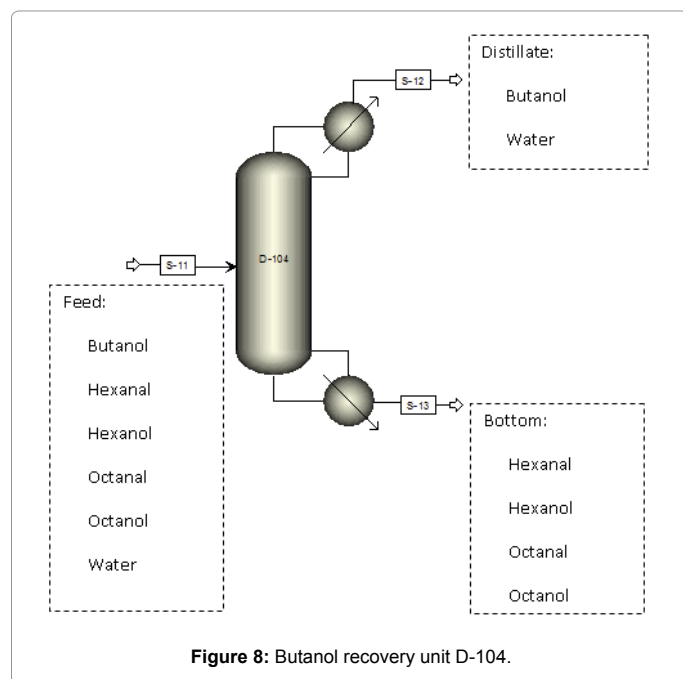


Figure 8: Butanol recovery unit D-104.

- Condensation of methanol and ethanol mixtures to branched alcohols is possible with the same technology. Opportunities arising from such a process should be evaluated.

Considering the existing market of higher alcohols and the broad mixture of existing applications of higher alcohols and derivatives thereof, it becomes conceivable that such products can become an important part of existing refineries or even chemical production sites without refineries, to introduce bio-based products into the portfolio in an affordable way. Ethanol as raw material could drastically lower the complexity of chemical production sites allowing further affordable and distributed back-ward integration, since capital intense unit operations of a refinery are not required anymore.

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