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Arjan Oudshoorn

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Prof. dr. ir. L.A.M. van der Wielen

Copromotor
Dr. ir. A.J.J. Straathof

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Rector Magnificus	voorzitter
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Summary

Product recovery is crucial for fermentative butanol production. Bio-based fermentative butanol production systems benefit from answering the question to what extent, and in which form, integration between fermentation and product recovery should be applied. The product recovery is applied in order to minimize the impact of butanol inhibiting during fermentation. This thesis addresses the product recovery methods applicable to butanol recovery. Two techniques are investigated in more detail, namely liquid demixing based-recovery and adsorptive-recovery. This work further provides a basis for process optimization for integrated product recovery and finally determines the economic potential of butanol production systems.

Butanol can be removed from the fermentation broth by means of direct phase transition (e.g. distillation or freeze crystallization), or by using auxiliary phase (e.g. extractive recovery or adsorption). The assessment of butanol recovery from aqueous solutions, shown in chapter 2, illustrates the wide range of recovery techniques which can be applied. Key efficiency aspect for product recovery is the selectivity of the recovery technique. The selection of the correct product recovery technique is paramount as is shown by the range in energy requirements for butanol recovery, ranging from 1.3 MJ/kg to 145 MJ/kg. Selectivity can be used as a parameter to qualify the energy demand of a production system. Selectivities of recovery can be a function of the initial product concentration in the fermentation broth, but to illustrate, for butanol recovery the highest product recovery selectivities are reported for extraction (S = 4100), liquid demixing (S = 750) and adsorption (S = 630). For the commonly applied distillation selectivity is lower, (S = 72). The selectivity is based on the liquid-gas phase equilibria. This lower selectivity implies that distillation will be carried out as a multistage operation and also that heat integration should be applied.

This thesis does not investigate the recovery by organic solvent extraction further as the method is extensively reported in literature and the extractive phase capacity for butanol is extremely limited, <0.003 kg butanol per kg organic extractive phase.

Liquid demixing is explored in chapter 3 as recovery method for butanol. The recovery makes use of the distinctive phase behavior of butanol-water mixtures, which shows a two liquid phases equilibria for a wide range of compositions. The organic phase of these two can be seen as a high concentrated product phase. Our analysis shows the liquid equilibria to be susceptible to chemical species used in fermentative production systems, namely salts

(LiCl, NaCl and $CaCl_2$) and carbohydrates (glucose, fructose and sucrose). The effects of carbohydrates on the liquid phase equilibria are less pronounced than the effect of the salts. The amount of salts needed for product recovery exceeds 250 g kg-1 and are too high for practical consideration. The amount of salt needed for product recovery goes down significantly the moment the butanol concentrations in the fermentation are closer to saturated conditions. An increase in solvent tolerance of microbial species are a favorable development for liquid-liquid based recovery, although butanol fermentations will not come close to saturated product concentrations 74 g L^{-1}.

Adsorptive recovery by high silica zeolites shows the zeolite affinity for butanol to be dependant on the zeolite structure and on aluminum content. ZSM-5 high silica zeolite, with a narrow pore structure, shows a very steep adsorption isotherm, indicating the beneficial effect of limited pore volume and hydrophobic nature of the pores for the selectivity of recovery. The butanol adsorption capacity for CBV28014 is actually limited by the available pore volume. Multi-component adsorption behavior for the investigated zeolites, when dealing with Acetone-Butanol-Ethanol (ABE) fermentations, can be estimated from the pure component adsorption isotherm in water by either simple multi-component Langmuir model or ideal adsorbed solution model. When modeling adsorption from fermentation broths, the acid content, e.g. butyric acid, needs to be taken into account, and should be present as an additional chemical species in the extended adsorption model.

Desorption of butanol from zeolite material by means of temperature operation is possible and is shown in detail in chapter 5. Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Adsorption (TGA) experiments show the heat effect of desorption of butanol from CBV901 and CBV28014 to be slightly above the enthalpy of evaporation, namely 1080 and 1160 $J \cdot g^{-1}$. Also the structurally more hydrofobic CBV28014 shows the least amount of water adsorption. The confined nature of the CBV28014 structure does show significantly slower desorption rates, with overall mass transfer coefficient being up to 10 times slower, compared to butanol desorption from the wider pore CBV901. The low heat capacity of silica material of around 1 $J \cdot g^{-1}$, the adsorptive phase capacity for butanol of approximately 0.1 $g \cdot g^{-1}$, the high product recovery selectivity and thermal stability of the material make adsorption based recovery a viable method for butanol recovery.

Carbon dioxide has an effect on the adsorption of butanol on high silica material in both liquid as well as in gas phase systems. Carbon dioxide can thus be used as a displacement agent to allow adsorptive phase regeneration. However, just as for most organic phases

applied in extractive based recovery, the butanol content in carbon dioxide is extremely limited.

The process evaluation carried out in chapter 6 show that for butanol both fermentation and product recovery are in the same range of importance. In-situ or integrated product recovery is necessary in order to optimize the expenditure of both unit operations. The capital expenditure (capex) and the operational expenditure (opex) for butanol recovery systems allow estimation of the costs related to bio-based butanol and these costs are currently estimated to be between 1.5 and 2 euro per kg.

Terugwinning van bio-butanol

Samenvatting

Productisolatie is belangrijk voor fermentatieve butanolproductie. Bio-gebaseerde fermentatieve butanolproductieprocessen halen voordeel wanneer antwoord wordt gegeven op de vraag hoeverre en in welke vorm integratie tussen de fermentatie en de productwinning moet plaatsvinden in het productieproces. Productisolatie wordt toegepast om de inhibiterende werking van butanol op de fermentatie te minimaliseren. Dit proefschrift behandelt productisolatiemethodes die toegepast kunnen worden op isolatie van butanol. Twee technieken worden in verdere details behandeld, namelijk vloeistofontmenging en adsorptiegebaseerde productisolatie. Dit proefschrift beschrijft ook een basis voor optimalisatiemethodologie voor geïntegreerde product processen voor productisolatie en laat tenslotte de economische mogelijkheden van butanolproductiesystemen zien.

Butanol kan verwijderd worden uit een fermentatiemedium door middel van directe faseverandering (bijv. destillatie of vrieskristallisatie), of door gebruik te maken van een hulpfase (bijv. extractie of adsorptie). Deze uiteenzetting van butanol-isolatiemogelijkheden uit waterige oplossingen, gepresenteerd in hoofdstuk 2, illustreert het brede scala dat kan worden toegepast. Vanuit het oogpunt van efficiëntie is de selectiviteit die gehaald wordt in de gebruikte methode cruciaal. De selectie van een correcte product-isolatietechniek is van het hoogste belang, zoals wordt geïllustreerd door de grote variatie in de energiebehoeftes van de verschillende technieken die voor butanolwinning kunnen worden gebruikt, variërend van 1,3 MJ/kg tot 145 MJ/kg. Selectiviteit kan als parameter gebruikt worden om een uitspraak te doen over de energiebehoeften van een productieproces. De selectiviteit van de isolatie van het product kan als functie van de initiële concentratie in de fermentatie uitgedrukt worden. Ter illustratie, de hoogste product selectiviteit (S) die is gerapporteerd is voor extractie S = 4100, voor vloeistof ontmenging S = 750 en voor adsorptie S = 630. Voor de standaard toegepaste destillatie is de selectiviteit lager, S = 72. Deze selectiviteit komt voort uit het vloeistof-gas fase-evenwicht. Deze lagere selectiviteit impliceert dat destillatie alleen uitgevoerd kan worden als meertraps operatie en dat warmte-integratie moet worden toegepast.

Dit proefschrift beschrijft isolatie van product door extractie met organische oplosmiddelen niet in detail, omdat extractie uitvoerig gerapporteerd wordt in de literatuur. Daarbuiten valt

nog op te merken dat de capaciteit voor butanol van de extractieve fase is extreem beperkt, <0,003 kg butanol per kg organische fase. Vloeistofontmenging is onderzocht in hoofdstuk 3 als mogelijke isolatiemethode voor butanol. De terugwinning maakt gebruikt van het onderscheidende fasegedrag van mengsels van water en butanol, wat vloeistofontmenging laat zien over een breed concentratiegebied. De organische fase kan hier gezien worden als een geconcentreerde productfase. De analyse laat zien dat de vloeistofevenwichten beïnvloed worden door chemicaliën die ook tijdens de fermentatie worden gebruikt, namelijk zouten (NaCl en $CaCl_2$) en koolhydraten (glucose, fructose en sucrose). Het effect van koolhydraten op de vloeistofevenwichten is minder uitgesproken dan het effect dat zouten hebben op de evenwichten. De hoeveelheid zout die nodig is voor fasescheiding is meer dan 250 g per kg en is vanuit praktisch oogpunt te hoog. De hoeveelheid benodigd zout gaat significant omlaag op het moment dat de butanolconcentratie in het fermentatiemedium dicht in de buurt komt van verzadiging. Een verbetering in tolerantie van het micro-organisme voor organische oplosmiddelen is een gunstige ontwikkeling op vloeistof-ontmenging gebaseerde scheidingstechnieken, al zal butanolfermentatie niet makkelijk in de buurt kunnen komen van de verzadigingsconcentratie, 74 g L^{-1}.

Adsorptie met behulp van silica zeoliet laat zien dat de affiniteit voor butanol van de zeoliet afhangt van de zeoliet structuur en de aanwezige hoeveelheid aluminium. ZSM-5 hoog silica zeoliet, met nauwe porie-structuur, laat een erg scherpe adsorptie-isotherm zien, wat het voordeel van beperkte porievolume en hydrofobe aspecten van de poriën op de selectiviteit van de scheiding illustreert. De adsorptiecapaciteit van CBV28014 voor butanol is gelimiteerd door het beschikbare porievolume. Multi-component adsorptiegedrag door de bestudeerde zeolieten van Aceton-Butanol-Ethanol (ABE) mengsels laat zien dat de adsorptie kan worden voorspeld aan de hand van de adsorptie-isothermen van de pure componenten indien gebruik wordt gemaakt van een simpel multi-component Langmuir-model of het ideal adsorbed solution (IAS) model. Voor het modelleren van de adsorptie uit fermenatiemedium is het belangrijk de aanwezige zuren in beschouwing te nemen, bijv. boterzuur, en deze moeten als extra component aan het model worden toegevoegd.

Desorptie van butanol uit zeoliet materiaal door middel van temperatuurverandering is mogelijk en wordt in detail behandeld in hoofdstuk 5. Differential Scanning Calorimetry (DSC) en Thermo Gravimetric Adsorption (TGA) experimenten met CBV901 en CBV28014 laten zien dat het warmte-effect van desorptie van butanol respectievelijk 1080 and 1160 $J \cdot g^{-1}$ bedraagt, iets boven de verdampingsenthalpie van butanol. Ook laat het meer hydrofobe CBV28014 significant minder wateradsorptie zien. De structuur van de

CBV28014 veroorzaakt meer massatransportlimitatie en de massatransportcoëfficiënt voor de totale overdracht is tot 10 keer lager dan voor desorptie van butanol uit het meer open CBV901. De lage warmtecapaciteit van silicamateriaal van ongeveer 1 $J \cdot g^{-1}$, de adsorptie capaciteit voor butanol van ongeveer 0.1 $g \cdot g^{-1}$, de hoge scheidingsselectiviteit en de thermische stabiliteit van het adsorptiemateriaal maken adsorptiegebaseerde processen een reëel toepasbare methode voor butanolproduct-isolatie.

Koolstofdioxide heeft een invloed op de adsorptie van butanol door silica materiaal in zowel vloeistof- als gassystemen. Koolstofdioxide kan zodoende gebruikt worden als verdringingsmiddel om de adsorptiefase te regenereren. Echter, net zoals voor de meeste organische oplosmiddelen die gebruikt worden in extractieve product-isolatieprocessen, is de oplosbaarheid voor butanol in koolstofdioxide beperkend.

Een procesevaluatie is uitgevoerd in hoofdstuk 6. Deze laat zien dat voor butanol zowel de fermentatie als de product-isolatie qua ordegrootte een gelijke invloed hebben op de proceskosten. In-situ of geïntegreerde product-isolatie is nodig om de kosten van beide operaties te kunnen minimaliseren. De investeringskosten en de operationele kosten voor productieprocessen voor uit fermentatie verkregen butanol geven een uiteindelijke kostenraming die ligt tussen de 1,5 en 2 euro per kg butanol.

Chapter 1: Introduction to bio-based butanol recovery

1.1. Bio-based microbial chemicals and fuels production

The world production of chemicals and fuels is at this time predominantly based on the conversion of non renewable raw materials, such as coal, natural gas and oil. Inevitably these resources will be depleted. The timescale on which these resources are depleted are a matter of debate, but our society will run out of these natural resources eventually.

From the standpoint of depletion, switching to a renewable resource for the production of chemicals and fuels is a logical step. Renewable resources are almost all derived from sunlight. Sunlight, wind, geo-thermal or hydro-electric systems can be used for energy production. The production of most chemicals and transportation fuels do require carbon based resources. The abundant carbon based material on the planet besides carbon dioxide is biomass. Plant material, algae and microbial biomass all can be converted into chemicals and fuels. Conversion of renewable carbon based feedstocks can take place by a wide range of processes from thermo-chemical and catalytic chemical conversion to enzymatic and microbial conversion.

Bio-based microbial production of bulk chemicals has existed since the start of the 20th century. Due to the rise and successfulness of the petrochemical industry the competition was lost after the 1950's and bio-based bulk production of most chemicals ceased. Currently, conversion steps are again increasing in competitiveness. Successful bio-based processes are on the market, with 1,3-propanediol, citric acid, lactic acid and ethanol being prime examples. 1-Butanol is currently joining these examples

1.2. Microbial 1-butanol production

Historically acetone-butanol and ethanol (ABE) fermentation was already occurring on large scale up to the late 1950's. Butanol as a biofuel has favorable properties over the already existing ethanol production in its higher combustion energy on mass basis and its lower polarity, allowing blending in biodiesels. Further, butanol is scientifically an interesting component with its hydrophobic carbon chain and its hydrophilic alcohol group, its interesting phase behavior with water, and its low saturated vapor pressure.

Microbial butanol fermentation occurs in water and the recovery of low concentration butanol from an aqueous phase is non-trivial and requires the investment of equipment and energy. In contrast industrial petrochemical conversions usually occur in an organic or vapor phase and its separation of choice, distillation, is predominantly the separation of

organic products from other organic components, while water is mostly used in the form of steam as heat transport agent. With the switch towards aqueous fermentative production, the product separation conditions significantly change. What is currently an optimal recovery need not be the optimum recovery for future renewable processes.

1.3. Towards bio-based butanol production

Large scale fermentations can be severely hampered by product inhibition. This means the microbial production is being limited as the produced products themselves negatively influence the microbes. Product toxicity effects can be limited if the product is continuously removed from the production system. Product removal can come in different process configurations and can be applied in-situ or in a multi-step integrated process. All of this applies to microbial butanol production, and as the transition to a more renewable resource based society is still in an early stage, it is the right time to investigate butanol recovery techniques, besides the currently dominant technique of distillation. This assessment can than allow a subsequent determination of the potential of bio-based butanol production, given the wide range of integrated production options.

This thesis thus systemically investigates the recovery of fermentative produced butanol from aqueous solutions; further investigates some specific promising techniques; provides a basis for integrated process optimization; and finally provides a basis for the determination of the economic potential of butanol production.

The approach used to investigate the microbial production of butanol can be used as a roadmap for the investigation of other microbial produced chemicals.

1.4. Outline of this thesis

In chapter 2 an assessment of selective separation techniques of butanol is made using a systematic approach, starting at the phase behavior of butanol-water mixtures. This assessment shows the current state of the recovery techniques and provides the background for the later chapters.

In chapter 3 the liquid-liquid demixing based recovery of butanol is explored, as it is identified as a currently underexplored technique in chapter 2.

In chapter 4 adsorptive recovery of butanol on high silica material is investigated, as adsorption is identified as a selective recovery technique in chapter 2.

As follow up on chapter 4, chapter 5 shows the thermal desorption characteristics of butanol from high silica material. Desorption of products from their sorbent is less frequently studied than adsorption, while its importance in relation to the overall recovery process is very high.

Chapter 6 shows the integrated production aspects of butanol production and provides the breakdown of capital and operational expenditure of its fermentative production. The actual butanol product concentration in the fermentation and downstream processing plays a crucial role in process optimization. This method is also applied to lactic acid and phenol production.

Chapter 7 provides an outlook on the product recovery of microbial produced butanol and microbial production of bulk chemicals in general.

Chapter 2: Assessment of options for selective 1-butanol recovery from aqueous solution

Abstract

The microbial production of 1-butanol occurs in aqueous fermentation broth, with up to ~ 20 g/L of product. Efficient recovery of butanol from this dilute aqueous phase determines, to a large extent, the efficiency of the production process. Starting from the thermodynamic (phase) properties of butanol and water systems, this paper presents a structured approach to determine the key characteristics of various butanol recovery methods. Analysis of reported separations, combined with fundamental phase properties, has resulted in both the characterization of the selectivity of recovery and estimations of the energy requirement during product recovery for a variety of recovery methods. Energy-efficient systems for the recovery of butanol from aqueous solution are pervaporation- and adsorption-based techniques. The applied method predicts the recovery energy requirement for both techniques to be < 4 MJ/kg of butanol, which, on an energy basis, is similar to ~ 10% of the internal combustion energy of butanol.

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2.1. Introduction

The anaerobic production of organic solvents by biological conversion of renewable feedstocks dates back to 1861 to Pasteur. Glycerol fermentations with its main products butyrate and butanol were later described by A. Fitz in 1876. Acetone, 1-butanol, and ethanol (ABE) fermentation was second only to ethanol production as a biological production route in the beginning of the 20th century. In the mid-20th century, economic factors and new petrochemical production methods led to the decline of the ABE fermentation industry, although in South Africa, the Soviet Union, and China,[1-3] production continued beyond this point. Increasing interest in sustainable industry, the increase in oil prices and renewable feedstock utilization has led to renewed attention for ABE fermentation from industry[4] and academia,[5] particularly for 1-butanol (hereafter referred to as butanol), although new developments also include 2-butanol and iso-butanol. Butanol can be used as a solvent, as a precursor for chemical synthesis, or as a biofuel. From a biofuel perspective, butanol has some advantages over ethanol. Butanol has a 31% higher combustion value, compared to ethanol. Also, the chemical properties of butanol, such as chain length, lower volatility, and polarity, allow blending in biofuels[6] more readily than ethanol does.

ABE fermentation is performed by a large variety of *Clostridia* strains at 25-37 ^{o}C and 1 atm. In ABE fermentations, butanol is usually the main product.[1,7] The final ABE composition can vary, but the maximum achievable total solvent concentration is ~ 20 g/L, mostly because of severe product inhibition and toxicity by butanol. Process synthesis approaches have focused on separation of the ABE mixture, without involving the fermentation.[8,9] We suppose that metabolic engineering approaches will be increasingly successful in minimizing acetone and ethanol formation in the future.

However, the achievable butanol concentration will remain modest. Therefore, we will focus here on in situ recovery of butanol without considering acetone and ethanol. By removing product during the fermentation, the productivity per volume of fermenter and per amount of cell mass can increase significantly. This concept has been commercially applied for ethanol production using the Biostil process, and other options (such as extractive lactate fermentation) are awaiting implementation. [10]

The fermentative production and recovery of butanol can be performed according to various schemes, allowing direct and indirect cell contact and internal and external product recovery.[11] The scheme shown in Figure 1 gives the best control possibilities and, therefore,

is assumed to be the most suitable option for a large-scale continuous process. The product capture step shown in Figure 1 consists of a downstream operation that leads to a smaller, more-concentrated butanol stream and a large, more dilute aqueous stream for recycle to the fermentation. This aqueous stream may contain the microbial cells; however, preferably, these are retained in the fermenter. This issue is not discussed in this paper, which will focus on the capture step. Complete recovery of butanol in the capture step is not necessary, assuming that the remaining aqueous stream, except for a small purge fraction, can be recycled to the fermentation.

The integrated butanol production system can be subunit of a (bio)refinery, where many streams will be available for further process integration. To avoid bias in evaluating the actual performance of the integrated system, stream integration with streams that do not stem from the butanol fermentation is not applied.

The separation of butanol and water in this operation will be based either on differences between the pure component physical properties or on their inherently different interaction with a third chemical species or auxiliary material. A favorably chosen ternary species, or mass-separating agent, will form an auxiliary phase in the capture step and will facilitate the recovery. To achieve product specifications, a final purification step may be required.

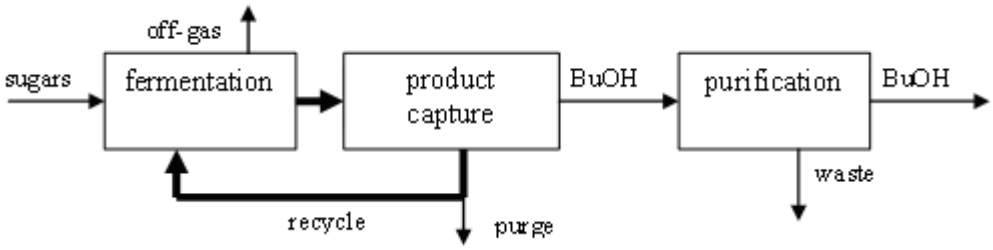

Figure 1. Butanol capture operation in its process context.

Ideally, the main costs in a butanol production process are due to feedstock consumption. Using cell retention and optimized fermentation techniques, the butanol yield on sugars can be maximized and feedstock costs will be fixed. Other large cost factors are due to the fermentation equipment, the capture equipment, and the overall energy consumption during recovery. An efficient capture operation will minimize all these costs, including the fermenter costs, if a less-inhibiting butanol concentration can be maintained in the

fermenter, according to the recovery scheme of Figure 1. Therefore, it will be crucial to select the type of operation for the capture step.

Distillation is the traditional recovery option, but the literature covers a wide range of alternative recovery options. These usually allow no straightforward comparison, because feed conditions and underlying assumptions vary from case to case.

Recovery information on an isolated separation step also provides limited information about its suitability within a process. Performing complete process designs on all possible systems is time-consuming. Ranking the possible butanol recovery options, however, is necessary for a rational choice. As mentioned previously, the energy consumption is a key cost factor of the recovery operation. We will use it as a parameter to rank recovery alternatives. The energy consumption influences not only operational costs but also investment costs through heat-exchange area. Therefore, our strategy to allow quantitative comparison of recovery alternatives is 3-fold and takes the mass and energy flows during the recovery operation into account separately. First, in Section 2, a phase-transition-based framework is used to compile and structure butanol and water separation possibilities on a thermodynamic basis. Section 3 characterizes the recovery options by their performance in separating butanol from water, using selectivity as a parameter. In Section 4, a short-cut method is presented, to allow ranking of the recovery options on an energy basis without having to perform labor-intensive process designs, while keeping the amount of necessary property data low.

Table 1. Recovery Operations for Butanol from Aqueous Solution

new phase	origin	membrane	operation
G	*P*/*T* shift	no	distillation [13,14]
L	*P*/*T* shift	no	liquid demixing
S	*P*/*T* shift	no	eutectic freeze crystallization
G	*P*/*T* shift or composition change	yes	Pervaporation[15-19]
L	*P*/*T* shift	yes	osmosis
G	composition change	no	gas stripping [1,20-23]
L/SC	composition change	no	extraction,[24-27] liquid demixing [28]
L	composition change	yes	perstraction [25,29]
S	composition change	no	adsorption [30-34]

Table 2. Phase-Transition Properties of Pure Butanol and Water[a]

property	melting point, T_m [°C]	boiling point, T_b [°C]	$\Delta H_{vap}(T_b)$ [kJ/mol]	$\Delta H_{fus}(T_m)$ [kJ/mol]	ΔH_{comb} [kJ/mol]
butanol	-88.6	117.7	43.29	9.37	2680
water	0	100	40.65	6.01	

[a] Data taken from ref 36.

2.2. Thermodynamics of Butanol and Water Mixtures

The recovery of butanol from aqueous solution is governed by the phase behavior of butanol during separation. After separation, the butanol product phase can be a vapor, liquid, solid, or supercritical phase. The separation operation can be classified as an energy, mass, or kinetic separation,[12] or a combination thereof. In energy-based separations, temperature and pressure are used as operational variables to introduce energy into the system. In mass-based separations, an auxiliary phase is introduced to facilitate separation. Here, variations in the chemical composition -and, to some extent, temperature and pressure- drive the separation. Differences in the transport properties of the components

allow kinetically based separations. Membrane-aided separations are clear examples of kinetic separations.

First, an overview of literature on butanol recovery operations from (cell-free) fermentation broth and model solutions is shown in Table 1. The recovery options have been primarily arranged by operating parameter. Second, a further subdivision is made by means of the butanol product phase characteristics. For *P*/*T* driven systems, membrane operations also are distinguished.

2.2.1. Pure Components. Liquid butanol and water can undergo phase transitions to vapor or solid phases. The enthalpy of these transitions is shown in Table 2. On a molar basis, the values for butanol are slightly higher; however, when recalculated on a mass basis, the enthalpies for water are ~3 times higher than that for butanol. The pure-component saturated vapor pressures, as a function of temperature for butanol and water,[35] are shown in Figure 2. Water has a 2-4-fold higher saturated vapor pressure.

2.2.2. Binary Systems. According to Gibbs' phase rule, the number of independent variables required to identify the intensive state of the system is 4 - the number of phases present for binary systems of butanol and water. This means only two degrees of freedom are available for biphasic systems, and the independent variables (temperature and pressure) can be used to define the composition of the system. To avoid three dimensional diagrams that cannot be read with a high degree of accuracy, only two-dimensional diagrams are shown here. The temperature versus composition diagram for butanol and water systems at 1 bar is shown in Figure 3. The vapor-liquid, liquid-liquid, and solid-liquid equilibrium lines are based on original data points.[37-39] By shifting the pressure, all individual equilibrium lines shift. As previously mentioned, ABE fermentations are usually performed in a temperature range of 25-37 ^{o}C. Starting with a butanol concentration of ~ 20 g/L, or 0.5 mol %, moving either up or down in temperature will lead primarily to a phase transition of water, rather than a phase transition of butanol. Unfortunately, this would recover ice rather than butanol crystals upon freezing. Upon boiling, the vapor is somewhat enriched in butanol.

In Figure 3, the temperature effect on the mutual solubility of butanol and water can also be seen. The aqueous solubility of butanol ranges from 2.8 mol % at 0 ^{o}C to 1.5 mol % at 60 ^{o}C.

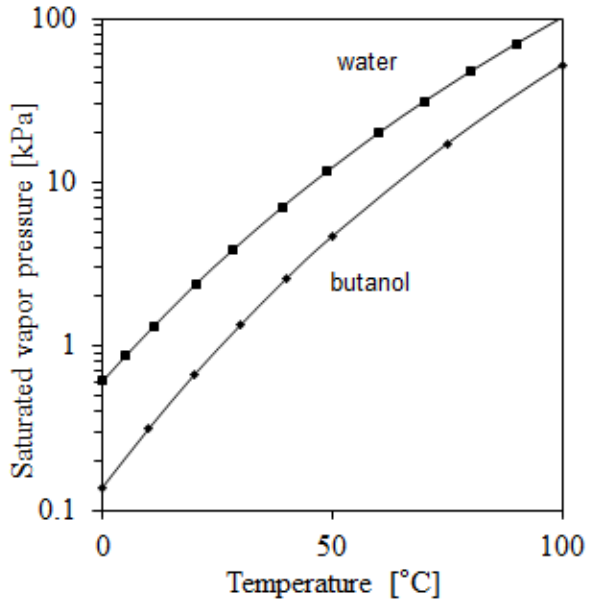

Figure 2. Saturated vapor pressure of butanol and water. (Data taken from ref 35).

The mutual solubilities of butanol and water increase with an increase in pressure (see Figure 4).[40] The temperature effect is shown by the multiple *P*-*x* curves. The pressures required to influence the solubility effectively are beyond those applied in conventional industrial large-scale systems. Conceptually, high-capacity, small-volume devices could allow pressure as an operational parameter for separation. The atmospheric vapor-liquid equilibrium in Figure 3 shows an azeotropic point at $x \approx 0.25$. Azeotropic behavior can severely complicate the direct distillation of a mixture. The liquid-liquid-vapor (L-L-V) equilibrium curve of a binary mixture is monovariant for a given composition when the temperature is fixed. The equilibrium vapor pressure can be determined for any composition and is shown in Figure 5. The pure-component vapor pressures of water and butanol are given at $x = 0$ and $x = 1$, respectively.

2.2.3. Ternary Systems. Besides temperature and pressure, an auxiliary component can be exploited to drive the separation of butanol from water. This third chemical species may lead to additional phase equilibria. Also, systems that contain more than three chemical species can be created; however, this investigation will be limited to ternary systems. Introduction of a fourth (or even more) species will require more-complex regeneration procedures and involve more phase equilibria. To illustrate the phase behavior of butanol and water mixtures, four types of ternary phase diagrams are shown subsequently. The ternary mixtures involve a solid, liquid, or gaseous compound with various mutual solubilities. Because the concentration of the butanol in the aqueous phase is close to the

outer edge of the ternary diagram, the examples have arbitrary axis units, to enhance clarity in illustrating the various types of phase behavior. The bottom axis of the diagrams shows the water-butanol binary mixture. Three points on this binary axis are common to all diagrams. The point on the left-hand side shows the liquid butanol concentration at feed composition, x^f_{BuOH}. The two remaining points give the liquid-liquid (L-L) equilibrium compositions. The addition of a ternary species to the initial butanol-water mixture will change the overall composition from point x^f_{BuOH} in a straight line to the top of the triangle. In each case, in the ternary phase diagrams, a tieline can be reached, such that the mixtures split into a relatively butanol-poor aqueous L1 phase and a relatively butanol-rich second phase. The ternary species shown in the diagrams are not necessarily the most efficient separating agent, but they are common in literature and representative for other ternary species.

2.2.3.1. Ternary Systems with a Soluble Solid Species.

Figure 6 shows the butanol-water-potassium iodide (KI) system. KI is an example of a solid that can dissolve partially in the aqueous phase and partially in the organic phase. The two solubility points of the salt are present on the outer edges of the diagram. The mutual solubility of butanol and water changes with the third species such that salting-out can occur.

A similar diagram can be expected with other inorganic compounds like NaCl or polar organic compounds such as amino acids.[41,42] Figures 7 and 8 show experimental solubility data for butanol and water solutions with NaCl and KI. The aqueous butanol equilibrium concentration decreases significantly when the salt content increases. Simultaneously the organic phase becomes less attractive for water. Predictive models for the salt effect on solubility have been developed.[43,44] Besides inorganic solids, organic solids can also have an effect on 1-butanol and water mixtures.[41]

2.2.3.2. Ternary Systems with a Gaseous Species. A gaseous species can also be present as a separate (gas) phase (see Figure 9). The gaseous phase will contain both butanol and water. A common stripping gas for microbiological systems is nitrogen. Nitrogen will dissolve in both the aqueous and organic phase. The effect on the L1 and L2 composition is small and the butanol and water contents in the gaseous phase are low. Besides allowing butanol to transfer to the gas phase under ambient conditions, no direct benefit, such as enrichment of the gas phase, relative to the vapor phase in the binary system, is expected. A gas that is inert, inexpensive, and insoluble in the aqueous solution is preferred. The Henry

coefficient can be used to describe the equilibrium partitioning of the compounds between the gas and liquid phases.

2.2.3.3. Ternary Systems with a Water-Immiscible Liquid Species. The ternary phase behavior of a water-immiscible liquid species with complete miscibility of butanol and the ternary component is shown in Figure 10, using octanol as the example. Two solubilities on the water-octanol axis are indicated. The organic phase (L2) is present at any binary butanol-octanol composition. Upon adding octanol to the feed composition x^{f}_{BuOH} a liquid-liquid phase split occurs with a relative high butanol: water ratio in the organic phase.

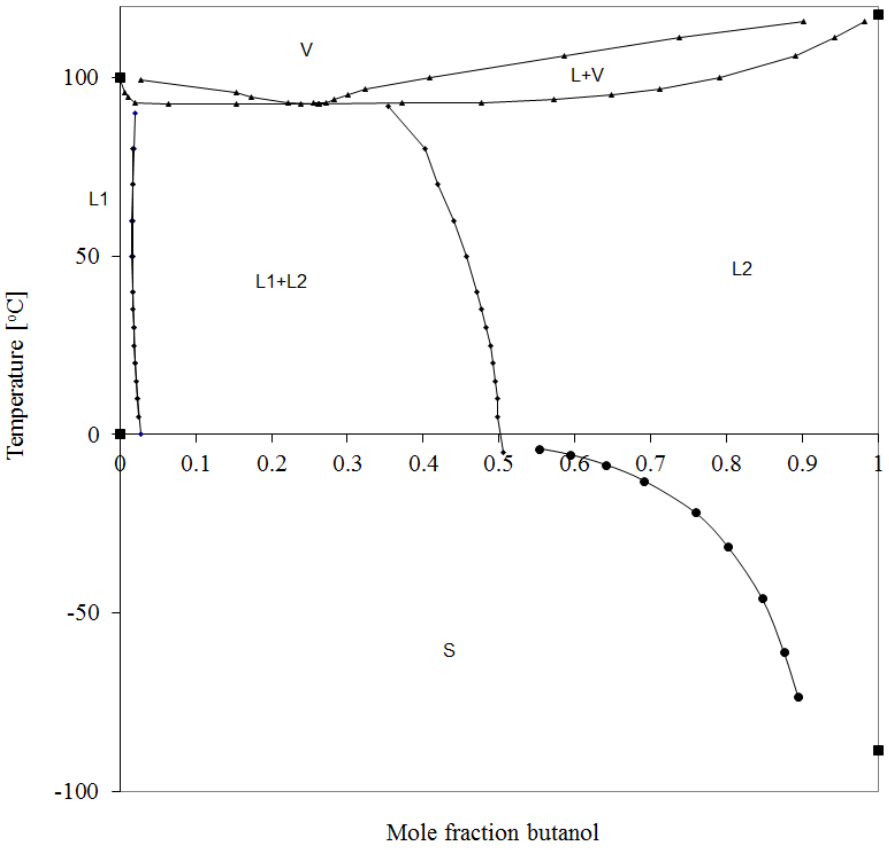

Figure 3. *T-x-y* data for the binary mixture of butanol and water at 1 bar. Experimental data points are indicated by markers ((▲) vapor-liquid equilibrium,38 (♦) liquid-liquid39 equilibrium, and (●) solid liquid equilibrium).[38] Lines are included to guide the eye. The square markers at the outer edges show the pure component fusion and boiling points for water (x = 0) and butanol (x = 1).

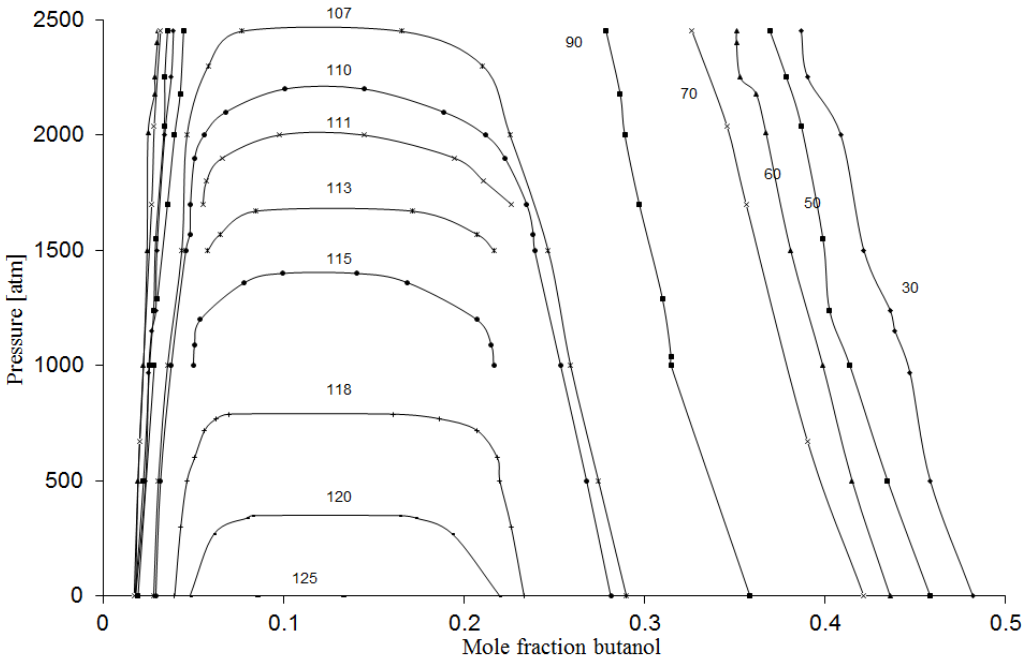

Figure 4. Butanol and water solubility isotherms. (Data taken from ref 40.) The temperature (displayed in degrees Celsius) is indicated at each isotherm.

The ternary phase data usually available for liquid ternary systems are expressed by partition coefficients. The partition coefficients of butanol and water between organic and aqueous phase are shown in Table 3 for various liquid nonpolar ternary species. The partition coefficient $m_{BuOH}^{org/aq}$ is the equilibrium ratio between the mass fraction of butanol in the organic phase and the mass fraction in the aqueous phase. Any $m_{BuOH}^{org/aq}$ value of > 1 indicates a preferable partitioning of butanol toward the organic phase. Table 3 gives some interesting candidates. The solubility of water in the solvent also can be expressed as a partition coefficient, $m_{H_2O}^{org/aq}$. This coefficient is needed to determine the overall selectivity of the separation. Selectivity can be defined as the ratio of the two partition coefficients. In integrated systems, such as that shown in Figure 1, the aqueous raffinate is recycled to the fermentation section and therefore the solubility of the organic solvents in the aqueous phase, $s_{Solvent}^{aq}$, must be considered. The solubility should be low, because it can disturb the fermentation, if the solvent is not recovered from the aqueous raffinate. Of course, the solvent should be easily recoverable from the extract to regenerate it. Some organic solvents do not mix completely with butanol. In these situations, the phase diagram may resemble Figure 9 rather than Figure 10, and the butanol solubility in the ternary species, s_{BuOH}^{org}, dictates the capacity for butanol and is an important parameter that influences the

total solvent requirement. Another situation occurs, for example, for the ternary mixture of the ionic liquid [C4mim][NTf2] with butanol and water at 15 °C and atmospheric pressure. This shows demixing in all three individual binary mixtures; however, complete mixing of water, butanol, and the ionic liquid occurs over a large composition range.[46] We refer to the literature for the phase diagram.

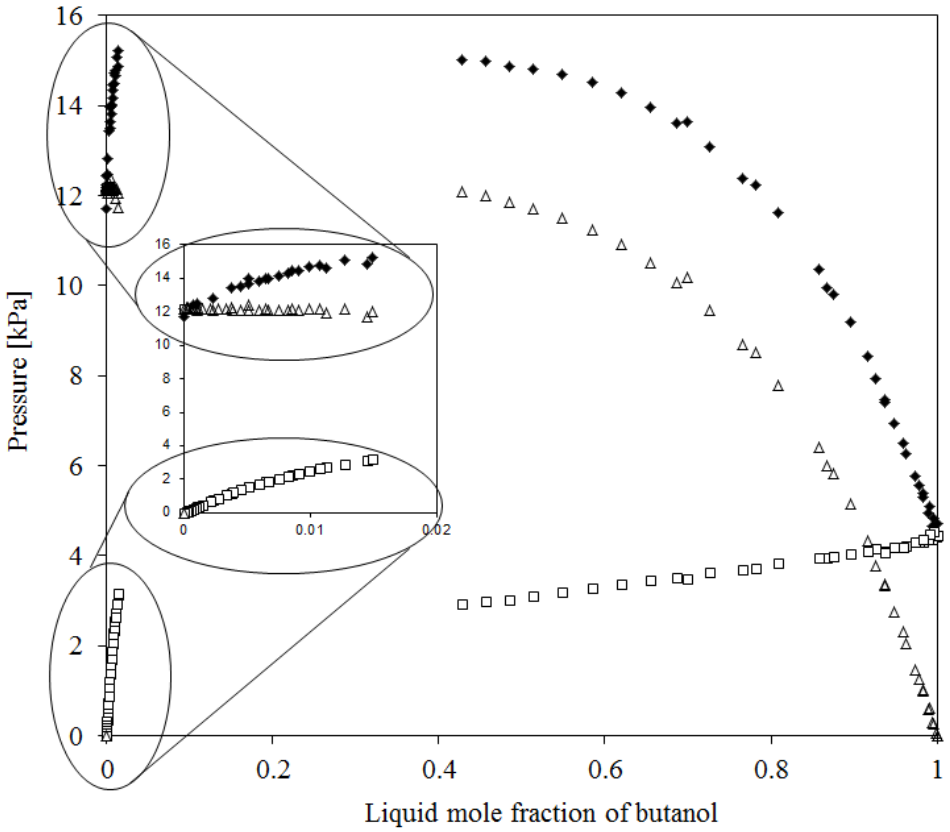

Figure 5. (♦) Saturated total vapor pressure and partial vapor pressure of (□) butanol and (Δ) water at T = 50 °C in binary mixtures. (Data taken from ref 35.) In the mole fraction range without data, liquid demixing occurs.

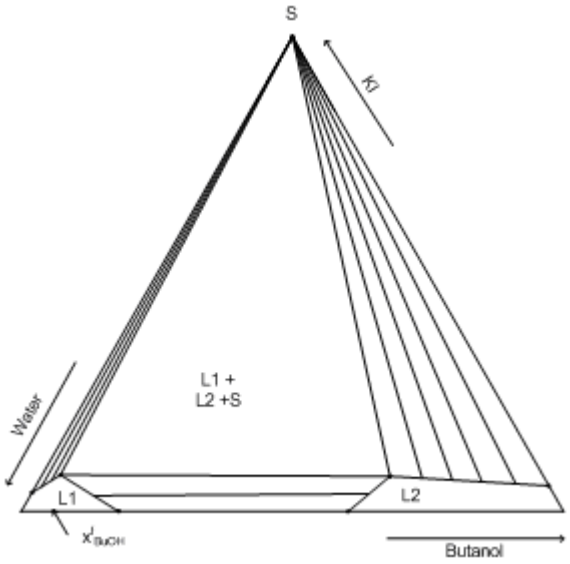

Figure 6. Schematic ternary phase diagram of butanol and water with a soluble (solid) species (example: potassium iodide (KI)).

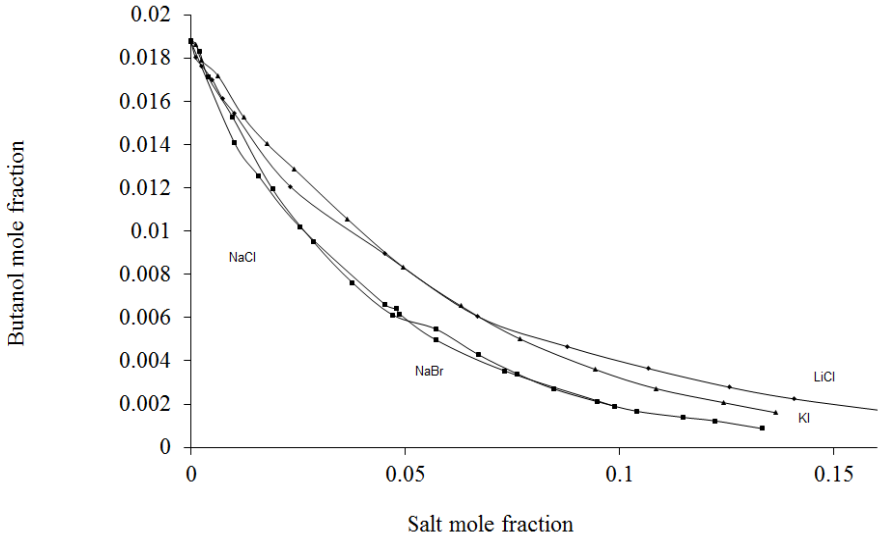

Figure 7. Salt effect on butanol solubility in the aqueous phase, as a function of salt content at T = 25 ^{o}C and P = 1 bar. (Data taken from refs 28 and 45).

2.2.3.4. Ternary Systems with an Insoluble Solid Species.

Figure 11 shows an example of a ternary system in which a solid is introduced that can contain butanol and water. The solid phase is silicalite, which is virtually insoluble in both the aqueous phase (L1) and the organic phase (L2). Again, adding this ternary species allows the presence of a new phase with a relatively high butanol:water ratio.

Silicalite is one of many solid species that can be used for butanol adsorption. Some have been listed in Table 4, with their adsorption capacity for butanol. Hydrophobic materials

prevail to minimize water adsorption. The butanol adsorption capacity ranges from 4% to 22% (m/m). The loading with adsorbate is a function of aqueous butanol concentration and temperature; however, these data are usually not available. An exception is silicalite-1,[50] for which the butanol adsorption isotherm is shown in Figure 12.[51] The initial slope of this line indicates an affinity from which the value of 2.16 for log $m_{BuOH}^{silicalite/aq}$ can be calculated. This compares favourably with the log $m_{BuOH}^{org/aq}$ values that are reported for the solvents in Table 3. Desorption of butanol can be achieved with an auxiliary fluid phase or by temperature or pressure shift, which requires additional isotherms, which are usually unavailable.

Adsorption data of butanol are mostly available in conjuncture with the recovery of ethanol and acetone.[31,51,54,55] However, the selectivity of the adsorption processes also is dependent on the binding capacity of the adsorbent for water. For zeolites, the water adsorption capacity is listed in Table 5. A decrease in the Si:Al ratio leads to a decrease in hydrophobicity and, consequently, an increase of water adsorption up to the micropore volume. Most $m_{H_2O}^{ads/aq}$ values in Table 5 are less favorable than the $m_{H_2O}^{org/aq}$ values in Table 3. However, the organic solvents will dissolve in the aqueous phase, whereas the adsorbents will not. Regeneration of the auxiliary phase is crucial for a successful operation. For regeneration of an adsorbent, temperature-swing or pressure-swing operations can be applied, as well as inert-purge or displacement-purge cycles operations, where an auxiliary species is introduced.[56]

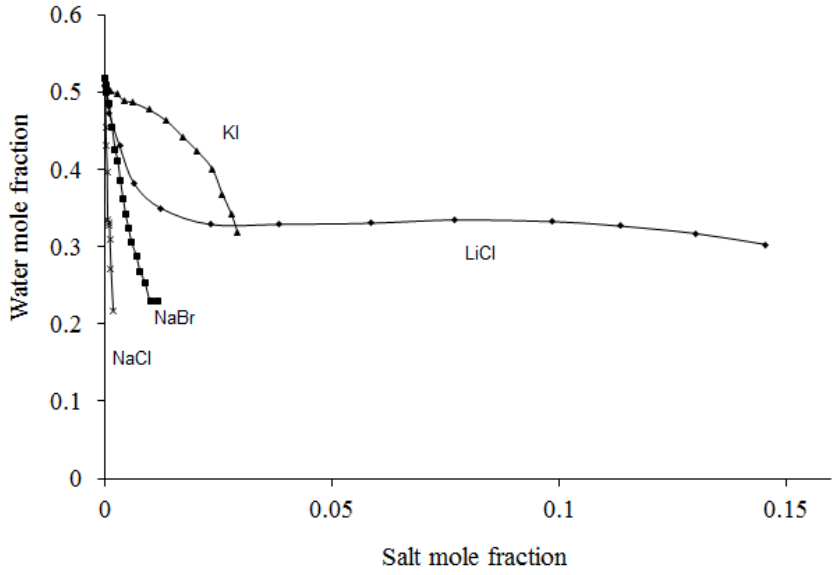

Figure 8. Salt effect on water solubility in organic phase as function of salt content at T = 25 °C and P = 1 bar. (Data taken from refs 28 and 45.)

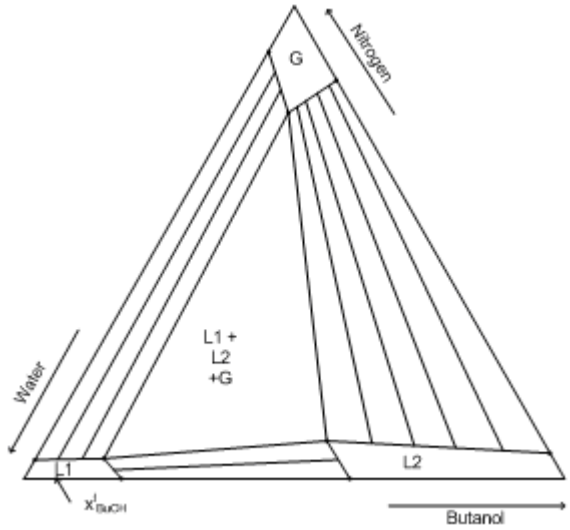

Figure 9. Schematic ternary phase diagram of butanol and water with a gaseous species forming a third phase (example: N2).

Table 3. Butanol and Water Partition and Solubility Data in Various Organic Solvents at 25 ^{o}C and 1 atm

solvent	ref(s)	$\log(m_{BuOH}^{org/aq})$	$\log(m_{H2O}^{org/aq})$	s_{BuOH}^{org} [g/L][47]	$s_{solvent}^{aq}$ [g/L][48]
cyclohexane	49	-1.12,-0.72		∞	0.058
hexadecane	49	-1.08			4 × 10-6
dodecane	25,49	-0.52,-0.96	-3.99		3.7 × 10-6
octane	25,49	-0.52,-0.81	-4.14		7.3 × 10-4
sesame oil	25	-0.52	-2.87		
carbon tetrachloride	49	-0.44		∞	0.65
benzene	49	-0.36	1.78	∞	
hexane	25	-0.30	-3.73	∞	0.0098
olive oil	25	-0.15	-2.83		
ethyl oleate	25	0.11	-0.66		
dibutyl phtalate	25	0.15	-0.33		0.0112
methyl laurate	25	0.26	-0.59		0.55[a]
dibutyl maleate	25	0.30	-0.18		15.9[b]
castor oil	25	0.41	-2.02		
trichloromethane	49	0.45			8.0
oleyl alcohol	24	0.48	-1.81	15.4	7 × 10-5
hexyl acetate	25	0.56	-0.14		0.20[b]
dodecanol	25	0.78	-1.37		4 × 10-3
diethyl ether	49	0.89		∞	64.2
octanol	25,49	0.88	-1.11	∞	0.54
hexanol	25	1.08	-1.12		6.0

[a] In dodecanoic acid at 20 ^{o}C. [b] At 20 ^{o}C.

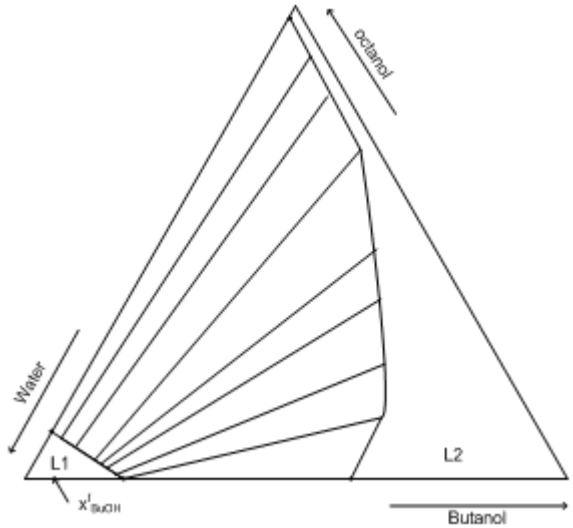

Figure 10. Schematic ternary phase diagram of butanol and water with a water-immiscible liquid species (example: octanol).

2.3. Selectivity of Recovery

Fermentation of butanol can be performed in batch, fed-batch, or continuous (continuous stirred tank reactor (CSTR) or plugflow reactor (PFR)) mode. Without going in the detail of the fermentation processes, one can note that all systems benefit from product removal. A general process scheme that describes a butanol production system with product recovery is defined in Figure 13. The defined streams are the feed stream Φ^f, the auxiliary phase stream Φ^a, the product stream Φ^p, and the recycle stream Φ^r. Depending on which operation is described in the literature, the latter two streams can also be called permeate or raffinate, respectively. In the literature, selectivity (S^f) is most often defined as the ratio of the butanol and water concentration ratio in the product and feed, as shown in eq 1.

The ratios can be expressed using either mass-based concentrations (C) or in mole fractions (x).

$$S^f = \frac{[C_{BuOH}/C_{H_2O}]^p}{[C_{BuOH}/C_{H_2O}]^f)} = \frac{[x_{BuOH}/x_{H_2O}]^p}{[x_{BuOH}/x_{H_2O}]^f} \qquad (1)$$

To be able to determine values for the reported recovery operations, we fix the feed at 20 g/L butanol at 25 ^oC, unless specifically mentioned otherwise.

2.3.1. Distillation. Distillation is the traditional method to recovery butanol from aqueous fermentation broth. Because water is the light key component, most of the energy consumption during distillation originates from the evaporation of the water in the feed. A binary azeotrope is obtained at 92.7 ^{o}C. Conversion of a feed of 20 g/L butanol into an azeotropic mixture at 1 atm leads to a selectivity of S^{f} = 72. It is possible to break the azeotrope by introducing a ternary compound or by changing the pressure. The specific energy requirement can be calculated and is a function of butanol feed concentration.[59] The performance of the distillation is directly related to the energy integration applied, because the energy consumption determines the largest portion of the operational costs. Energy integration options are dependent on the scale and the processing plant. In conclusion, pure butanol can be obtained at the cost of energy and investment in equipment.

2.3.2. Liquid-Liquid Demixing. Butanol and water can form a biphasic liquid; however, at the upper limit in fermentative concentration (~20 g/L), all butanol is still soluble in the aqueous phase. The addition of salts might be pursued to cause a phase split. The salt contents required in the aqueous phase to reduce the solubility of butanol to 20 g/L for sodium chloride (NaCl), lithium chloride (LiCl), sodium bromide (NaBr), and kalium iodide (KI) are 160, 188, 270, and 430 g/L, respectively. Liquid demixing will also provide a butanol phase. The composition of the butanol phase, in comparison to the liquid feed composition, leads to a selectivity of 310-750 for the salt contents that have been mentioned. Subsequently, the salts would enter the fermenter according to Figure 13, and then these salt concentrations would be too high for normal clostridial fermentations. A microbial cell strives to maintain a constant intracellular environment. For larger salt gradients over the cell membrane, more energy is spent on maintaining the cells' internal conditions, usually at the expense of growth or product formation. The key factor still remains to be the overall product yield on the substrate. Nevertheless, some micro-organisms live in medium- to high-saline environments, such as soda lakes, but these organisms have not been used for butanol production.

For most other polar compounds, the effect on water and butanol demixing has not been reported; however, it is expected that liquid-liquid demixing cannot be readily applied, because it will require the addition of large amounts of auxiliary chemicals, which might easily disturb the fermentation in the case of the recycle described in Figure 13. Whenever the fermentation is not fully inhibited by the addition of large amounts of additional chemicals, liquid-liquid demixing might be conceptually feasible.

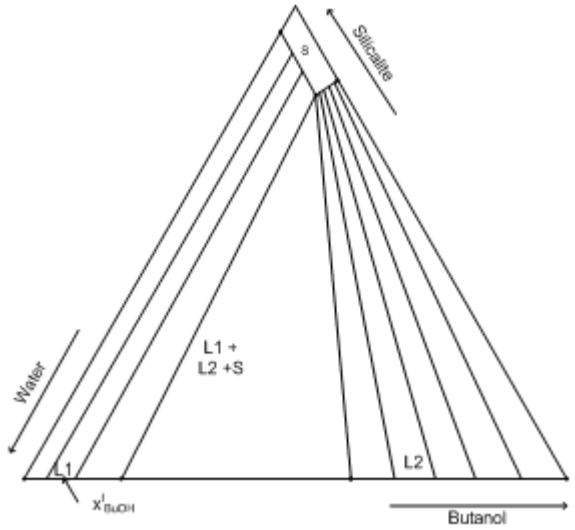

Figure 11. Schematic ternary phase diagram of butanol and water with an insoluble porous solid species (example: silicalite). L1 and L2 phases are located on the horizontal axis.

Table 4. Adsorbent Capacity for Butanol Recovery from Model Solutions at T = 20 °C[51-53] and T = 37 °C,[30] 1 atm

adsorbent	ref	butanol capacity [g/g]
Norit ROW 0.8	30	0.22
Norit W52	30	0.22
silica gel	52	0.15
Silicalite-1	51	0.10
XAD 4	30	0.0975
XAD 4	53	0.083
Bonopore	53	0.074
XAD 7	53	0.069
Bonopore, nitrated	53	0.055
XAD 2	30	0.05
XAD 8	30	0.04

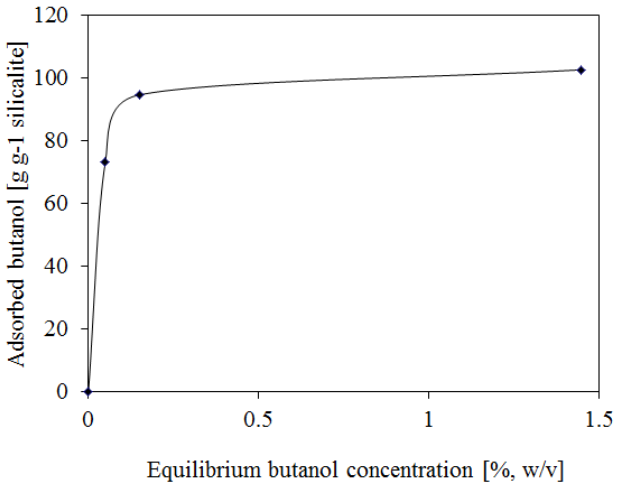

Figure 12. Equilibrium isotherm on silicalite from aqueous solution at T = 25 °C.[51]

Table 5. Water Binding Capacity in Zeolites and Silicalite at T = 25 °C[57] and T = 50 °C[58]

adsorbent	water capacity [g/g]	$\log(m_{H2O}^{ads/aq})$	micropore volume [cm^3/g]	Si/Al ratio
Silicalite[58] ∞	0.016	-1.80	0.180	∞
H-ZSM-5[58]	0.072	-1.14	0.180	20
NaZSM-5[57]	0.077	-1.12	0.102	15
NaA-mordenite zeolite[57]	0.13	-0.89	0.169	5.0
Na, K-erionite A zeolite[57]	0.16	-0.80	0.190	3.0
NaA zeolite[57]	0.26	-0.59	0.287	1.0
NaY zeolite[57]	0.29	-0.54	0.310	2.6
NaX zeolite57	0.30	-0.52	0.311	1.2

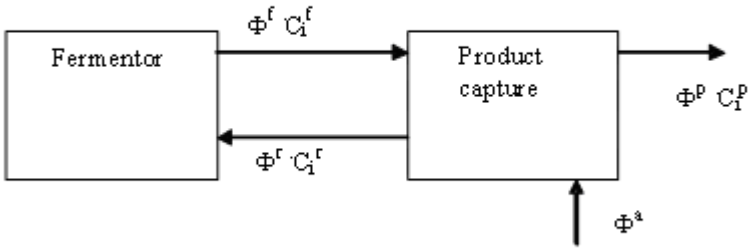

Figure 13. Stream definitions recovery operation.

2.3.3. Freeze Crystallization. The enthalpies required for liquid-to-solid phase transition of either butanol or water are substantially lower than those for their respective liquid-to-vapor phase transition (see Table 2). From this perspective, freeze crystallization may be energetically more favorable than distillation.

However, process plant investment for solids handling will be significantly higher than that for vapors, usually by a factor of 2. The energy advantage must balance the additional costs introduced by the handling of the solid bulk water phase. No freeze recovery systems for butanol have been described in the literature. According to Figure 3, bringing a system of 20 g/L butanol to a temperature of -20 ^{o}C will result in a butanol product stream with a selectivity of 150.

2.3.4. Pervaporation. Pervaporation as recovery technique is a combination of membrane permeation and evaporation.[60] Pervaporation is commercially applied mainly for dehydration of organic solvents.[61] A low vapor pressure or vacuum can be used instead of sweep gas to increase transport flux and selectivity. Membrane modules can vary from simple sheet membranes to more-complex systems (such as tubular systems). The product flux through the membrane and the selectivity of recovery are a function of the composition of the aqueous phase and gas phase, membrane properties, membrane area, temperature, and pressure. The flux through a membrane is inversely proportional to the membrane thickness. As the membrane provides selectivity, more-selective membranes experience relative lower product flux. Hydrophobicity of the membrane has a strong effect on selectivity, because it limits the water flux. Silicalite, zeolite, liquid, and organic polymer membranes are all possible considerations. In the literature, various compilations of membrane-aided separation of butanol are available.[19,62]

Usually, these report batch operations with a (internal) recycle to the feed vessel and measurement of the concentration occurs using the effluent. Therefore, the reported selectivities should formally be denoted as S^r, with a superscript "r" instead of superscript "f" in eq 1. In practice, most experiments are operated in fully mixed batch systems, without an actual distinction between feed and recycle composition. A selection of pervaporation data is shown in Table 6. Overall, the aqueous butanol concentration was in the range of 0.37-78 /L. The selectivity is in the range of 2.7-209.

Flux is dependent on membrane thickness. The membrane thickness varied in the studies; however, it is usually 0.025-2 mm. The total flux through the membrane varied between 3 g m^{-2} h^{-1} and 2100 g m^{-2} h^{-1}.

Flux increases with butanol feed concentration. It is reasonable to assume a standard butanol product flux of 20-100 g m^{-2} h^{-1} to be feasible today when handling fermentation broth.

Most membranes can be considered to be close to their performance limit, although some membrane types (such as silicalite/silicone membranes) are considered to be improvable.[63]

Flux limitations can be overcome by influencing the process kinetics. The kinetics can be influenced by process temperature or by product phase concentration. For example, the butanol content of the product phase can be reduced using a strip gas that dilutes the system but increases the driving force for the separation. Alternatively, a vacuum can be applied, which leads to an increase in volume.

2.3.5. Reverse Osmosis. Traditional reverse-osmosis membranes materials dissolve in acetone. Therefore, the presence of acetone is considered to be a main factor for the absence of studies on osmosis as a recovery technique.[62] Alternative membranes have not been reported; however, the application of reverse osmosis as a separating technique still remains very interesting.

2.3.6. Gas Stripping. Several gas-stripping recovery systems for butanol have been described.[1,20-23] Primarily, nitrogen is used as the stripping gas. Butanol fermentations require anaerobic conditions, and exposure to oxygen should be avoided. Stripping can occur in the reactor or in an external unit, the latter of which allows heating of the liquid without disturbing the fermentation. Not only batch and fed-batch fermentation have been conducted: some

continuous cultures also have been run on a laboratory scale, using gas stripping as a recovery technique. In all cases, the product recovery improved the productivity and product yield of the fermentation. An important advantage of stripping as a recovery

technique is the low risk of fouling or clogging of the auxiliary phase.[1] The mass-transfer area is determined by the gas/liquid interface, which is a function of the gas bubble size. A compilation of operation parameters and selectivities obtained in stripping systems is shown in Table 7.

Table 6. Pervaporation Systems and Butanol Selectivity

membrane	ref	temperature, T [^{o}C]	C_{BuOH}^{aq} [g/L]	total flux [g m^{-2} h^{-1}]	S^{f}
polytetrafluoroethylene	62	30-55	3-30	35-2100	2.7-4.8
polypropylene	16, 62, 64	35-50	2-16. 7	3-1600	4-61
polyurethane	62, 65	50	10	7-88	9
poly(methoxy siloxane)	62	50	10-70	150-400	10-15
silicone	17, 18, 62, 66-68	37-78	1-60.0	4.42-270	13-58
poly(dimethyl siloxane)	62, 65, 69	40-62	5-50	26-1000	15-58
zeolite membrane Ge-ZSM-5	70	30	50	5	19
polyether block amide	62, 65	50	10-52.5	46-800	20-23
zeolite-filled PDMS	62	40	10-50	100-230	36-45
poly[1-(trimethylsilyl)-1-propyne]	69	25-37	10-35	100-650	38-135
thin-film silicone	63	30-70	10	~25-200	42-49.6
silicalite-filled PDMS	62	78	0.37-78	90-237	55-209
silicalite-silicone	18, 71	78	10-12	89-119	70-97
thin-film silicalite-silicone	63	30-70	10	~40-500	86-111
oleyl alcohol liquid membrane	59		40	400	180

2.3.7. Extraction and Supercritical Extraction. The feasibility of liquid extraction of butanol, among others, is dependent on the aforementioned partition coefficient of butanol and water and on the solubility of the organic solvent in the aqueous phase.[24,25] Usually, the objective is to concentrate butanol in a higher-boiling solvent, enabling distillation of

butanol more efficiently than via direct distillation from the dilute aqueous solution. Selectivity of the extraction is a function of butanol and water solubility of the solvent and ranges from 1.2 to 4100.[24,25] High selectivities are attained when extremely nonpolar extractants are used. Although water does not readily

dissolve in such strongly nonpolar solvents, an increase in hydrophobicity adversely affects the solubility of butanol in the solvent. This means that selective solvents have a low capacity for butanol. For extraction with a selective solvent such as oleyl alcohol, the selectivity at equilibrium is 105, with a capacity of only 1.8% (m/m).

The extractant will usually saturate the aqueous phase and can become toxic to the microorganisms when the aqueous phase is recycled to the fermenter. The toxicity of an extractant to a micro-organism can be determined experimentally, but it can be correlated to the octanol-water partitioning coefficient.[72,73]

In this case, it is fortunate that very nonpolar solvents are the least toxic ones. Supercritical CO_2 ($SCCO_2$) extraction differs from extraction only in the definition of the phase. By reducing the pressure, the CO_2 can be easily removed for recovery of the extracted products. Under extraction conditions, $m_{BuOH}^{SSCO_2/aq} = 2.2$, which is a good indication of the selectivity that one equilibrium stage can bring. Because of the multistage operation, the selectivity is reported as S^r at a pressure of 100 bar and a temperature of 40 ^oC, as a function of the butanol raffinate concentration, and ranges in value from 139 to 6020.[27] Recycle concentrations were in the range of 0.7-0.14 g/L, whereas the feed contained 50 g/L. The selectivity increases with an increase in the amount of solvent stream, relative to the feed stream. At a CO_2:feed mass ratio of 1.2, the selectivity of butanol recovery is ~ 400. The CO_2 capacity for butanol is modest (1.6%-6.9% (m/m)).

2.3.8. Perstraction. In the literature, most applications of extraction are perstraction operations.[25,29] The membranes keep the organic and aqueous phases physically separated, avoiding a settling compartment for the two liquid phases, avoiding contamination of the organic phase by the cells, and reducing the toxicity of the organic phase to the cells. Membranes do introduce an additional mass-transfer limitation. In the long run, any recycle system, as shown in Figure 13, will operate under saturated conditions.

2.3.9. Adsorption. The selectivity of an adsorption process is dependent on the relative binding of the adsorbent of butanol versus water. Because of the high water concentrations and low butanol concentrations, hydrophobic material is desired. The highest adsorption capacity for butanol in Table 4 is 22% (m/m) for activated coal. Activated coal is generally

used to remove organic contaminants from water. The regeneration of activated coal is more cumbersome and the activated coal's stability and homogeneity are less favorable, in comparison to silica-based adsorbents. Because of the high affinity for butanol, even at feed concentrations of < 1 g/L, the selectivity can be very high. The overall selectivity of hydrophobic zeolite adsorbents is estimated to be 130-630. When working with a feed composition of 20 g/L, the selectivity can be ~270. Desorption is an issue that has been studied much less. It has been noted that gradual heating might allow the stepwise desorption from silicalite-1 and therefore enable the recovery of an enriched butanol fraction.[51,74]

2.3.10. Overview of Butanol Recovery Operations. Table 8 gives an overview of the estimated selectivities of butanol recovery. Although distillation and extraction are mature and widely applied in the chemical industry, Table 8 also contains recovery options, such as adsorption and membrane separation, which are much less accepted, in terms of scaleup. Still, the latter are applied on a scale larger than that required for butanol recovery. For example, a total adsorption bed volume of 640 m^3 is used for the desugarization of molasses in an Applexion plant,[75] and more than 300 000 m^2 of membrane area will be installed in the Sulaibiya wastewater treatment plant for Kuwait City.[76] With a change from hydrocarbon to carbohydrate feedstock, the chemical industry may also have to adopt such less-mature recovery operations at very large scale.

Distillation, gas stripping, freeze crystallization, and pervaporation show a relatively low selectivity. Liquid demixing and adsorption allow a more-selective capturing operation for butanol. The reported selectivity is predominantly based on a single-stage equilibrium operation. Operations such as distillation and extraction can easily be performed in multistage contactors. Multistage equilibrium operations will allow higher selectivities, compared to the single equilibrium stage.

Table 8 is limited to single-equilibrium-stage operations. On a mass basis, the highest capacities are achieved for adsorption and extraction. However, for extraction, capacity is inversely coupled to the overall selectivity of recovery. For liquid demixing, the known salting-out agents are not compatible with the fermentation.

Based on these data, several recovery operations will be evaluated further.

2.4. Energy Requirement Estimates per Recovery Operation

The energy requirement of the recovery system contributes significantly to the operational costs of a recovery system, as mentioned in the Introduction. The internal combustion energy of butanol (36.2 MJ/kg) is clearly beyond the upper limit amount of energy to be

spent on recovering butanol. A target value of 10% of the combustion energy seems reasonable, which would give an operational energy requirement limit of 4 MJ/kg. The product-capturing step concentrates the butanol to a much smaller stream, similar to that indicated by Figure 1. This process step is more intensive, with regard to the investment of equipment and the energy requirement, than the subsequent purification step of the enriched organic phase. When concentrating butanol to 50%, the capturing step consumes ~ 90% of the energy requirement of the product recovery. For systems such as gas stripping that do not achieve such a 50% concentration, still 75% of the energy is consumed by the capturing step. To avoid the need for detailed product specifications, depending on too many variables (such as byproduct and production site-specificintegration options), only the product-capturing step is investigated in detail. It is the crucial process step when determining the process performance. Most process energy estimates are based on process flowsheet calculations. A simple quantitative approach to evaluate a set of recovery options is presented here. We propose to neglect the process-specific details altogether and describe the product-capture operation as a general steady-state flow process.

Steady-state flow processes can be described as shown in eq 2.

In the absence of a change in kinetic or potential energy, the enthalpy difference between feed and product streams of the steady-state process is dependent on the heat and work applied to the capture operation.[77]

$$\Delta H = Q - W_S \qquad (2)$$

Because process-dependent characteristics are not taken into account, the heat and work are not specified.

The course of ΔH is variable throughout the product capture operation and is dependent on the local temperature and pressure. The recovery energy requirement is estimated using the enthalpy extremes as illustrated in Figure 14 and eq 3. The product flow is taken to be a specific fraction of the feed flow. The product flow is evaluated as only the mass in the feed flow that will eventually comprise the final product flow. For simplicity, the difference in enthalpy between the various streams are taken as a function of temperature and pressure and not of composition. In other words, the mixing effect is neglected. Only the enthalpy change of the product part of the feed flow will be taken into account; this is called ΔH^p. We assume the remainder of the feed flow to leave the system as recycle to the fermenter at the original feed enthalpy level.

$$\Delta H^{p} = H^{p}(T^{p,|max|}, P^{p,|max|}) - H^{p}(T^{f}, P^{f}) \qquad (3)$$

Note that energy input has been calculated from the enthalpy value of the final product stream; it is not the actual reversible work performed on the system. Under relevant conditions, the enthalpy is more sensitive to temperature than to pressure. In the case of work-intensive operations that involve pressure, the energy requirement calculation is an underestimation, because the work is assumed to be ideally applied. Butanol and water enthalpies were calculated in Aspen Engineering Plus 12.1, using the NRTL property method. The energy requirement for any recovery operation *j* is expressed per mass amount of butanol product:

$$E^{p}_{BuOH}(j) = \frac{\Delta H^{p}}{x^{p}_{BuOH}}\left(\frac{1}{M_{w,BuOH}}\right) \qquad (4)$$

Equation 1 can be used to express the product butanol composition as a function of selectivity and feed composition.

Substitution of eq 1 in eq 4 will yield eq 5. Equation 5 expresses the energy estimated for recovery operation *j* for the recovery of 1 kg of butanol from an aqueous feed mixture and is only a function of the selectivity. Thus, the energy requirement per kilogram of butanol in the product phase can easily be calculated using the tabled selectivities:

$$E^{p}_{BuOH}(j) = \frac{\Delta H^{p}}{M_{w,BuOH}} \cdot \left(\frac{1}{S} \cdot \frac{x^{f}_{H_2O}}{x^{f}_{BuOH}} + 1\right) \qquad (5)$$

If an auxiliary phase is present, its energy change also must be taken into account. A simpler method was applied with the assumption that the ternary species does not experience a change in phase or pressure. Thus, the enthalpy requirement for the auxiliary phase (ΔH^{p}_{a}) is estimated using its heat capacity, c^{a}_{p}.

For convenience, the heat capacities are expressed on a mass basis, because the capacities are expressed on a mass basis.

$$\Delta H^{a}(j) = c^{a}_{p}\,(T^{p} - T^{f}) \qquad (6)$$

The enthalpy effect of the temperature change of the auxiliary phase, combined with the amount of butanol in the auxiliary phase (L^{a}_{BuOH}), given in Table 8, gives an estimate for the energy requirement of the auxiliary phase per kilogram of butanol.

$$E^{a}(j) = \frac{\Delta H^{a}(j)}{L^{a}_{BuOH}} \qquad (7)$$

Table 7. Selectivity of Integrated Recovery System by Gas Stripping

operating mode fermentation	ref	C_{BuOH} [f] [g/L]	selectivity
batch	21	1.5-12.3	10-14
fed-batch	22	< 10	10.3-22.1
continuous	23	2.5	4

Table 8. Selectivity and Capacity Estimates Per Recovery Operation[a]

operation	ref(s)	selectivity estimate	capacity [kg/kg]
distillation	13, 14	72	*a*
liquid demixing		310-750	*a*
freeze crystallization		150	*a*
pervaporation	15-19	2-209	*a*
supercritical extraction	26, 27	550	0.050
gas stripping	1, 20–23	4-22	0.00064
extraction	24, 25	1.2 - 4100	0.003-0.12[b]
adsorption	30-33	130-630	0.11

[a] No auxiliary phase involved. [b] Low capacity at high selectivity.

Table 9. Energy Requirement Estimates per Kilogram of Butanol

operation, *j*	*S*	T^f [^oC]	T^p [^oC]	Energy Requirement Contribution [MJ/kg] E^p	E^a	total
gas stripping[a]	4	25	25	31		31
gas stripping[a,b]	19	25	70	14		14
pervaporation[c]	60	70	70	4.5	140[d]	145
pervaporation[c]	200	25	25	2		2
extraction[e]	104	25	120	1.9	5.8	7.7
adsorption[h]	10	25	160	27	6	33
adsorption[h]	274	25	160	1.2	0.1	1.3

[a] Gas phase product. [b] No heat is assumed to be lost to fermentation broth. [c] Work of vacuum operation is assumed at 100% efficiency. [d] Not for the auxiliary phase but for heating of the liquid feed to the recovery temperature. [e] Using oleyl alcohol. [h] The heat capacity of the adsorbent is assumed to be 1 kJ kg^{-1} $^oC^{-1}$.

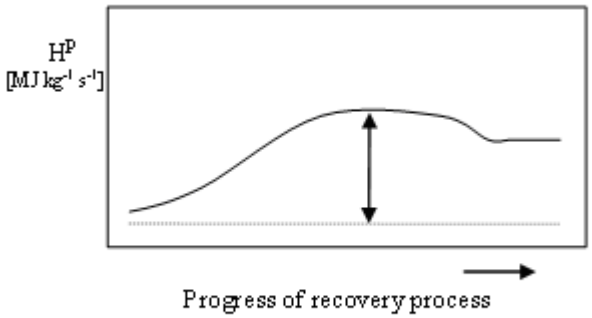

Figure 14. Enthalpy during recovery.

Table 10. Energy Requirement of Butanol Recovery Systems[a]

operation	Energy Requirement (MJ/kg)		
	butanol (from ref [31])	butanol (from ref [59])	ABE[b] (from ref [14])
steam stripping distillation	24	>50	
gas stripping	22		21
pervaporation	14		9
extraction/perstraction	9		14
adsorption	8		33

[a] Results have been normalized per kilogram of recovered butanol. [b] Acetone, 1-butanol, and ethanol.

Both contributions are reported separately in Table 9, to provide a clear picture of the energy requirements of the recovery options. Low-energy-requirement estimates can be observed for selective adsorption processes and pervaporation processes without preheating the feed stream. It is necessary to have a highly selective system and to avoid high energy demands in the auxiliary phase to remain below the already-mentioned target value of 4 MJ/kg butanol. Table 9 lists the energy requirements for each recovery operation and conditions. The contribution of auxiliary phase to the energy consumption can be considerable and corresponds to a large investment in heat-transfer equipment. The operations listed with footnote (c) correspond to processes mentioned in the literature,[14] as shown in Table 10.

The applied method ranks the recovery operations in similar order to the predictions in the literature on process estimates (shown in Table 10). The short-cut method results shown in Table 9 underestimate the required energy, when compared to Table 10. This is expected as the short-cut method evaluates the internal enthalpy change and not the actual heat and work performed on the system. The processes with energy requirements below the target value of 4 MJ/kg are, according to this short-cut method, pervaporation and adsorption, provided that high selectivities are achieved.

2.5. Conclusions

The thermodynamic properties of binary and ternary butanol-water mixtures lead to a wide range of options available for the recovery of butanol from dilute aqueous solution, by varying temperature, pressure, or composition. Recovery options that have not yet been explored include freeze crystallization and liquid-liquid demixing. From an energy requirement perspective, both operations are interesting.

Complete process designs for the recovery of butanol are scarce. Most operational data have been reported only for model systems using batch recovery. The available recovery data have been ranked by the selectivity of the recovery of butanol versus water. Highly selective processes are adsorption-based recovery processes using nonpolar adsorbents and some extraction systems. Selective extraction systems show a very low capacity for butanol. Ranking of the energy consumption of the recovery alternatives has been achieved using a short-cut model, which only takes into account the enthalpy change during the recovery operation. According to this assessment, the most attractive recovery options are adsorption-and pervaporation-based recovery operations.

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2.7. Nomenclature

Symbols

C = mass concentration [g/L]
c_p = heat capacity [J g-1 K-1]
E = mass-specific energy requirement [MJ/kg]
F = molar flow rate [mol/s]
G = Gibbs energy [J/mol]
H = specific enthalpy [J/mol]
L = capacity [kg/kg]
M_w = molar mass [g/mol]
m = distribution coefficient

P = pressure [atm]

Q = mass-specific heat [J/kg]

s = solubility [g/L]

S = selectivity

T =temperature [^{o}C]

W_s = mass-specific shaft work [J/kg]

x = mole fraction in liquid phase

y = mole fraction in vapor phase

Φ = stream volume flow rate [m^3/h]

Subscripts

b = boiling

BuOH = butanol

comb = combustion

fus = fusion

H_2O = water

j = process operation

m = melting

vap = vaporization

∞= infinite

Superscripts

a = auxiliary phase

aq = aqueous phase

f = feed

org = organic phase

p = permeate/product

r = recycle/retentate

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Chapter 3: Exploring the potential of recovering 1-butanol from aqueous solutions by liquid demixing upon addition of carbohydrates or salts

Abstract

BACKGROUND: Fermentative production of 1-butanol yields dilute aqueous solutions. Recovery of the butanol from these solutions is most commonly performed by energy-intensive distillation. This work investigated the liquid-liquid (L-L) phase behavior of mixtures of butanol and water to explore the potential of using L-L phase separation as a recovery possibility for 1-butanol. The phase behavior is preferably influenced by compounds already present in the fermentation, such as carbohydrates and salts.

RESULTS: The L-L phase equilibria of butanol and water were determined in the presence of glucose, fructose, sucrose, NaCl, LiCl and CaCl2. The aqueous and organic phase split is more pronounced in the presence of salts than in the presence of carbohydrates. Demixing is achieved with about 0.3 kg salt kg−1 aqueous phase containing 40 g of butanol.

CONCLUSION: Operation of L-L based recovery using salts or carbohydrates requires extreme concentrations of those compounds. For feed material containing 40 g kg−1 butanol, the tested carbohydrates do not influence the phase equilibria sufficiently to allow butanol separation. Fermentative butanol concentrations up to 70 g kg−1 are required to create an effective L-L phase split. The remaining residual aqueous carbohydrate solution might be used as feed for a following fermentation.

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3.1. Introduction

The dominant transportation fuels today are gasoline, diesel and kerosene. Sustainability concerns are a major driving force behind the development of technologies enabling renewable feedstock conversion into energy carriers,[1–3] in particular into ethanol.[4] However, higher alcohols, e.g. 1-butanol, provide better product characteristics, such as higher energy content on a mass basis. 1-butanol can be produced by Clostridia using acetone–butanol–ethanol (ABE) fermentation.[5] Due to product inhibition, the overall concentration of the solvents in the production broth reaches only around 20 g kg^{-1}.[6–8] This total solvent concentration might be improved significantly by organism choice, because the highest butanol tolerance has been reported to be 48 g kg^{-1}.[9] Owing to the product concentration, separation and purification of the dilute aqueous stream by traditional recovery techniques, such as distillation, require a relatively high energy input when compared with the energy content of butanol.[10] Alternative recovery techniques are pervaporation, adsorption, and extraction.[11] All these techniques use the introduction of a new product-enriched phase in order to separate the product from the bulk fermentation broth. A mostly unexplored technique, which is more direct, is liquid demixing. Butanol and water are not fully miscible under most conditions. At ambient conditions, 74 g kg^{-1} butanol dissolves in water. The liquid–liquid equilibria can be influenced by pressure, temperature and chemical composition.[12–14] We will not explore temperature and pressure influences on the phase equilibria here, but will focus only on chemical composition. This work explored the use of polar solutes, some of which were already present in the fermentation process, to influence the chemical composition of a two-phase organic and aqueous system containing butanol. The feed material used for fermentations contains mostly carbohydrates, but also some salts are added as nutrient. Salts are further introduced in the form of acid and base dosing for pH control. The aim is to show the possibilities and (operating) boundaries for an integrated recovery process using L-L phase behavior as the separating technique. To that end liquid–liquid phase equilibria between butanol, water and a ternary species, carbohydrates as well as various salts are determined by batch equilibrium experiments. The equilibria are used to calculate the potential of using the various chemical species to perform a L-L phase separation process, as is depicted in Fig. 1.

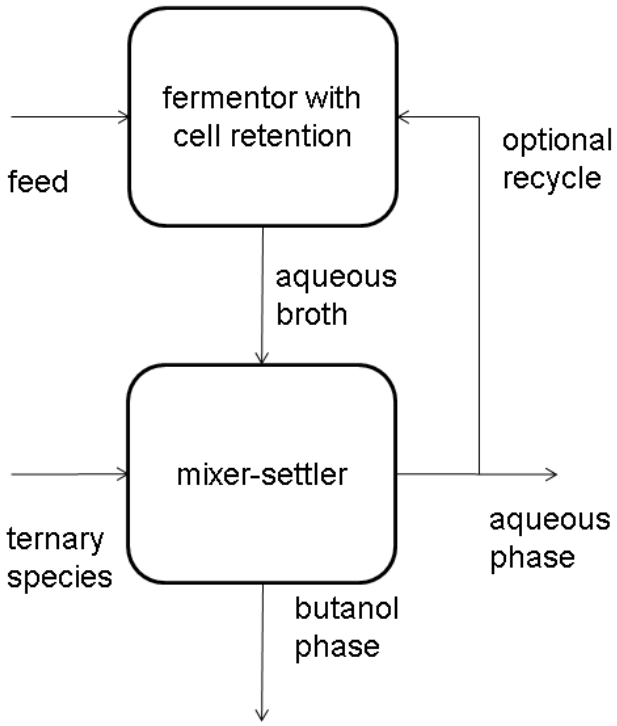

Figure 1. General process scheme for 1-butanol production using L-L separation based product recovery.

3.2. Experimental section

3.2.1.Chemicals

D-glucose (>99.0%), D-fructose (>99.0%), sucrose, CaCl2•2 H2O (>99.5%) and, phosphoric acid (85%) were supplied by Merck (Schiphol-Rijk, the Netherlands); NaCl (99.7%) and LiCl (>99.6%) by Baker (Deventer, the Netherlands); and 1-butanol (>99.5%) by Acros (Geel, Belgium).

3.2.2.Miscibility experiments to determine phase equilibria

The equilibrium experiments were performed by adding a set mass of water, butanol and a carbohydrate or salt species into a 250 mL vessel. The mixture was stirred magnetically for about 4 h and then transferred into a separating funnel. The funnel was placed inside an oven kept at 25 ◦C. After approximately 24 h of settling, the two liquid phases were separated. Their mass was determined and they were stored at 5 ◦C for further analysis.

3.2.3.Analytical methods

A high performance liquid chromatograph (HPLC,Waters,Milford, MA, USA) was used to determine the butanol concentration in all samples, with a 2414 Refractive Index (RI) detector (Waters, Milford, MA, USA), a 515 HPLC pump and a 717plus autosampler. A BioRad Aminex (Biorad, Hercules, CA, USA) HPX- 87H (7.8 mm, 300 mm) column was used, with a dilute phosphoric acid solution as mobile phase, to determine the aqueous and organic phase concentrations of fructose and glucose. Sucrose concentrations were determined by an enzymatic assay, using a sucrose/D-glucose kit from R-Biopharm (Darmstadt, Germany).

Absorption was measured at 340 nm on a Tecan (MTX Lab Systems, Vienna, VA, USA) GENios, with a costar3631, flat-bottom, non-treated microtiter plate. ICP-OES was used to determine the salt concentrations in the organic phase, using a PerkinElmer (Waltham, MA, USA) Optima 5300dv; all samples were diluted 100 times and were brought to acidic conditions with 0.5 mol L−1 nitric acid. Non-volatile residues were measured gravimetrically, after overnight drying in an oven, to determine the salt content in aqueous samples. Density measurements were carried out on a vibrating-tube Anton Paar GmbH (Ostfildern, Germany), DMA48, to enable the use of mass balances (over the species and phases) to calculate the water content of each phase.

3.3. Results

All results are at 25 ◦C and 1 atm. The mass fractions for the two phase systems of butanol, water and dissolved carbohydrate are shown in Tables 1 to 3 for glucose, fructose and sucrose, respectively. Comparable trends are seen for the three carbohydrates.

Table 1. Mass fractions in liquid-liquid phase equilibria of butanol, water and glucose

Aqueous phase			Organic phase		
BuOH	glucose	H_2O	BuOH	glucose	H_2O
0.072	0.000	0.928	0.804	0.000	0.196
0.060	0.098	0.841	0.825	0.006	0.168
0.053	0.185	0.763	0.838	0.010	0.151
0.040	0.278	0.682	0.852	0.014	0.134
0.032	0.367	0.601	0.854	0.015	0.131
0.026	0.442	0.532	0.879	0.017	0.104
0.021	0.548	0.431	0.900	0.017	0.083

Table 2. Mass fractions in liquid-liquid phase equilibria of butanol, water and fructose

Aqueous phase			Organic phase		
BuOH	fructose	H_2O	BuOH	fructose	H_2O
0.061	0.083	0.856	0.783	0.004	0.213
0.052	0.166	0.782	0.800	0.008	0.192
0.042	0.250	0.707	0.795	0.009	0.196
0.034	0.355	0.611	0.823	0.013	0.163
0.027	0.442	0.531	0.833	0.013	0.155
0.025	0.481	0.495	0.841	0.013	0.146
0.022	0.502	0.476	0.831	0.013	0.156
0.012	0.559	0.429	0.844	0.013	0.142
0.017	0.601	0.382	0.841	0.014	0.145

Table 3. Mass fractions in liquid–liquid phase equilibria of butanol, water and sucrose

Aqueous phase			Organic phase		
BuOH	sucrose	H_2O	BuOH	sucrose	H_2O
0.059	0.096	0.844	0.804	0.005	0.191
0.055	0.171	0.774	0.789	0.007	0.204
0.047	0.236	0.717	0.805	0.008	0.187
0.038	0.318	0.643	0.815	0.010	0.175
0.034	0.374	0.592	0.863	0.011	0.126
0.030	0.388	0.582	0.841	0.010	0.149
0.027	0.416	0.557	0.838	0.011	0.151
0.028	0.436	0.536	0.855	0.010	0.135

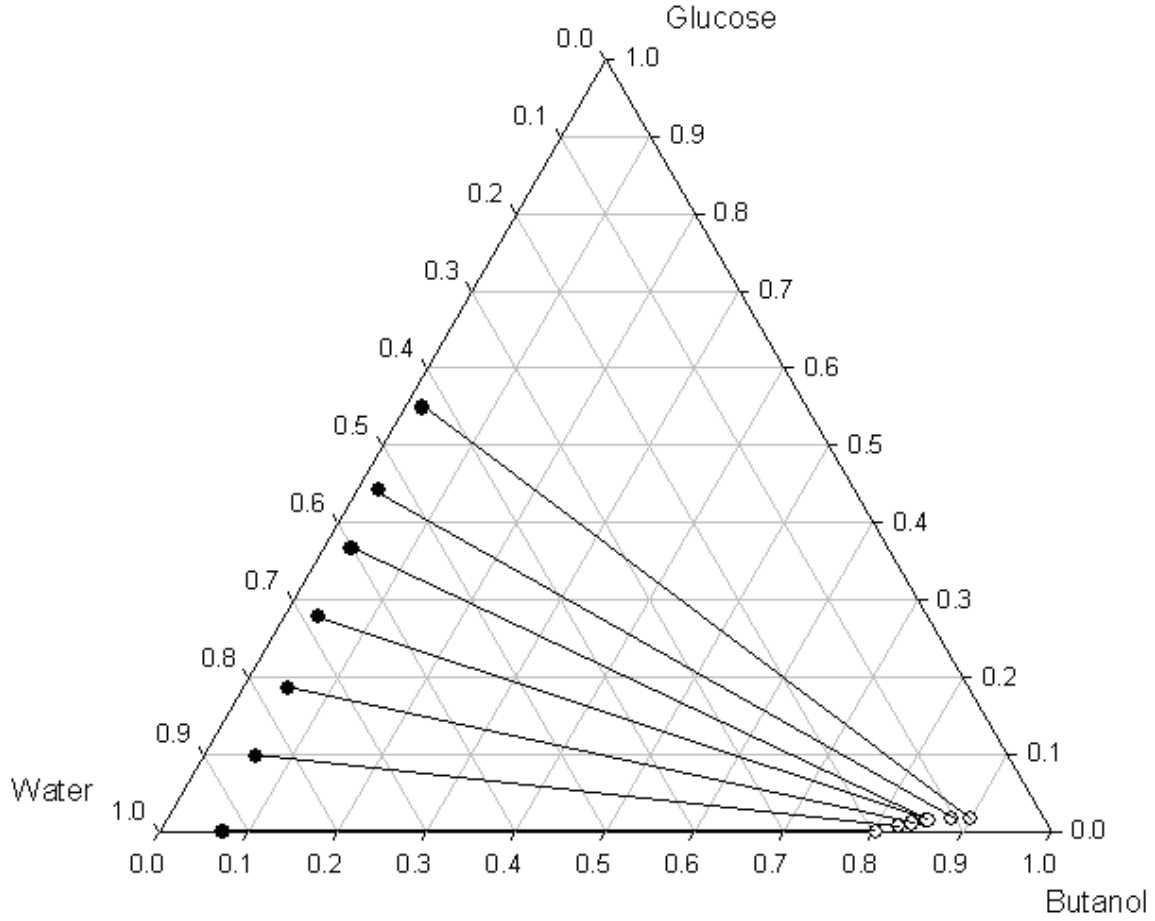

Figure 2. Ternary phase diagram for water, butanol and glucose two phase system. Compositions are given for mass fractions. Tie-lines are shown between the organic and aqueous phase equilibria points.

Table 4. Mass fractions in liquid–liquid phase equilibria of butanol, water and NaCl

Aqueous phase			Organic phase		
BuOH	NaCl	H_2O	BuOH	NaCl	H_2O
0.035	0.084	0.882	0.819	0.000	0.181
0.024	0.127	0.849	0.828	0.000	0.172
0.016	0.167	0.816	0.803	0.001	0.196
0.010	0.209	0.781	0.846	0.001	0.153
0.009	0.227	0.764	0.868	0.001	0.131
0.007	0.250	0.743	0.888	0.001	0.112
0.008	0.247	0.745	0.868	0.001	0.131
0.007	0.260	0.733	0.880	0.001	0.120

Table 5. Mass fractions in liquid–liquid phase equilibria of butanol, water and LiCl

Aqueous phase			Organic phase		
BuOH	LiCl	H_2O	BuOH	LiCl	H_2O
0.037	0.081	0.882	0.807	0.001	0.193
0.028	0.121	0.851	0.808	0.002	0.190
0.022	0.159	0.819	0.815	0.002	0.183
0.016	0.215	0.769	0.805	0.005	0.190
0.014	0.231	0.755	0.809	0.006	0.184
0.011	0.266	0.723	0.793	0.009	0.198
0.009	0.301	0.690	0.761	0.013	0.227
0.006	0.336	0.657	0.757	0.015	0.227

In the concentration range studied, addition of the carbohydrates decreases the butanol/water ratio in the aqueous phase and the water/butanol ratio in the organic phase by values in the range 30–70%. The equilibrium data for the glucose–butanol–water system are shown graphically in a ternary phase diagram (Fig. 2). The L-L mass fractions for butanol, water and salt solutions (NaCl, LiCl and $CaCl_2$, respectively), are presented in Tables 4 to 6. The salt mass of $CaCl_2$•$2H_2O$has been corrected for water of hydration. The water of hydration was added to the total amount of water present in the system for mass balance calculations when determining water content. On mass basis, the decrease of butanol solubility in water is more pronounced for the addition of salts than for the addition of the carbohydrates investigated, according to Fig. 3. The addition of $CaCl_2$ or LiCl leads to a local maximum of the organic phase butanol mass fraction of 0.89 and 0.82, respectively, at ~ 0.002 mass fraction of ternary species, according to Fig. 4. For ~ 0.001 mass fraction NaCl in the organic phase there is a local maximum that is less clear, but also at 0.89 mass fraction butanol. The addition of carbohydrates leads to an increase of butanol mass fraction in the organic phase from ~ 0.78 to ~ 0.90, (see Fig. 5).

Table 6. Mass fractions in liquid–liquid phase equilibria of butanol, water and $CaCl_2$

Aqueous phase			Organic phase		
BuOH	$CaCl_2$	H_2O	BuOH	$CaCl_2$	H_2O
0.037	0.092	0.871	0.827	0.001	0.172
0.030	0.121	0.850	0.834	0.001	0.165
0.020	0.181	0.799	0.862	0.001	0.137
0.015	0.212	0.773	0.864	0.002	0.134
0.014	0.239	0.747	0.892	0.002	0.106
0.010	0.270	0.719	0.889	0.004	0.107
0.008	0.299	0.693	0.881	0.005	0.114
0.006	0.327	0.667	0.847	0.013	0.140
0.005	0.355	0.640	0.846	0.015	0.138

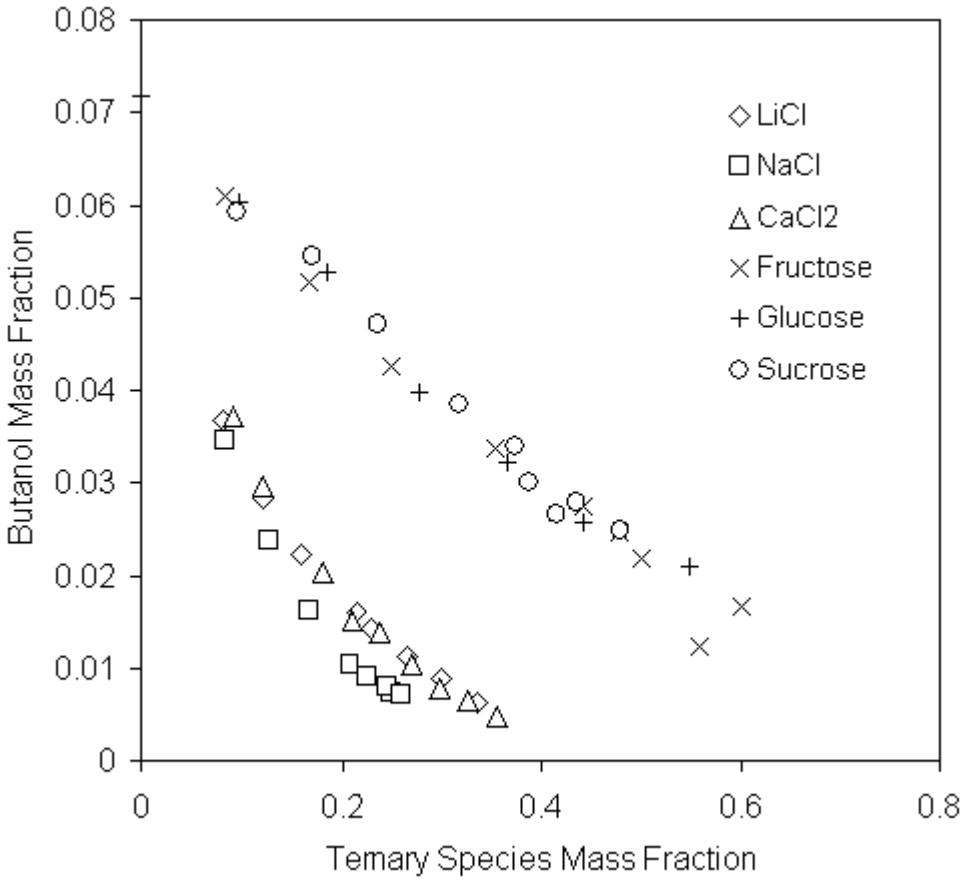

Figure 3. Butanol fraction versus salt and carbohydrate mass fraction in the aqueous phase.

3.4. Discussion

L-L based phase separation, when using a dilute aqueous butanol phase, requires accurate determination of liquid phase compositions at low concentrations, because experimental and measurement errors can significantly influence the recovery performance calculations. Butanol–water–NaCl compositions of the aqueous phase from this study agree with those in the literature.[15,16] The organic phase compositions show some stronger deviations from those in the literature. This can be explained because the organic phase compositions are more difficult to determine accurately than the aqueous compositions, in particular with respect to butanol content. Butanol and salt content of the organic phase have been calculated using species mass balances by some authors,[16] to avoid direct butanol measurements of the organic phase.

Figure 3 shows that in saturated aqueous solutions containing a desired low mass fraction of butanol, about three times more carbohydrate than salt must be present. When

minimizing the amount of ternary component necessary to perform phase separation, NaCl, LiCl and $CaCl_2$ are used preferably to glucose, fructose and sucrose.

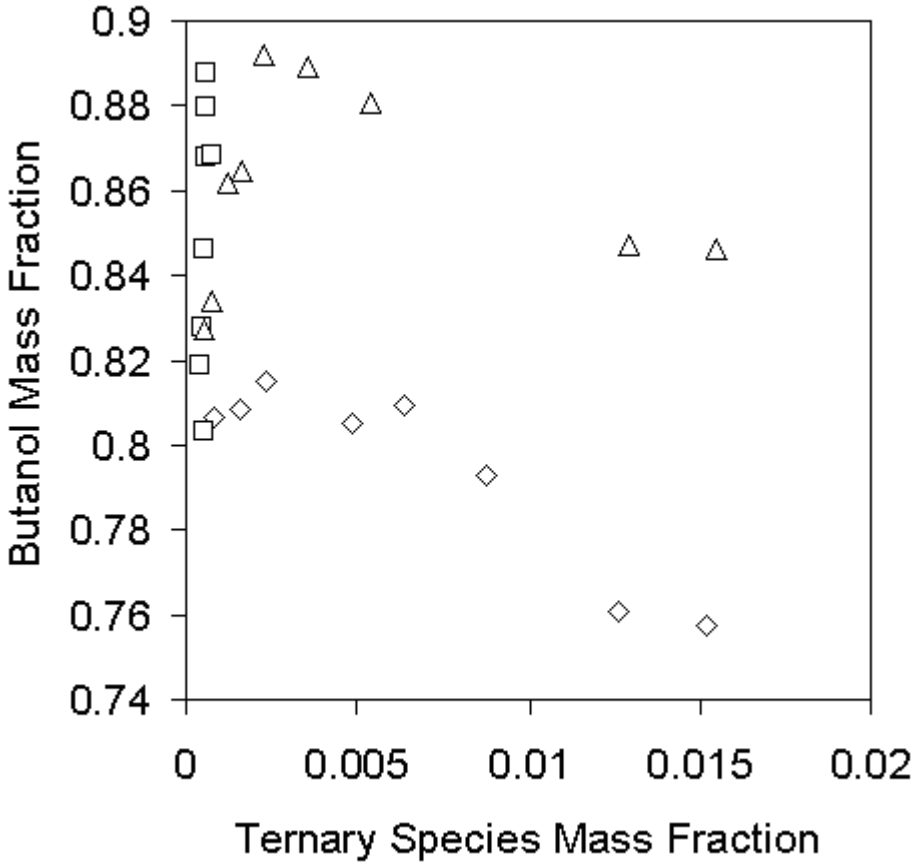

Figure 4. Butanol fraction and salt mass fraction in the organic phase (Δ, CaCl2) (◊, LiCl) (□, NaCl).

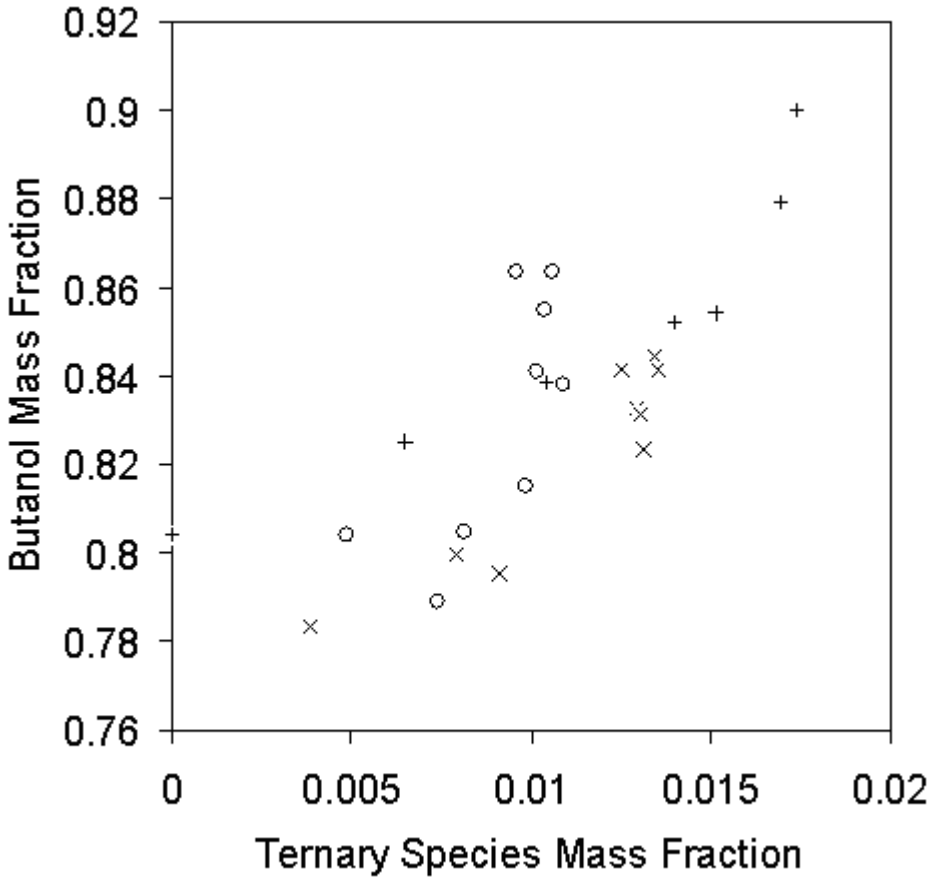

Figure 5. Butanol fraction and carbohydrate mass fraction in the organic phase (+, glucose) (×, fructose) (◦, sucrose).

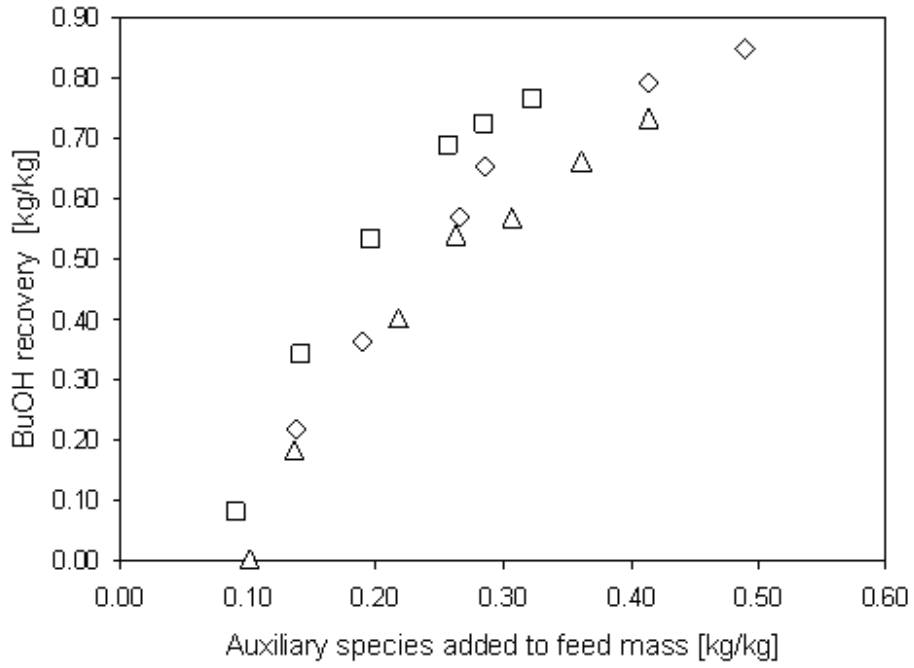

Figure 6. Butanol recovery of the feed, versus the amount of auxiliary species added to the feed (◊, LiCl) (□, NaCl) (Δ, CaCl2).

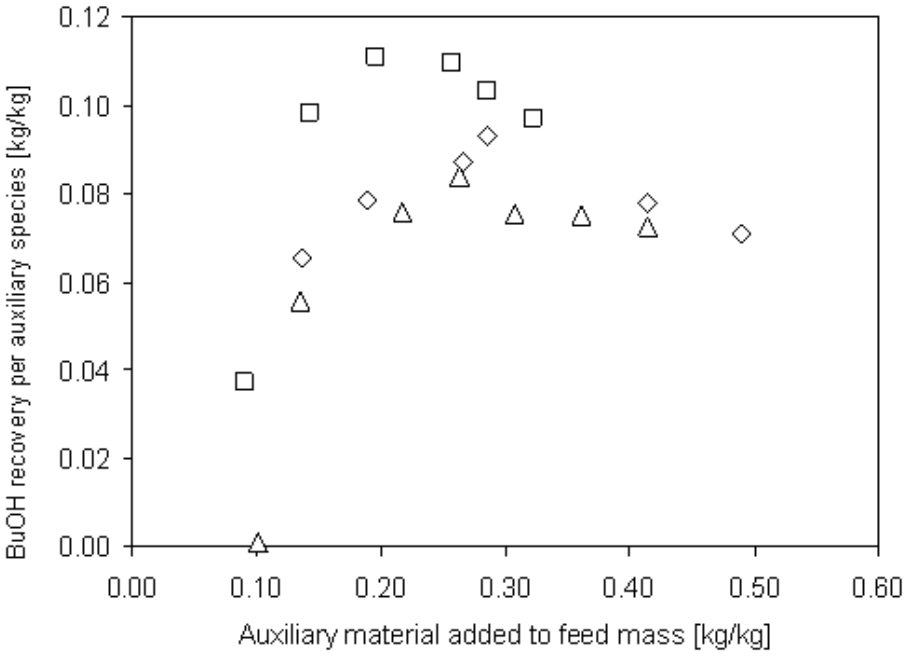

Figure 7. Butanol recovered per amount of auxiliary material added, versus the amount of auxiliary species added to feed (◊, LiCl) (□, NaCl) (Δ, CaCl2).

For salt based recovery, the selectivity of separation, as defined in Chapter 2 equation 1, when starting with a feed containing 20 g/L butanol, the maximum selectivity are 388, 208 and 412, for NaCl, LiCl and $CaCl_2$, respectively. However, at those levels most of the butanol will be in the aqueous phase and only a small, highly enriched, organic phase will be present.

Figure 6 shows the amount of ternary species necessary when performing a demixing operation on an aqueous 40.8 g kg^{-1} butanol solution. The results are obtained by calculating the masses of the species in organic and aqueous phase at equilibrium. Recovery of 70 to 80% butanol requires addition to the feed of about 400 g kg^{-1} of NaCl, LiCl or $CaCl_2$. The costs of the cheapest ternary compound (NaCl) may be ~0.15 \$ kg^{-1}, so if 10 kg NaCl is spent to produce 1 kg of butanol, which may be worth~1.8 \$ kg^{-1}, this approach is unaffordable because there will be other major costs. Besides, using such large proportions of salts in industry is inconvenient.

The capacity of the auxiliary material, which is defined here as the amount of butanol recovered per amount of auxiliary material introduced, is shown in Fig. 7 as a function of the amount of auxiliary species that has to be added to reach the new equilibrium. Similar mass ratios are found for many separation systems using an auxiliary phase.[10]

Unfortunately, the effect is less pronounced for the carbohydrates than for the salts. An important incentive for using carbohydrates in a L-L based recovery system is that the carbohydrates can be consumed upstream. This can be accomplished by recycling the remaining aqueous phase as feed for the fermentation section, see also Fig. 1. Continuous feeding might be applied to prevent that the microorganisms operate at too high sugar concentrations, and storage tanks may have to be implemented. To prevent microbial contamination, the location of the sterilization of the sugar solutions needs careful consideration.

As long as the carbohydrate consumption matches the amount required for liquid phase split, no additional input to the process is necessary. However, on a mass basis carbohydrate consumption is only about twice the butanol production, as butanol production yield on glucose has a maximum of 0.42 g g^{-1}.[17] A typical consumption of carbohydrate would thus be ~40 g kg^{-1} water, which is much lower than the amount of carbohydrate required for liquid demixing. Carbohydrates that have a stronger demixing effect would be required for this approach to be effective. A compound like sodium gluconate, which combines carbohydrate and salt properties, might behave much better, but

is too expensive to be converted into butanol. The viscosity, density and surface tension of a carbohydrate mixture complicates the process further.

Growth of microorganisms under saline conditions has been shown to be possible under severe conditions. Growth up to 4mol L^{-1} Na+ has been reported.[18] However, this has not been combined with the production of butanol or butanol-producing microorganisms. Also, sugar tolerant microorganisms like yeasts can grow on media containing up to 220 g kg^{-1} total sugar.[19] A butanol-producing metabolic pathway might be introduced into such a microorganism, but obtaining a sufficiently efficient strain would be very complicated.

As mentioned, the influence of the carbohydrates investigated on the L-L phase equilibria is less pronounced than for the salts, so the recovery is lower. When starting with 70 g kg^{-1} butanol, addition of 150 g of carbohydrate will provide an organic phase containing only 5% of the butanol present.

It might be interesting to study this approach for other alcohols that can be produced by fermentation, such as isobutanol and pentanols[20,21] to see if a stronger effect on the L-L phase behaviour can be found.

3.5. Conclusions

Demixing aqueous 1-butanol into an aqueous and butanol phase requires addition of large amounts of salts, exceeding 250 g kg^{-1} total solution, in order to recover 70% of the product, for aqueous phase containing 40 g butanol per kg. Demixing might become useful for recovery of butanol from aqueous fermentation solution if the butanol concentrations would be almost at saturation, i.e. ~74 g kg−1.

3.6 Acknowledgements

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Chapter 4: Adsorption equilibria of bio-based butanol solutions using zeolite

Abstract

1-Butanol can be produced by clostridial fermentations with acetone and ethanol as by-products. The butanol can be present up to ~20gL-1 depending on process conditions and microbial strain. The high-silica zeolite CBV28014 has been proven to adsorb butanol selective over water, while showing higher affinity for butanol than for acetone and ethanol. Multi-component acetone–butanol–ethanol (ABE) adsorption on CBV28014 has been modeled using a single site extended Langmuir adsorption model and the ideal adsorbed solution (IAS) theory model. The IAS model describes multi-component adsorption of ABE in synthetic mixtures and ABE in filtered fermentation broth by CBV28014 more accurately than the single site extended Langmuir model.

Keywords:
Bioseparations Adsorption Bioresources Biofuels Butanol Zeolite

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4.1. Introduction

Production of biofuels is currently one of the key strategies in developing a sustainable economy. In all probability a whole range of biofuels, from hydrogen and ethanol to biodiesel, will appear on the transportation fuel market in the first half of this century [1]. In comparison to ethanol, e.g., 1-butanol is an attractive biofuel candidate as it has positive fuel characteristics such as carbon chain length, volatility, polarity and combustion value. Butanol can be biologically derived from carbohydrates by means of clostridial fermentations, with acetone and ethanol as principle by-products [2]. The highest butanol concentration obtained in clostridial fermentations is around 20 g L^{-1} [3]. This limitation occurs because butanol increases the permeability of the microbial cells' membrane. Maintaining homeostasis becomes increasingly more difficult at higher butanol concentrations, leading to a complete stop of all microbiological activity. Microorganisms with a higher butanol tolerance are being discovered and developed, but elimination of the inhibiting characteristics of butanol is unlikely. Therefore, efficient recovery of butanol from dilute aqueous solutions is a prerequisite for development of a biobutanol production process. Adsorption has been shown to be a promising recovery technique [4]. Adsorption should allow separation of the butanol from the bulk aqueous fermentation broth, so that further downstream processing operations need to be performed on a relatively small amount of organic product phase only; thus providing the basis for energy efficient recovery. Hydrophobic adsorbents potentially show the desired high selectivity for butanol over water. Zeolitic hydrophobic sorbents have additional positive features such as stability, homogeneity and low heat capacity. The hydrophobicity of zeolites increases with increasing SiO2/Al2O3 ratio, with silicalite containing no alumina. Silicalite-1 (ZSM-5 structure) has been shown to adsorb low amounts of water [5]. Commercially available zeolites with high silica over alumina content have been shown to adsorb organic components selectively over water [6]. Adsorption of butanol from fermentation broth has been reported for various zeolites for binary mixtures and some multi-component systems, e.g., with ethanol and acetic acid [7,8]. However, there is a lack of data on butanol adsorption by high silica zeolites in the presence of acetone and ethanol. Also, the butanol adsorption behavior of commercial high silica zeolites from aqueous mixtures or fermentation broth is lacking. Therefore, we have determined the adsorption of butanol and water by three structurally different commercially available high-silica zeolites. The competitive adsorption of acetone, butanol and ethanol from aqueous mixtures and fermentation broth has also been measured and mathematically modeled.

4.2. Materials and methods

4.2.1. Materials

The powdered zeolites, CBV28014, CBV901 and CBV811C-300 (abbreviated to CBV811) were from Zeolyst International, Conshohocken, PA, USA. All zeolites were calcined at 600 ^{o}C for 8 h. Further details on the zeolites are shown in Table 1.

Table 1: Manufacturer's specifications of zeolite adsorbents and pore volume estimates.

Name	Zeolite type	SiO_2/Al_2O_3	Nominal cation	Surface area (m^2/g)	Estimated pore volume (cm^3/g)
CBV28014	ZSM-5 (MFI)	280	Ammonium	400	0.19
CBV811	Beta (BEA)	360	Hydrogen	620	0.24
CBV901	Y (FAU)	80	Hydrogen	700	0.50

The pore volumes of the specific zeolites listed in Table 1 are not reported in the literature. For silicalite-1 (alumina free ZSM-5, MFI framework) the pore volume is 0.19 cm^3/g [5]. The MFI framework has an intersecting channel system with both channel systems being 10-ring channels (0.53 nm × 056 nm) and (0.55 nm × 0.51 nm) [9].

Beta-type zeolites consist of faulted intergrowth of two separate 3-dimensional 12-ring pore structures. The two structures have a pore structure of channels with (0.73 nm × 0.60 nm) and (0.56 nm × 0.56 nm) dimensions [9].

The pore volume for CBV901 has been estimated at 0.24 cm^3/g [10], but this value is surprisingly low in comparison to reported volume for NaY zeolites. The FAU-type framework of the zeolite has a large void volume, ~50%, which is easily accessible. FAU-type zeolites have 12-ring pore openings and a 3-dimensional channel system (0.74 nm × 0.74 nm) [9].

1-Butanol (Acros, purity 99.5%), acetone (Merck, purity 99.9%) and ethanol (Merck, purity 99.9%) were used. Samples from two clostridial fermentations were obtained from the Wageningen University and Research Centre. One sample was directly taken from the main fermentation broth. The other sample was filtered fermentation broth and contains no microbial cells. The fermentation broth contained 2.33, 9.02, 0.25, 0.45 g L^{-1} acetone, butanol, ethanol and butyrate, respectively, according to gas chromatography (GC)

analysis. The filtrate contained 1.72, 4.84, 0.14, 0.5 g L^{-1} acetone, butanol, ethanol and butyrate. The pH of the fermentation broth and filtrate were 5.16 and 5.36, respectively.

4.2.2. Experimental methods

Experiments were carried out at temperatures in the range of 22–25 ^{o}C.

4.2.2.1. Gas phase equilibration experiments

Gas phase equilibrium experiments were performed in a closed desiccator. A known amount of the calcined zeolite was placed next to an amount of liquid butanol or water. The mass increase of the zeolite after 72 h was used to calculate its adsorption of the species involved. The adsorption of the sorbate via gas phase equilibrium was measured after 90 h. It was verified equilibrium had been reached because no deviation in adsorption was seen after 264 h.

4.2.2.2. Liquid phase equilibration experiments

Liquid phase adsorption equilibrium experiments were carried out in closed stirred vessels of 35–40 mL. The vessels contained known amounts of butanol, acetone, ethanol, water and adsorbent. Typically 0.25–1 g adsorbent was used. After 48 h equilibration, acetone, butanol and ethanol liquid phase concentrations were determined. The adsorption q of a sorbate (*i*) on a zeolite (*z*) was calculated by means of mass balance as shown in Eq. (1). Over the concentration range the density of the mixtures varies by less than 0.3%. Therefore the density of the liquid phase was considered to be constant at the density of pure water. The volume was calculated using the initial total mass of acetone, butanol, ethanol and water. Competitive water adsorption by the zeolite material could not be measured by us and was not taken into account. The error that imposes on the calculation of the amount of adsorption of the other compounds is up to 3 times smaller than the error in the adsorption due to the GC measurements. The accuracy of a calculated adsorption is a function of the ratio between the aqueous concentration and available solid zeolite material used

$$q_i = \frac{(C_{i,0} - C_i) \cdot V_0}{m_{z,0}} \qquad (1)$$

The measured adsorption isotherms were modeled using a Langmuir-type equation for single site adsorption, neglecting water adsorption. For multi-component mixtures

containing (*j*) species the Langmuir model for adsorption of component (i) is shown in Eq. (2)

$$q_i = \frac{q_{m,i} \cdot K_i \cdot C_i}{1 + \sum_j K_j \cdot C_j} \qquad (2)$$

The ideal adsorbed solution (IAS) theory has originally been developed to describe gas phase adsorption of volatile components. The IAS model has been modified to describe liquid phase adsorption [11]. IAS theory makes use of the spreading pressure (π), defined as the difference between the interfacial tension of the pure solvent–solid interface and the solution–solid interface area (A), given for a specific amount of solid phase. The following Gibbs relation (Eq. (3)) shows this relation [11]. The superscript o denotes that the system is seen as a single-solute system. IAS calculations require the single solute and solvent properties to be expressed on a molar basis

Table 2: Gas phase single-component equilibrium adsorption [g g^{-1}] at 25 ^{o}C.

Sorbent	Water	Butanol
CBV28014	0.061 ± 0.009	0.12 ± 0.011
CBV811	0.27 ± 0.015	0.34 ± 0.004
CBV901	0.47 ± 0.012	0.37 ± 0.007

$$\frac{\pi \cdot A}{R \cdot T} = \int_0^{C_i^o} \frac{q_i^o}{C_i^o} dC_i^o \qquad (3)$$

The IAS model uses the single-solute adsorption at equilibrium, q_i^o, to calculate the spreading pressure for each solute *i*. The basis of the IAS model is given by Eq. (4) and links the (total) solvent concentration in a multi-component mixture to the actual solid phase loading in a multi-component mixture. $C_i^o(\pi)$ is such, that solute *i* adsorbs singly from solution, at the same temperature and spreading pressure as the mixture does. The adsorbed species in the solid phase can be calculated for any liquid phase composition. For the complete derivation of Eq. (4) we refer to the original authors [11]

$$C_T \cdot x_i = C_i^o(\pi) \cdot z_i \qquad (4)$$

The IAS model equations and variables can be solved with the following additional relations. The fraction of species *i* in the solid phase, z_i, is calculated from the total adsorption of the solid phase q_T, and is shown in Eq. (5)

$$q_T = \sum_i \frac{z_i}{q_i^o} \qquad (5)$$

The spreading pressure for all species should be equal at equilibrium. Furthermore, the sum of each fraction equals one, as shown in Eq. (6)

$$\sum_i z_i = \sum_i x_i = 1 \qquad (6)$$

The solid phase loading can be calculated for any multi-component adsorption system, using the relations given in (5) and (6), by simultaneously solving Eqs. (3) and (4) for all components. After solving the equations, the results can be converted from molar to mass basis.

4.2.2.3. Analytical methods

Determination of the concentrations of acetone, butanol and ethanol in the aqueous phase was performed by means of GC, Thermo Electron Corporation, model GC-Focus, with an autosampler, AS3000. The GC column was Innowax 19091N-133 (30 m × 0.20 mm, with coating of 0.25 μm) from Agilent Technologies Inc. Mobile carrier gas phase through the column was helium at 6 mL/min. The temperature of the column was at 70 ^oC for 1 min and increased to 130 ^oC with a heating rate of 10 ^oC min^{-1} after which the column was kept at 130 ^oC for 5 min. A flame ionization detector was used. 1-Pentanol was added to the samples as internal standard.

4.3. Results

4.3.1. Single-component equilibration

Gas phase equilibrium experiments were carried out in triplicate to determine the equilibrium adsorption for single components. The results are shown in Table 2. Like expected, CBV28014 shows the lowest amount of adsorption of water [7]. The measured adsorption is slightly higher than the literature values, which are 0.046–0.050 g g^{-1} for adsorption of water on ZSM-5 zeolite material [5,7,12]. CBV811 and CBV901 show a high adsorption capacity for both water and butanol. The adsorptions show a positive correlation with the pore volumes of Table 1. CBV28014 seems to be far more selective than the other two zeolites when directly comparing the single-component adsorption capacities, with a butanol capacity of 0.11 g g^{-1} to a water capacity of 0.06 g g^{-1}.

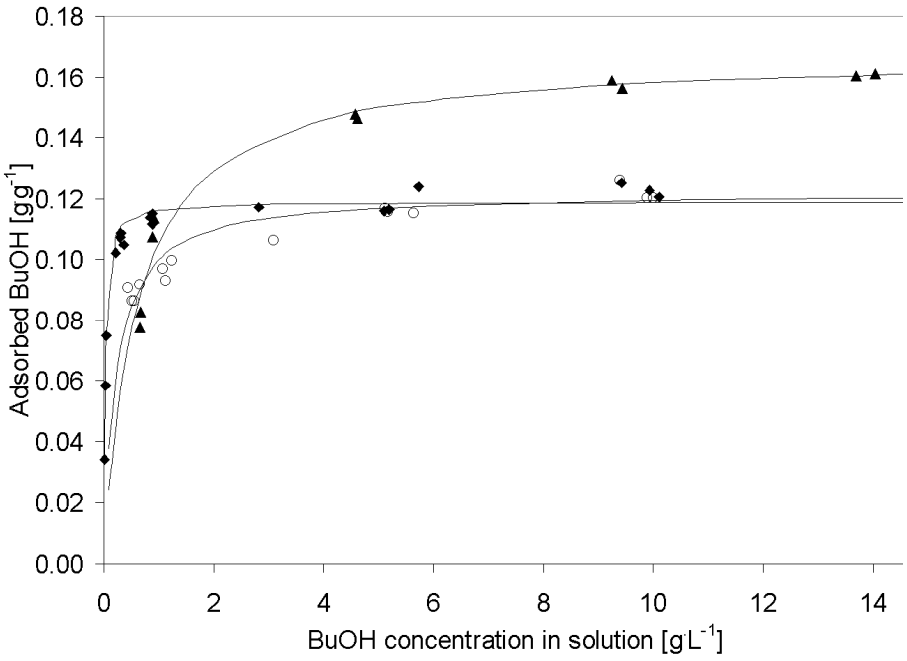

Fig. 1. Experimental adsorption of butanol on CBV28014 (♦), CBV901 (▲) and CBV811 (○) at 25 °C, with full lines for the Langmuir model.

4.3.2. Liquid phase equilibration of binary mixtures

The adsorption of butanol from aqueous solution is shown in Fig. 1. CBV28014 has the highest affinity for butanol at low concentrations. CBV811 and CBV28014 have similar butanol adsorption over a large concentration range, and a similar maximum adsorption

capacity, but CBV901 shows an approximate 25% higher capacity for butanol, 0.16 g g^{-1} at butanol concentrations exceeding 7g L^{-1}, maybe due to its higher internal volume. For CBV811 and CBV901 the observed adsorptions are far below the single-component butanol adsorptions of Table 2. This suggests that severe competition by water may occur. In contrast, for CBV28014 the single-component butanol adsorption is already reached with ~1g L^{-1} butanol in water, suggesting that competition by water does not play an important role for this case. Therefore, CBV28014 is used subsequently.

For CBV28014, comparison of adsorption isotherms of different solutes shows a decrease in affinity for the sorbate with an increase in polarity from the sorbate, from butanol to acetone to ethanol, see Fig. 2. This is in line with the hydrophobicity of the zeolite and might facilitate consecutive desorption in a column operation [6,13]. The behavior of butyric acid is not in line with this. Butyric acid is slightly more polar than butanol but shows a higher affinity. Specific interactions between butyric acid and the zeolite might play a role.

A two parameter Langmuir equation was fitted to the single solute isotherms data using the non-linear Marquardt method to a two parameter Langmuir isotherm. For butyric acid the data were transformed to a linear relationship [1/q vs. 1/C] and fitted by the least square method. Figs. 1 and 2 show that acceptable fits were obtained. The fitted Langmuir parameters in Table 3 indicate that for CBV28014 the affinities are widely different for the different solutes, but the maximum amounts of adsorbed species are in a relative narrow range.

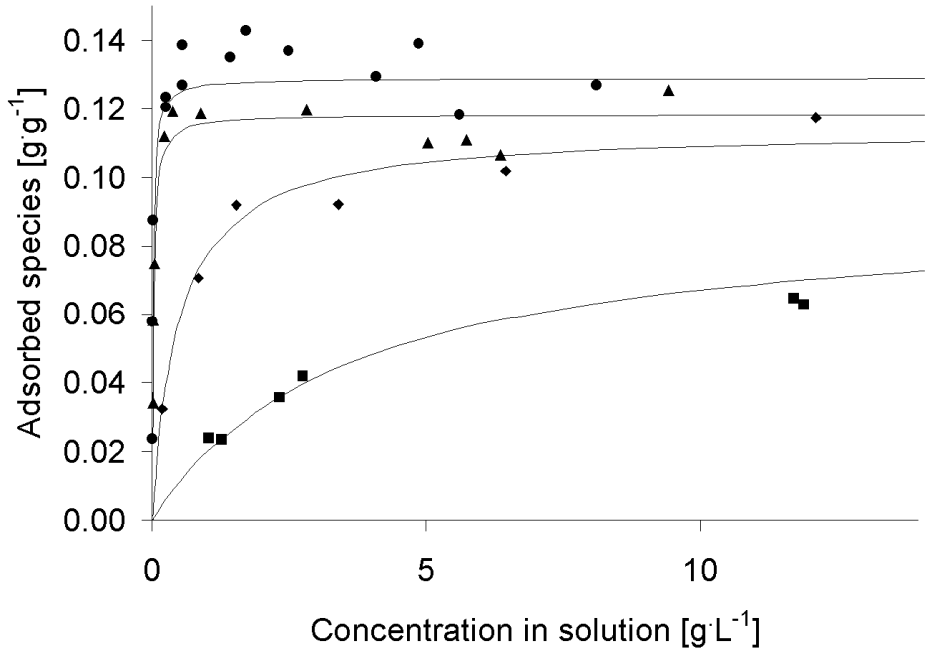

Fig. 2. Experimental adsorption isotherms at 25 .C for acetone (♦), butanol (▲), butyric acid (●) and ethanol (■. on CBV28014, with full lines for the Langmuir model.

4.3.3. Liquid phase equilibration of ternary and higher mixtures

A limited number of equilibrium experiments with CBV28014 and aqueous mixtures of acetone, butanol and ethanol was performed in relevant concentration ranges, in order to be able to describe competitive adsorption. Table 4 shows that ethanol adsorption is very low at these conditions, <0.003 g g^{-1}, which is within the measuring sensitivity of the experimental set-up. The acetone data, when compared to Fig. 2, clearly indicate that competition by butanol occurs.

Table 3: Langmuir parameters.

Zeolite	Adsorbate	K (L g^{-1})	q_m (g g^{-1})
CBV901	Butanol	3.14 ± 0.94	0.168 ± 3.6 × 10-3
CBV811	Butanol	1.68 ± 0.18	0.126 ± 7.1 × 10-3
CBV28014	Butanol	42.8 ± 6.6	0.118 ± 2.6 × 10-3
CBV28014	Acetone	1.65 ± 0.42	0.121 ± 5.9 × 10-3
CBV28014	Ethanol	0.34 ± 0.11	0.093 ± 7.2 × 10-3
CBV28014	Butyric acid	139 ± 30	0.130 ± 2.5 × 10-3

Table 4: Measured equilibrium adsorption of synthetic mixtures of acetone, ethanol and butanol by CBV28014 at 22–25 ^{o}C.

Aqueous concentration (g L^{-1})			Adsorbed species (g g^{-1})		
Acetone	Ethanol	Butanol	Acetone	Ethanol	Butanol
1.26	0.98	0.37	0.021	0.003	0.088
1.04	1.50	4.96	0.002	0.002	0.116
5.41	0.94	0.40	0.052	0.001	0.059
5.25	1.04	5.65	0.015	0.000	0.107
1.30	0.99	0.44	0.020	0.002	0.090
1.03	1.50	5.01	0.003	0.001	0.117
5.31	0.92	0.39	0.057	0.002	0.059
5.18	1.03	5.58	0.019	0.001	0.111

Table 5: Measured equilibrium adsorption of acetone, ethanol, butyric acid and butanol from filtered medium (first two entries) and fermentation broth (last two entries) by CBV28014. Ethanol adsorption is too low for accurate determination at 22–25^{o}C.

Dissolved concentration (g L^{-1})				Adsorbed species (g g^{-1})			
Acetone	Ethanol	Butanol	Butyric acid	Acetone	Ethanol	Butanol	Butyric acid
1.59	0.15	2.73	0.36	0.006	-0.0000921[a]	0.098	0.007
1.61	0.14	2.70	0.36	0.005	0.0000367	0.099	0.007
2.24	0.24	6.57	0.36	0.004	0.000193	0.117	0.004
2.22	0.25	6.80	0.37	0.005	-0.000079[a]	0.100	0.004

[a] Negative values due to too small aqueous concentration differences to calculate adsorption.

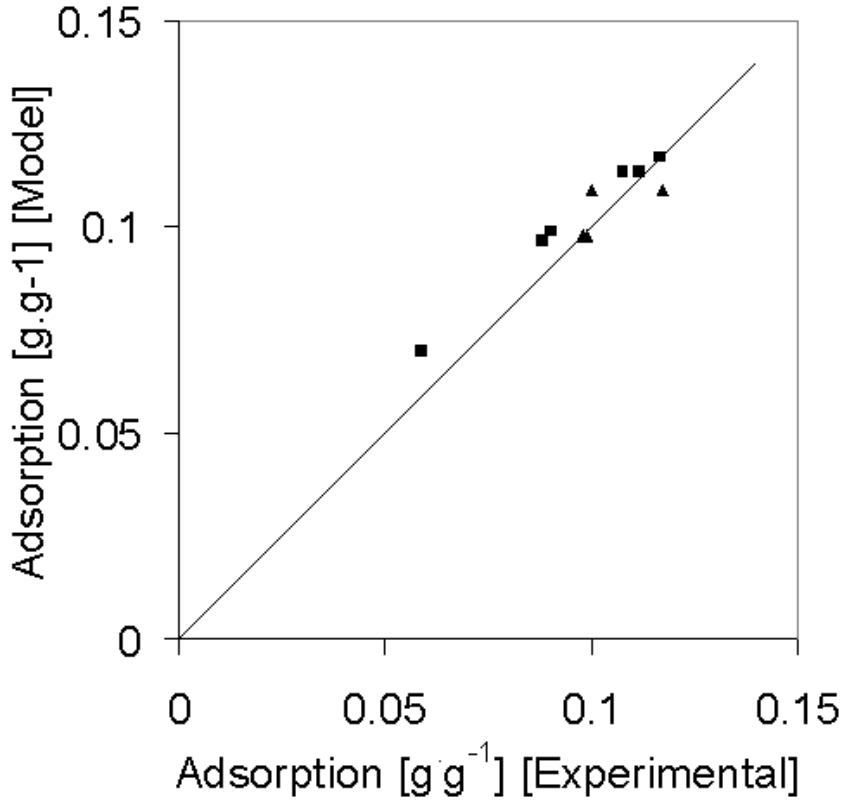

Fig. 3. Parity plot multi-component Langmuir model predictions vs. experimental butanol adsorption. (■) Butanol adsorption from synthetic ABE mixture by CBV28014. Butanol (▲) adsorption from fermentation broth as shown in Table 5.

Competitive adsorption also occurred when using fermentation broth and filtered fermentation broth (Table 5). In this case, butyric acid was also included.

Adsorption of butanol and acetone and butyric acid from fermentation broth and cell free filtered broth behave similarly. Butyric acid adsorption at these conditions is approximately 0.005 g g^{-1}. The results indicate that butyric acid displaces butanol. To show this more clearly, using the parameters in Table 3, multi-component adsorption of acetone, butanol, butyric acid and ethanol was predicted by the extended Langmuir model.

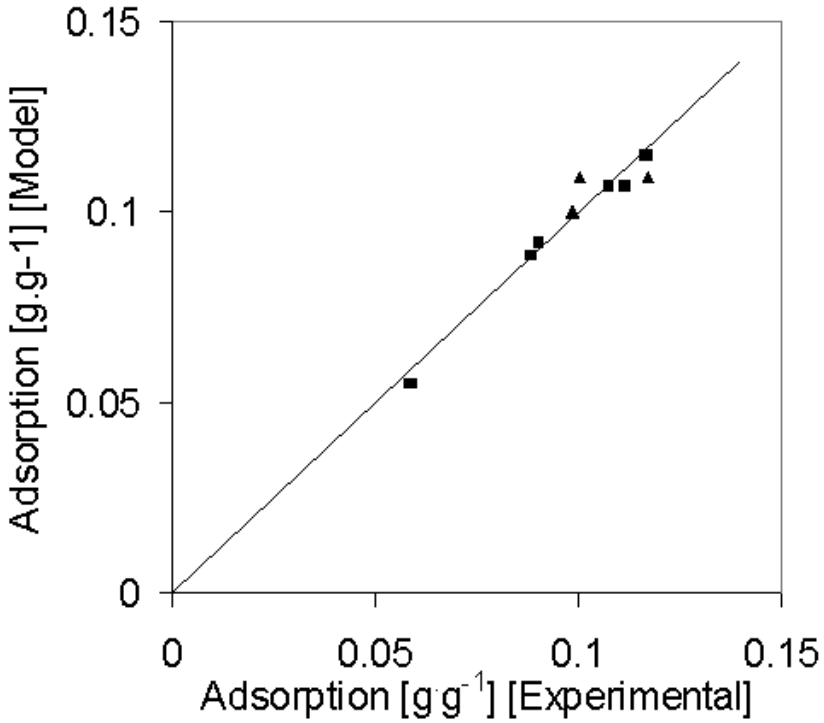

Fig. 4. Parity plot IAS model predictions vs. experimental butanol adsorption. (■) Butanol adsorption from synthetic ABE mixture by CBV28014. Butanol (▲) adsorption from fermentation broth as shown in Table 5.

Fig. 3 shows the comparison of extended Langmuir model predictions with the experimental data from Tables 4 and 5. The highest deviations from the experimental results occur at low concentrations and corresponding adsorption equilibria. The IAS model results are shown in Fig. 4. The IAS model predictions are closer to the experimental data than the simple extended Langmuir model. The maximum adsorption capacity for each of the individual species on the zeolites differs, which can more adequately be handled by the IAS model. The average difference between the adsorption predicted by both models and experimental adsorption is 0.0032 and 0.0054 g g^{-1}, respectively.

4.3.4. Qualitative description of adsorption equilibria*.

The octanol/water partitioning (see table 6) follows the trend butanol>butyric acid>acetone>ethanol. This is mostly in line with the affinity following from the adsorption isotherms (see figure 2). The Hildebrand and Hansen parameters show the affinity of the specific compound for water to follow ethanol>butanol>acetone. Acetone and butanol behave off key. Clearly not only compound and its interaction with water play a role, but also the hydrophobicity of the sorbent. This is observed behavior, as e.g. [Ref 15]. Using a

Hildebrand/Hansen parameter will not provide a full picture and also hydrophobicity does have a significant effect on the difference between water and solvent adsorption.

Table 6: Solubility data sorbates

Compound	Log $P_{o/w}$ [14]	Hildebrand Parameter [$Pa^{0.5}$] [14]	Hansen Parameter [15]
Butyric acid	0.79		
Butanol	0.84	23.05	28.5
Acetone	-0.24	19.7	35.8
Ethanol	-0.30	26.4	24.1

Table 7: Polarity scales for sorbents

Compound	Type	Si/Al ratio	Hydrophobicity Index (c)-Hexane/water	Hydrophobicity Index [18] Toluene/water
CBV901	ZSM-5	80	20 [ref 17]	0-19[a]
CBV28014	FAU	280	23 [ref 16]	15.2[b]

[a]Function of Si/Al ratio. Specific data not available, [b] 1-silicalite

The hydrophobicity index for the used zeolites, see Table 7, are, if data is not directly available for the specific zeolite, related to the Zsm-5 or Y-type structure with comparable Si/Al content. The HI indices are approximately similar for CBV901 and CBV28014 as both are high silica zeolites. The differences in adsorptive behavior are thus not only due to direct surface interactions. The difference in structure plays a role [Ref 19]., namely a micropore ZSM-5 type material (CBV28014) and micropore/mesopore containing Y-type (CBV901), leading to an overall increase in water content. This difference in structure changes the overall adsorptive properties of the silica crystals and results in the selectivity of recovery for CBV28014 and CBV901 to be far more favorable for CBV28014, namely 274 to only 12.

4.4. Conclusions

CBV901 has the highest adsorption capacity for butanol of the three zeolites investigated, but CBV28014 shows the highest affinity for butanol at aqueous butanol concentrations below 2 g L^{-1}. The competitive adsorption on CBV28014 showed a correlation with hydrophobicity of the sorbate with the highest affinity for butanol > acetone > ethanol. Single solute isotherms were successfully used for predicting multi-component adsorption. The ideal adsorbed solution model predicts the competitive adsorption of butanol, acetone and ethanol on CBV28014 more accurately than extended single site Langmuir model. Adsorption from fermentative mixtures was also predicted successfully but butyric acid needed to be taken into account as additional minor component.

4.5. Acknowledgments

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4.6. References

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4.7. Nomenclature

A surface area of adsorbent (m^2 kg^{-1})

C liquid phase concentration (kg m^{-3})

C^o single solute equilibrium liquid phase concentration (mol m^{-3})

K Langmuir constant (m^3 kg^{-1})

m mass (kg)

q mass equilibrium solid phase concentration (kg kg^{-1})

q^o single solute equilibrium concentration in solid phase (mol kg^{-1})

q_m maximum adsorption capacity (kg kg^{-1})

R gas constant (J $mol^{-1}K^{-1}$)

T temperature (K)

V liquid volume (m^3)

x solvent free liquid phase mole fraction (–)

z adsorbed phase mole fraction (–)

Greek symbol

π spreading pressure (N m^{-1})

Subscripts

i sorbate species i

j all sorbate species

z sorbent

0 initial condition

T total

Superscript

o single-solute

Chapter 5: Desorption of butanol from zeolite material

Abstract

Sorption-based recovery of 1-butanol from aqueous solution has been investigated focusing on the recovery of butanol by desorption from the sorbate. Sorption isotherm, thermogravimetric adsorption and differential scanning calorimetry experiments have been used to determine the desorption behavior of butanol and water for two high-silica zeolite adsorbents, CBV901 and CBV28014.

Carbon dioxide can be used as displacement agent for butanol recovery, with the butanol-carbon dioxide equilibria determining the carbon dioxide mass requirement for such a process.

For CBV901 desorption requires 2440 J per g of water and 1080 J per g of butanol. The heat effects for CBV28014 are 2730 J/g (water) and 1160 J/g (butanol). A significant difference in water content can be seen between both zeolite materials, with CBV28014 showing the least amount of water adsorption. The desorption rate of butanol from CBV28014 is significantly slower than from CBV901.

A catalytic reaction, most probably dehydration, occurs around 200 ^{o}C during temperature programmed desorption of butanol from CBV28014.

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5.1. Introduction

Microbial butanol production from renewable feedstocks has been receiving continuous attention, because butanol has favorable fuel properties [1]. The microbial production of 1-butanol will provide aqueous fermentation broth with approximately 10 to 20 g/L butanol or total organic solvents [2,3,4]. Distillation is generally applied for product recovery, but this is relatively energy-intensive [5,6]. Alternative recovery techniques are much less developed. Frequently proposed alternative downstream processing methods are adsorptive, extractive and pervaporation based recovery techniques. For adsorptive recovery of butanol, high silica zeolites are selective and stable adsorbing agents [7,8,9,10]. Desorption of butanol from the adsorbed zeolite phase is less frequently mentioned, but this is a crucial process operation and needs to be taken into account when designing a complete recovery process.

Desorption of adsorbed species from a sorbent can be done by 1) pressure swing operation, 2) purge gas stripping, 3) displacement desorption, and 4) thermal swing operation [11]. Recovery by pressure swing operation is impractical, due to the very low vapor pressure of butanol at ambient temperature. Recovery by purge gas stripping will require, also due to the low vapor pressure, extreme volumes of purge gas. Therefore this paper focuses on displacement desorption and thermal swing operation for desorption of butanol from high silica zeolite.

Regeneration of an adsorbent using thermal swing operation is probably the most used regeneration technique [11]. Thermal swing operations use the shift in adsorption behavior as a function of temperature. Displacement of butanol from zeolite can occur if a newly introduced displacement agent is adsorbed by the sorbent. After displacement, regeneration of the sorbent phase by removal of the displacement agent is necessary if the sorbent is to be reused. To allow relatively easy removal of the displacement agent from the sorbent, in our opinion gaseous compounds at elevated pressures should be used. Fermentative production of butanol will involve carbon dioxide [12], so this compound might be useful if it shows sufficient adsorptive behavior.

Essential data necessary for the design of adsorptive recovery of butanol from fermentation broth using high silica adsorbents will be determined.

5.2. Materials and Methods

5.2.1. Materials and sample preparations

1-Butanol (BuOH) was from Acros (purity 99.5 %). The powdered zeolites, CBV28014 (ZSM-5-Type) and CBV901 were from Zeolyst International, USA. All zeolites were calcined at 600 ^{o}C for 8 h. For further details on the zeolites see table 1. The structure of MFI and FAU crystals are described in literature [13,14].

Table 1: Manufacturer's specifications of zeolite adsorbents and pore volume estimates.

Name	Zeolite Type	SiO_2/Al_2O_3	Nominal cation	Surface area m^2/g	Estimated Pore volume cm^3/g
CBV28014	ZSM-5 (MFI)	280	ammonium	400	0.19
CBV901	Y (FAU)	80	hydrogen	700	0.50

5.2.2. CO_2 and butanol competition

The adsorption of butanol on the investigated zeolites in the presence of dissolved carbon dioxide was measured using a setup and experimental method similar to one previously described [15]. The aqueous butanol concentration was determined by gas chromatography.

5.2.3. Gaseous butanol and water adsorption isotherm determination

The gas phase equilibria between butanol, water and zeolite (CBV901 and CBV28014) were determined by gas phase pressure measurements in an enclosed temperature controlled system (1,270 ml pressure vessel combined with a WIKA, EN 837-1 manometer). The loading of adsorbed species was determined by following the pressure changes in the system at various amounts of sorbate introduced into the system. The liquid phase butanol or water was injected into the system, in portions of approximately 0.1 to 0.15 gram per injection, up to a total amount of around 2.5 g. The amount of adsorbed species was calculated from the difference between the observed pressure and the pressure the total volatile species injected should have reached at that temperature if no adsorption had occurred. In the loading calculation the ideal gas law was used to convert pressure into

mole of gas. Total volatile pressure in the system was always below the saturated vapor pressure, to make sure no internal condensation could occur.

5.2.4. Differential scanning calorimetry (DSC)

Temperature programmed differential scanning calorimetry (Perkin-Elmer DSC-7) was used to determine endothermic heat flow to zeolite and zeolite loaded samples during the temperature change. This allowed the determination of the heat capacity of the zeolite material and the heat uptake of adsorbed water or butanol when desorbing from the zeolite sorbent.

Sample and reference containers were aluminum cups. For each DSC desorption run, the heat uptake of an aluminum sample cup was measured and subtracted from the values of the subsequent desorption run to obtain the net heat effect of the sample. The sample was continuously flushed with nitrogen gas at 20 ml/min to remove desorbed components. The DSC analyses were carried out using a programmed temperature profile, which applied a heating rate of 10 ^{o}C/min, starting at 25 ^{o}C. By integration of the heat flow over time it is possible to calculate heat effects per mass amount of sample. Integration of the DSC endothermic heat flow allows calculation of the heat of desorption of the volatile species, and also allows the calculation of the heat capacity of the zeolite materials. Similar heating profiles have been used to determine desorption of volatile organics from micropore material and activated carbon [16,17]. Initial isothermal steps of 5 min were programmed to allow baseline correction. The samples of CBV901 and CBV28014 were loaded with butanol, water or a mixture thereof by gas phase equilibration in a temperature controlled vessel (25 ^{o}C) in the presence of liquid volatile species during 48 h. No difference in adsorbed mass on the zeolite could be seen after 48 h equilibration compared to 72 and 168 h of equilibration. Liquids were pure water, pure butanol or 20 g/L butanol in water. An amount of the loaded sorbent was then placed in an aluminum cup, after which a desorption run was carried out. The mass of the sample with the cup was measured before and after the run. The amount of sample material was usually between 10 and 15 mg total loaded zeolite sample, including approximately 1 to 2 mg volatile component.

5.2.5. Thermogravimetric adsorption (TGA)

Thermogravimetric adsorption (Perkin-Elmer), was applied to sorbate-containing zeolite. During the measurement the mass of a specific sample was monitored. The TGA analyses were carried out using the same temperature program as in the DSC experiments (a heating rate of 10 ^{o}C/min, starting at 25 ^{o}C). Also for the TGA experiments the samples of CBV901 and CBV28014 (approximately 10 to 15 mg total sample mass) had been equilibrated with butanol, water or a butanol-water mixture, following the same method as described in the DSC section. The loaded sorbent was then placed in an aluminum cup, after which a desorption run was carried out. TGA was performed at atmospheric pressure, using nitrogen or air, 80 ml/min, as purge gas.

5.3. Results and discussion

5.3.1. Recovery by displacement

To be able to evaluate the potential of CO_2 as butanol displacement agent, the isotherm of butanol in the presence of carbon dioxide was measured for CBV28014 (figure 1). A decrease of butanol adsorption on CBV28014 is observed with increasing CO_2 pressure. The difference between the data for 0 and 1 bar (CO_2-saturated aqueous solutions containing butanol) indicates that during adsorption the solute CO_2 competes with butanol and diminishes the total amount of butanol adsorption. Previously, this competition had not yet been taken into account [9], but it can play a role especially as anaerobic fermentation broths will usually be saturated by 1 bar CO_2, corresponding to ~ 1.5 g/L in aqueous solution. In figure 4, at 9 bar CO_2 the aqueous butanol concentration is still relatively high, indicating that this pressure is relatively low for using it to efficiently desorb butanol. Our equipment did not allow higher pressures to be evaluated. Our results are in line with those of [18], who preferred 1-butanol to CO_2 for desorption of succinic acid from CBV28014. Equilibria between 1-butanol and CO_2 at elevated pressure show a low butanol content. For CO_2-based displacement at elevated pressure the CO_2 the gas phase capacity for butanol then determines to the economic effectiveness as it dictates the CO_2 flow requirements. Increase of pressure will allow larger butanol fractions at pressures over 60 bar [19], as will an increase in temperature, at 333 K the fraction butanol is 3 to 4 times larger than at 303 K [20]. As 1-butanol is only of the possible C4 alcohols, it should be noted that for 2-butanol the alcohol-CO_2 gas phase equilibria are significantly more favorable, when compared to 1- butanol and CO_2, making this concept more feasible for this product.

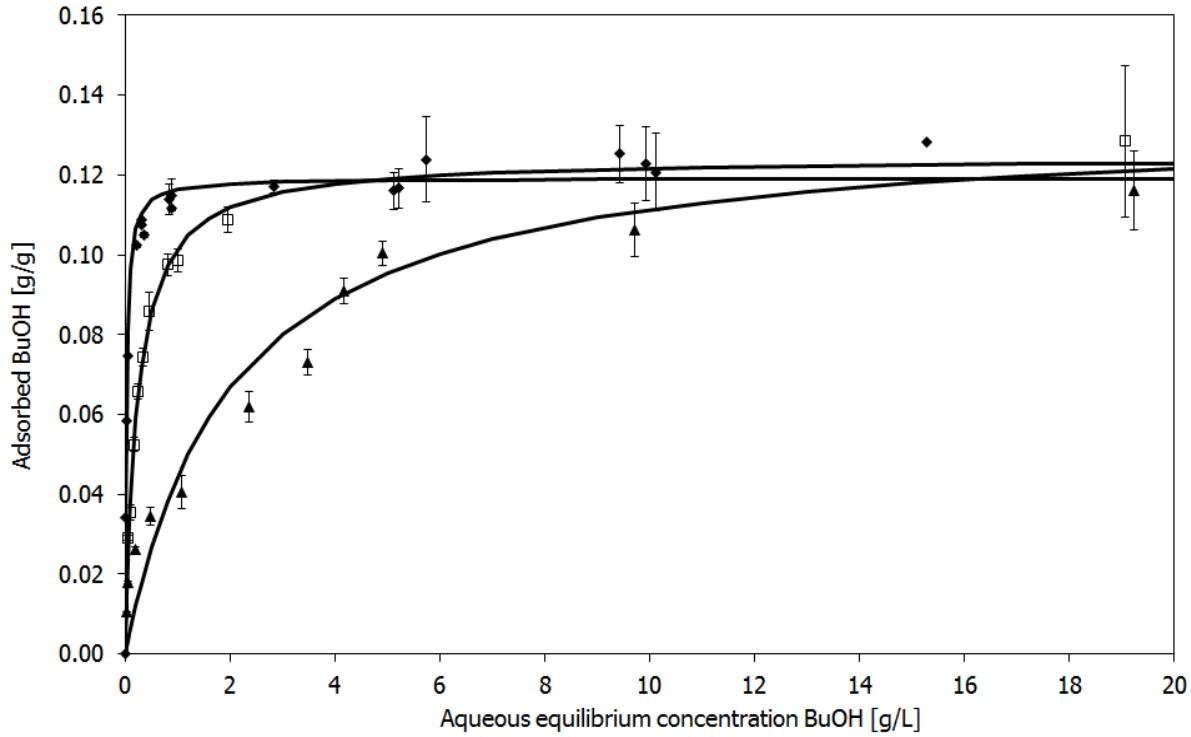

Figure 1: Competitive adsorption of butanol from aqueous solution at 25 °C for CBV28014 under no (♦), 1 bar (□), and 9 bar (▲) CO_2 -gas phase pressure. Lines have been added to guide the eye.

5.3.2. Recovery by thermal swing

At 25°C, CBV901 can adsorb butanol up to 0.16 g/g and CBV28014 up to 0.12 g/g [9]. Adsorption isotherms of butanol from butanol vapor at elevated temperature are shown in figure 2. At 110 °C the equilibrium loading of butanol is significantly lower on CBV901 than on CBV28014. The loading on CBV901 was reduced much further by increasing the temperature to 150 °C. No data are given at 150 °C for CBV28014 because the observed pressures were larger than expected on basis of the amount of butanol introduced in the system. This suggests a catalytic reaction to occur producing additional gaseous molecules.

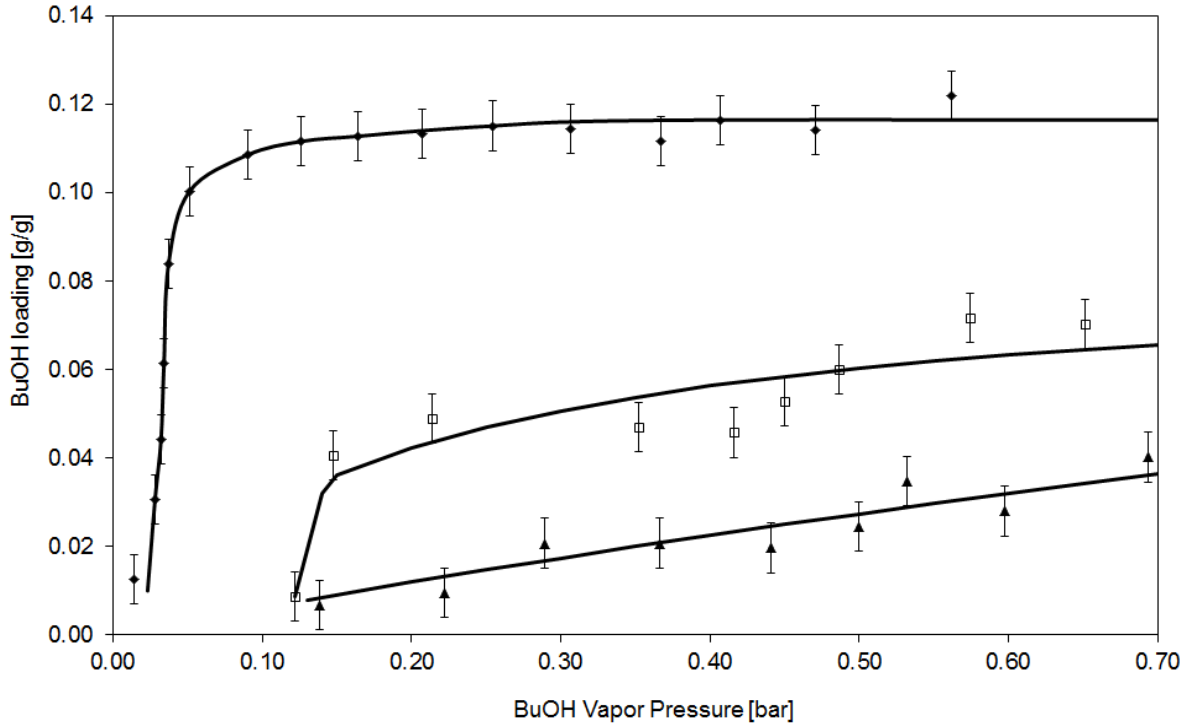

Figure 2: Butanol equilibrium loading on zeolite as function of butanol vapor pressure for CBV28014 at 110 °C (♦) and for CBV901 at 110 °C (□) and 150 °C (▲). Lines have been added to guide the eye.

5.3.3. Desorption rates

The desorption rates of butanol and a butanol and water mixture from CBV901 were followed using TGA. Figures 3 and 4 are a function of temperature. The second abscissa shows the time progression of the experiment. The observed sample mass has been normalized to the amount of adsorbent present at the end of the experiment, assuming all sorbate had been desorbed.

TGA desorption profiles normalized on final mass are shown in figure 3. The two top TGA profiles show a significant amount of water to be present in comparison to pure butanol adsorption. The large slope of the two top samples from 400 to 800 s indicates water is removed at that stage. As all curves start behaving more similar after 800 s, it is assumed that the remaining butanol is being removed in this stage.

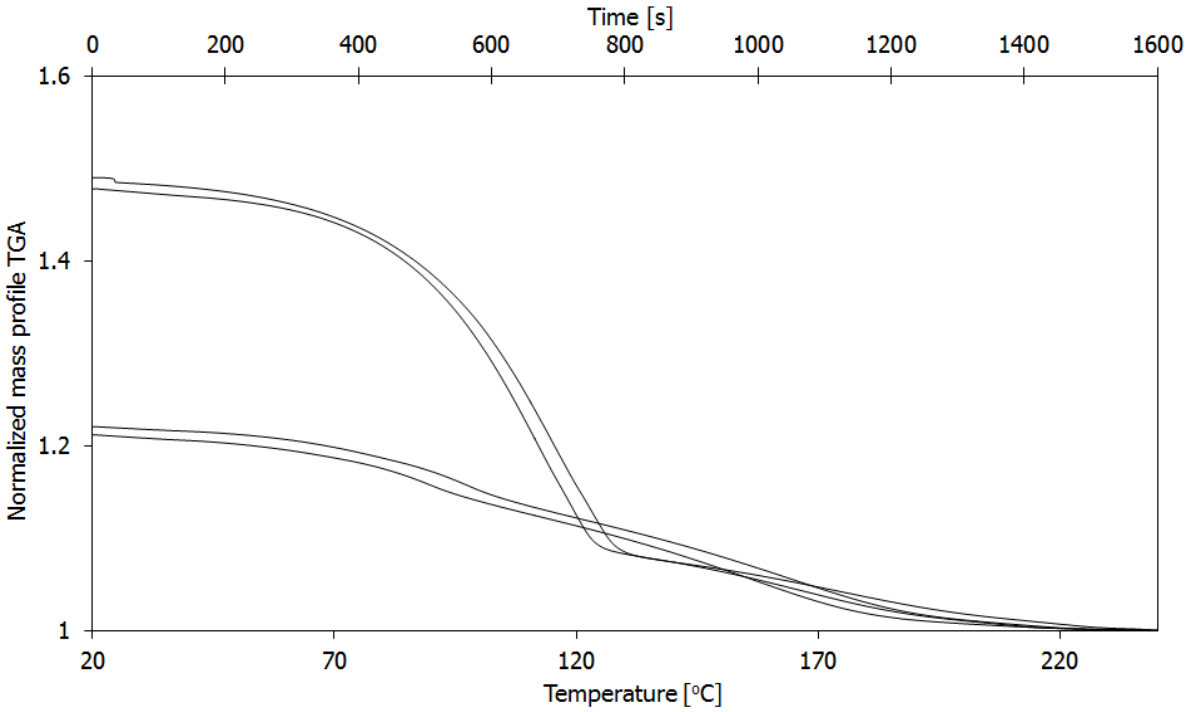

Figure 3: Duplicates of TGA profile of the desorption of butanol (bottom lines) and butanol/water mixture (top lines) from CBV901. Reading from top to bottom, the initial mass of volatiles present in the samples were 6.91, 5.87, 2.50 and 1.55 mg. See Materials and Methods for further sample preparation information.

Similar to the experiments on CBV901 the desorption of water, butanol and a mixture of water and butanol from CBV28014 was determined. In figure 4 the normalized mass profile can be seen. CBV28014 has a MFI channel structure and is very hydrophobic in nature. This effect is seen by the additional water mass profile in figure 4. The overall water content in the sample is very low, when the zeolite has been equilibrated with water. The difference between butanol and butanol-water is thus also very small, as water is not present in significant quantity, this opposed to CBV901. CBV901 showed significant water uptake to occur [9]. Complete desorption of butanol from CBV28014 can be achieved at temperatures below 200 ^{o}C. At ~ 200 ^{o}C a pronounced change in the slope of butanol-containing samples can be seen, indicating a change in mechanism. This will be explained in the later section when also looking at its heat effect.

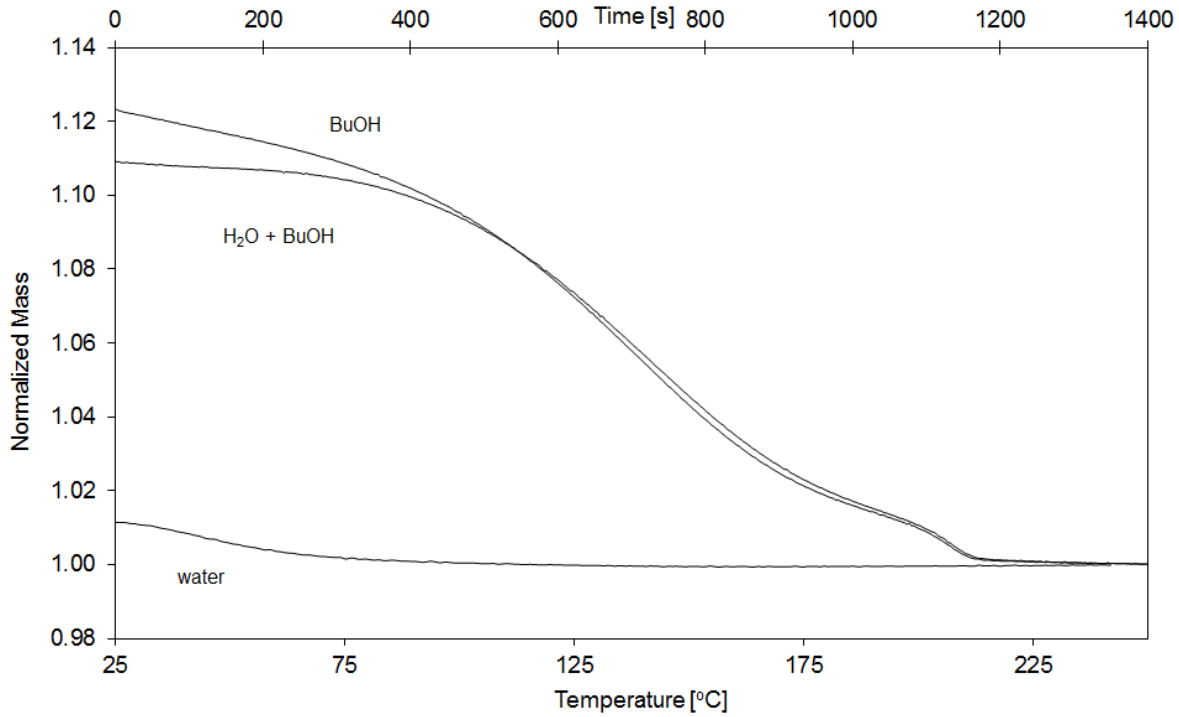

Figure 4: Desorption profile of CBV28014 with three different loadings: butanol, butanol/water and water. Reading from top to bottom the initial amount of volatiles present were 2.5, 2.5 and 0.25 mg, respectively.

The mass transfer of butanol and water from the sorbent to the vapor phase was modeled using a linear driving force relation, in order to obtain an estimate for the overall mass transfer coefficient (k_o) during the desorption runs:

$$-\frac{\mathrm{d}q}{\mathrm{d}t} = k_{o_{BuOH}^{zeolite}} \cdot (q - q^*)$$

A relatively large flow of inert stripping gas was applied, so that the volatile species concentration in the gas phase could be assumed to be close to zero. This implies the equilibrium loading of the sorbate (q^*) to be approximately zero, $q^* = 0$. The current actual loading of the zeolite (q) is seen as an average actual loading (q) of the zeolite. In general for a gaseous system the overall mass transfer coefficient for a particle is determined by the resistance in a gaseous film (external mass transfer resistance), the resistance in the internal structure of the particle (pore diffusion), and the surface diffusion resistance of the sorbates to the specific adsorption sites e.g. [21]. Due to the high temperature and purge gas flow the external mass transfer resistance is probably not limiting. The observed overall mass transfer is then mainly influenced by particle size and shape and by internal diffusion through the pore structure of the zeolite. Structural differences between the zeolite particles

show the pore structure to be more constrained for MFI than for FAU types. Therefore a stronger mass transfer limitation and lower mass transfer coefficient is expected for CBV28014.

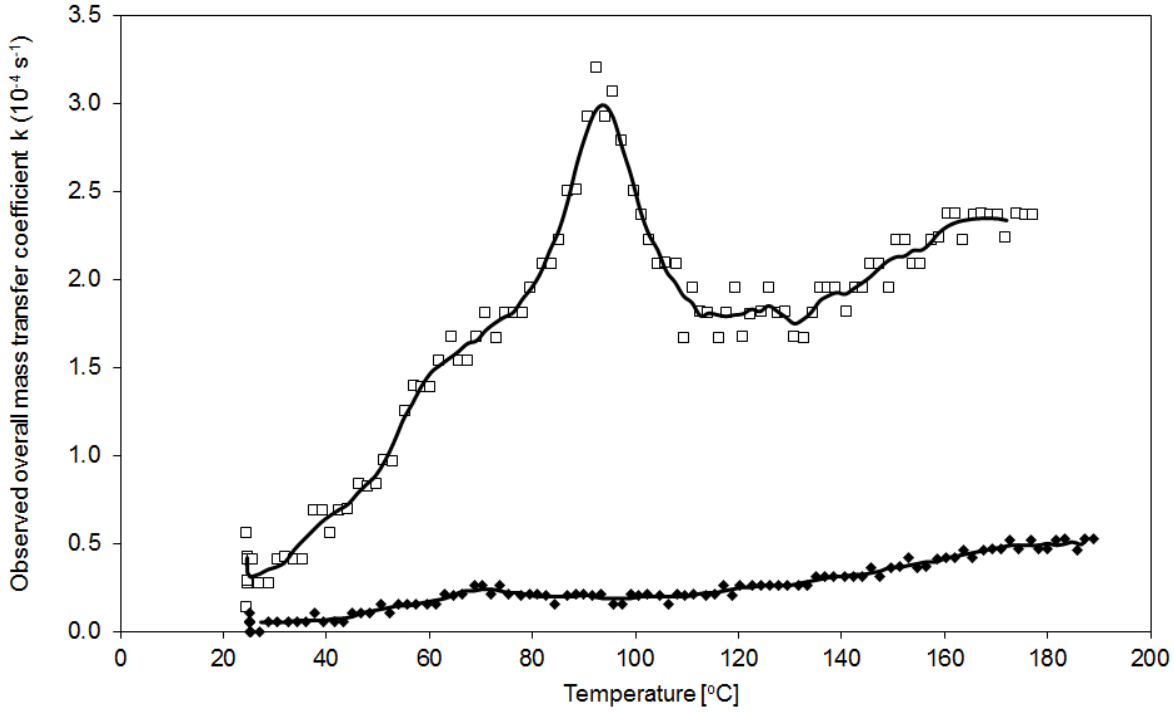

Figure 5: The observed overall mass transfer coefficient of desorption of butanol from CBV28014 (♦) and CBV901(□). Lines have been added to guide the eye.

The mass transfer rates, see figure 5, increase with temperature, as is expected and reaches a maximum for CBV901 at around 95°C. The wide structure of the CBV901 in all probability allows easy desorption of a large fraction of relatively loosely adsorbed butanol. This is also later illustrated by the observed heat effects. The observed overall mass transfer coefficient for desorption of butanol is lower for CBV28014 than for CBV901. The butanol adsorption isotherm also showed a higher affinity for CBV28014 than for CBV901 [9]. This all shows the butanol on the CBV28014 to be stronger bound. For CBV901, after reaching 90 °C, most of the sorbate has been removed and the low amount of butanol present on the zeolite is limiting the overall mass transfer. The heat effects after 90 °C behave in line with the decrease in sorbate removal rate, as can be seen later in figure 7, implying no strong difference in binding energy or different adsorption sites play a role.

5.3.4. Heat capacities and heat of desorption

The DSC method monitors the endothermic heat flow ($H_{heating}$) in time necessary for the system to follow the preset heating profile. The specific heat capacity (C_p) for a specific non-volatile species can be calculated if the total measured heat effect is determined by the DSC, as long as the sample mass (m) and heating range (T_{end}-T_0) are known. The average heat capacity of a zeolite sample is then:

$$C_{p,zeolite} = \frac{H_{heating}}{m_{zeolite} \cdot (T_{end} - T_0)}$$

The heat capacities of CBV901 and CBV28014 as a function of temperature are shown in figure 6. As can be seen from figure 3 the heat capacity of both zeolites increases slightly with temperature and ranges for the listed temperatures from 0.85 to 0.98 J/(g·°C) for CBV28014 and 0.95 to 1.1 J/(g·°C) for CBV901. This is in line with the reported heat capacity of 1.0 J/(g·°C) for 1-silicalite [7]. The difference in heat capacity between the two zeolites is expected as the zeolites structure differs strongly (ZSM-5 versus Y-Type). The heat capacity is relatively low for the zeolites compared to water (the bulk of the original aqueous feed phase). This is favourable with respect to the energy required for usage of high silica in thermal desorption processes. Table 2 summarizes the heat properties of the investigated components.

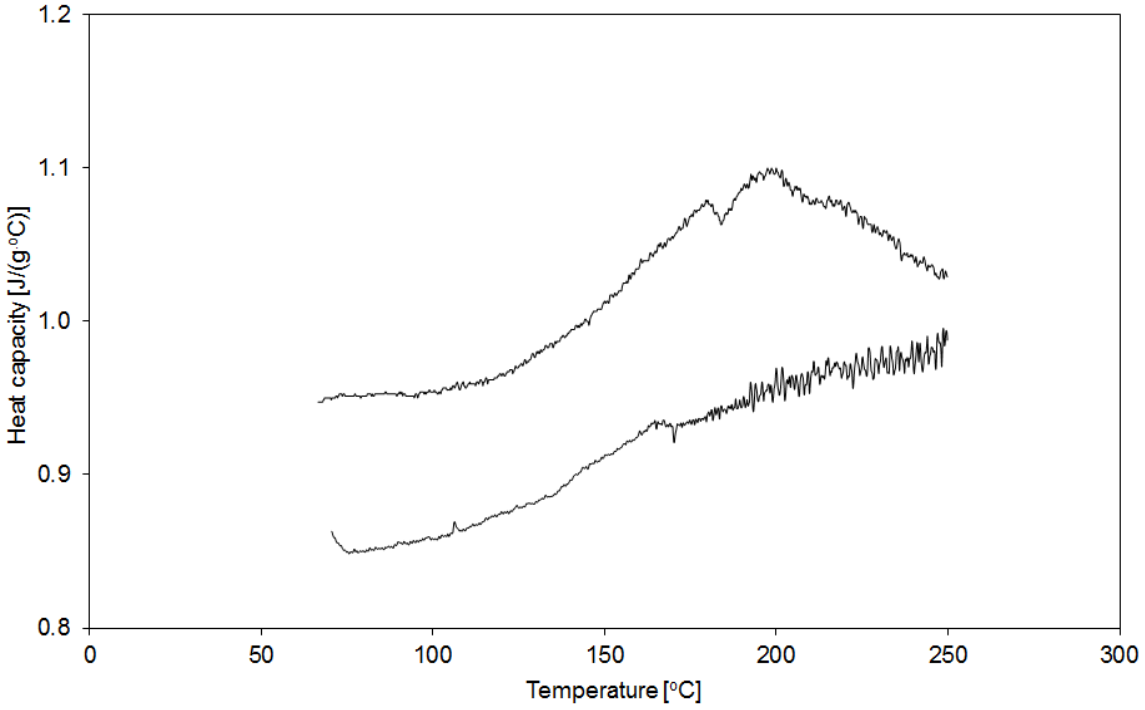

Figure 6: Heat capacity as function of temperature of CBV901 [Top line] and CBV28014 [Bottom line].

Table 2: Heat capacity and enthalpy of evaporation

Component	C_p [J/(g·K)]	Sensible heat [J/g]	Evaporation enthalpy [J/g]	Reference
BuOH	2.3919 [a]	220[c]	585[e]	[22]
Water	4.1833[a]	314[c]	2258[e]	[22]
CBV901	0.85 [b]	105[d]	N.A. [d]	This paper
CBV28014	0.95 [b]	95 [d]	N.A. [d]	This paper

[a](at 25°C), [b](at 75°C), [c]Calculated from $(T_b\text{-}T_0)\cdot C_p$, with T_0 = 25 °C, [d](per 100 °C). : Not applicable, [e]at boiling temperature T_b.

For validation of the DSC method the heat of evaporation of pure water was measured in the same setup, using the applied temperature profile. The measured heat was 2570 J/g. This corresponds to the sum of the sensible heat of water between 25 and 100 °C and the evaporation enthalpy at its boiling point, according to the data in Table 2.

Similar to the heat capacity the heat of desorption was monitored using DSC. Integration of the DSC signal allows calculation of the overall desorption heat. The heat uptake for butanol and water are shown in figures 7 and 8 for CBV901 and CBV28014, respectively as a function of temperature. The second abscissa shows the time progression of the experiment.

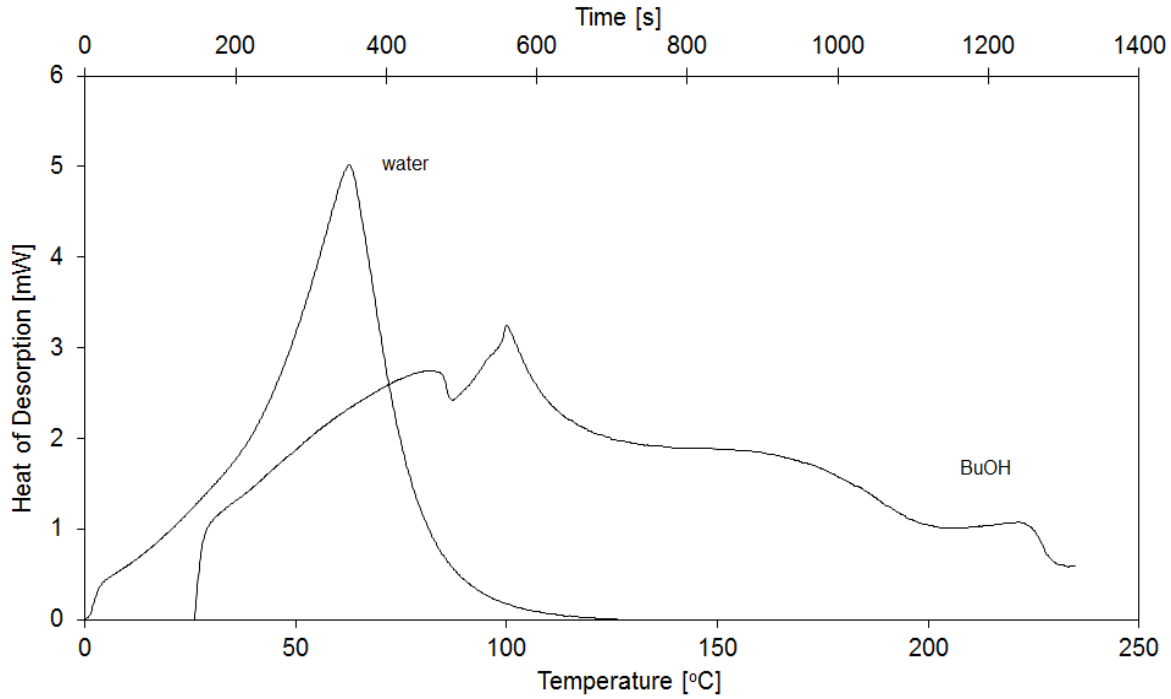

Figure 7: Heat of desorption of water and of butanol from CBV901 (0.50 mg and 2.24 mg, respectively).

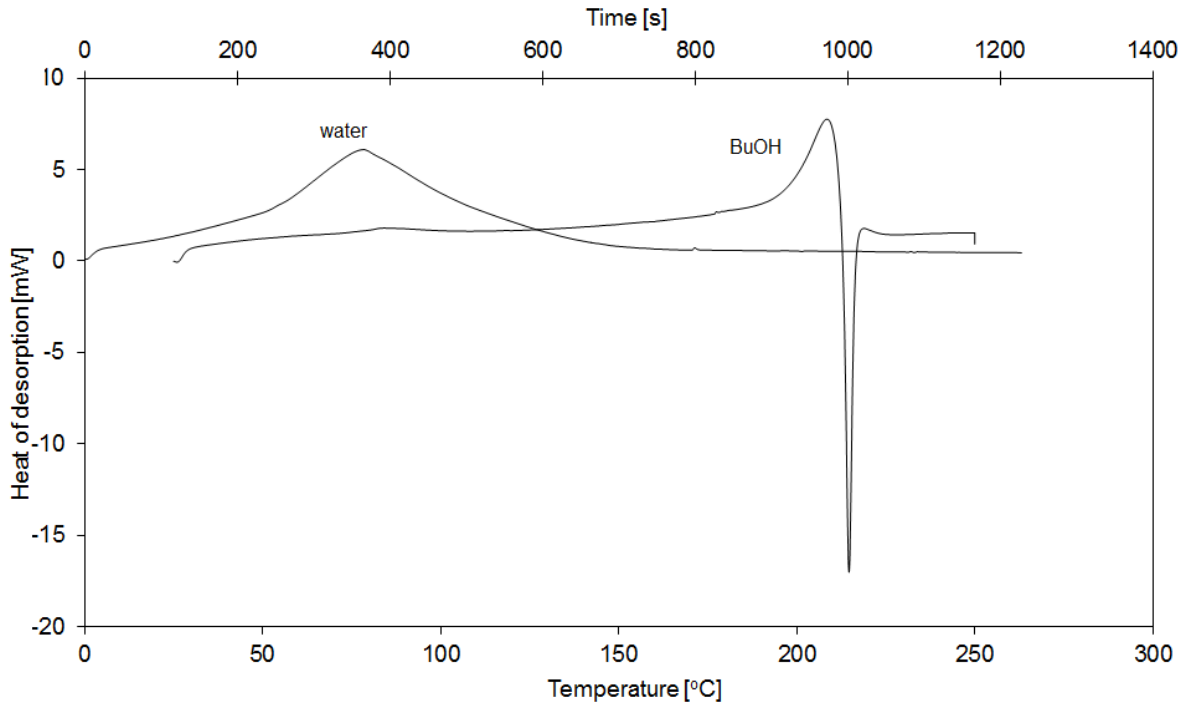

Figure 8: Heat of desorption of water and of butanol from CBV28014 (0.70 mg and 2.14 mg, respectively).

Figure 7 and 8 show water to desorb predominantly at low temperatures compared to butanol. The relative high amount of water present in CBV901 is desorbed easily and the water is thus not strongly bound, which results in the peak in the desorption profile. However, figure 7 does show butanol to desorb over the entire temperature range, which is in line with the TGA profile in figure 3. The difference in desorption heat profiles between water and butanol is more significant for CBV28014. This indicates a significant difference in butanol adsorption to exist between both zeolite structures. This large difference in desorption temperature between both components can be used to perform temperature programmed desorption, in which almost pure fractions of water and butanol are obtained, which has already been mentioned for 1-silicalite [23].

The heat required for the desorption of volatile components from the investigated zeolites is close to the sum of heat of evaporation and sensible heat of the volatile species investigated. This means the heat of adsorption is small when compared to the heat of evaporation. Figure 4 shows the desorption rate to change significantly around 200 ^{o}C. The heat effect of the desorption in figure 8 also shows a change in behavior to occur here. The desorption of butanol from CBV28014 shows an endothermic peak at around 200 ^{o}C. This endothermic behavior can occur from a chemical reaction occurring. The heat effect seen in

figure 8 is probably due to a dehydration reaction, leading to butene formation. This reaction has been observed using granulated zeolites of CBV28014 [24].
In table 3 the total heat of desorption of desorbed volatile species is shown. The overall heat of desorption is shown per gram of desorbed component, under saturated loading.

Table 3: Heat effect of desorption per amount of BuOH and water.

Zeolite	Component	Heat uptake [J/g]
CBV28014	BuOH	1160
CBV901	BuOH	1080
CBV28014	Water	2730
CBV901	Water	2440

The heat of desorption is less pronounced for butanol than for water. This is not unexpected when comparing their evaporation enthalpies (Table 2). The heat of desorption for butanol is 275 J/g and 355 J/g above the heat of evaporation of the pure species, for CBV901 and CBV28014, respectively. The heat of desorption of water shows a ~5 % deviation from the heat of evaporation of the pure species. The differences are -130 and 160 J/g for CBV901 and CBV28014, respectively. This inversely indicates that the adsorption heat at 25^{o}C will be relatively high for butanol as compared to water, which is a consequence of the stronger adsorption of butanol. The measured heat effects for CBV28014 also indicate stronger molecular interactions between the volatiles and this zeolite, compared to CBV901. The stronger hydrophobic interactions between CBV28014 and butanol increase the difficulty of thermal desorption.

5.4. Conclusions

The adsorption isotherm of aqueous butanol on CBV28014 changes significantly if the aqueous solution is at equilibrium with up to 9 bar of gaseous carbon dioxide. This difference can be exploited in a pressure swing desorption operation.

The small competitive adsorptive behaviour of CO_2 relative to butanol should be taken into account when adsorbing butanol from fermentation broth saturated by 1 bar of carbon dioxide.

The heat capacities of CBV901 and CBV28014 are (at 75 ^{o}C) 0.95 and 0.85 J/(g·^{o}C), respectively. These relative low heat capacities pose no direct limitation on usage of high silica in thermal swing desorption processes.

Desorption of butanol from CBV901 and CBV28014 by thermal swing operation shows the overall desorption heat effect for water to be marginally affected. Butanol is bound stronger by CBV28014 than by CBV901. The heat of desorption for butanol is 275 J/g and 355 J/g above the heat of evaporation of the pure species, for CBV901 and CBV28014, respectively. Also, the desorption of butanol from CBV28014 shows a catalytic reaction to occur around 200 ^{o}C.

The desorption rate of butanol from CBV28014 is significantly slower than from CBV901. The increased mass transfer resistance can be caused by a difference in pore diffusion characteristics due to the smaller pore channels of CBV2014. Complete regeneration of both zeolites is possible using thermal operation.

5.5. Acknowledgements

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Chapter 6: Short-cut calculations for integrated product recovery options in fermentative production of bio-bulk chemicals

Abstract

Micro organisms are generally sensitive to high concentrations of products that they excrete. Such product inhibition and toxicity effects can significantly be reduced by the integration of fermentations with separation technologies to remove the products continuously. Cost-calculations are required to select the preferred integration method. This paper presents a shortcut calculation method that provides easy interpretable results to assist the reader in making rational design choices. The method distinguishes four main cost categories, being capital and operational expenditure for both fermentation and product recovery. We have applied these cost correlations to the production of three typical bio-based bulk chemicals. The results show the origin of the most significant costs in the investigated integrated bio-processes. The presented method can be used to direct future research efforts and might assist in evaluating the impact of integrated product recovery techniques on total production costs of bio-chemicals.

Keywords: Integrated product recovery, Lactic acid, Butanol, Phenol, Review, Cost calculations, Fermentation, Separation technology

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*Co-Authors, both authors contributed equally

6.1. Introduction

Fermentative conversions of substrates into desired chemical products have been commercialized over time by pharmaceutical and chemical industry. Biocatalysts usually show a high selectivity towards the product and therefore biological conversions can be used in a wide range of fields. Currently, there is a focus on sustainable resources and production systems. This paper deals with the production of bulk chemicals by de novo fermentative conversions with integrated product recovery. Microbial production of bio-based chemicals is often hampered by product inhibition or product toxicity [1]. The performance of product inhibited fermentations can be enhanced by removal of the product during fermentation, usually referred to as integrated product recovery [2]. Integrated product recovery is not just a downstream operation, but is directly influencing the performance of the fermentor. Thus, a direct coupling exists between the performance of the fermentation and product recovery (see Fig. 1). The system shown in Fig. 1 can be seen as an integrated production system. The (economic) performance of the integrated production system is an optimization problem involving multiple unit operations. Table 1 shows some available integrated product recovery operations for bio-chemicals. This paper details the integrated microbial production of lactic acid, 1-butanol and phenol. The main goal of this work is to show the economic effect of integrated product recovery on production systems. The results only interpret the effect of product recovery. Other possibilities for stream integration, e.g. substrate utilization and waste management, are not taken into consideration. The obtained economic outline can be used to further focus research and development efforts of integrated product recovery designs.

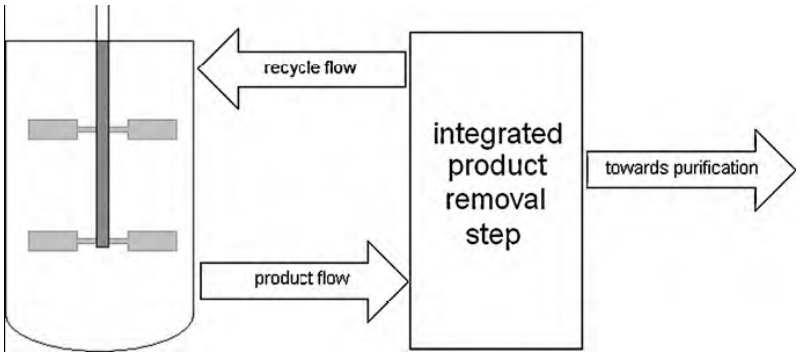

Fig. 1. Fermentation with integrated product recovery.

Table 1 Some possible recovery operations for bio-based bulk chemicals from fermentation broths.

New Phase	Origin	Membrane	Operation
Gas	P/T shift or composition change	Yes	Pervaporation [3–6]
Gas	Composition change	No	Gas stripping [7–10]
Liquid/supercritical	Composition change	No	Extraction [11–15]
Liquid	Composition change	Yes	Pertraction [16–20]
Solid	Composition change	No	Adsorption [21–26]

6.2. Product characteristics

6.2.1. Fermentation

Fermentations can be quantified by product yield, volumespecific productivity and critical concentration. Table 2 lists the fermentation performance data that are used to define the specific fermentations in this paper. Extensive literature on the production of these chemicals is available. Lactic acid shows the highest critical concentration, volume-specific productivity and yield. The butanol case can be characterized by a moderate volume-specific productivity, product yield and critical concentration. Phenol is the most inhibiting of the three compounds, with the lowest critical concentration, volume-specific productivity and yield.

6.2.2. Lactic acid

Lactic acid, when compared to butanol and phenol, has the highest aqueous solubility and a negligible vapor pressure. The negligible vapor pressure renders recovery options involving an auxiliary gas phase (such as pervaporation) non-feasible. Therefore, only recovery by adsorption, extraction and pertraction are evaluated. Adsorptive based recovery involves adsorbents, which can range from (organic) resins to inorganic materials, like zeolites [35,36]. Only lactic acid adsorption on zeolite is considered in this paper, because the high stability of the zeolite adsorbent material is assumed to be favorable.

Solvent selection [37–39] is crucial in the design of extractive recovery systems. Among the best extractants for L–L extraction/pertraction of lactic acid is tri-n-octylamine, which has a lactic acid partition coefficient of 4 and dissolves a low amount of water (0.51 mass%). Regeneration of the extractant will be performed using a base/acid wash.

Overall mass transfer coefficients for pertraction based recovery have been reported by Huang et al. [40]. Desorption and extractant phase regeneration operations are also

constrained by the negligible vapor pressure. Desorption needs a chemical auxiliary, introduced in the form of a base or solvent wash. For the adsorption case, desorption using an ethanol washing step is assumed[41].

The energy demand during regeneration is then determined by ethanol evaporation, see also Section 6.4.4.

6.2.3. Butanol

Due to the moderate aqueous solubility of butanol a wide range of possible product recovery techniques is available [42,43]. Furthermore, butanol has the highest vapor pressure of the three cases, explaining the relatively large amount of literature concerning gas-phase product recovery [44].

Table 2 Product characteristics for evaluating fermentation.

Product	Critical concentration (kg/m^3)	Maximum volume specific productivity ($(kg/m^3)/h$)	Maximum yield (C-mol product/C-mol glucose)
Lactic acid	91.9[a]	11.2[b]	1[c]
1-Butanol	20.9[d]	4.6[e]	0.67[f]
Phenol	0.5[g]	0.013[h]	0.067[g]

[a] [27], [b] [28], [c] [29], [d] [30],. [e] [31].,[f] [32].,[g] [33].,[h] [34].

Numerous adsorptive recovery operations, with various adsorption materials, can be used [43,45]. Often zeolite material has been suggested, and this can be used in a granulated form, allowing easier handling of the material due to increased particle sizes. However, additional water will be adsorbed due to the presence of macropores. Macropores can make-up 40% of the material [46].

The extractant considered for L–L extraction/pertraction of butanol is Cyanex-923, which is a liquid phosphine oxide with a butanol partition coefficient of 14.8, which is the highest butanol partition coefficient recorded to our knowledge. Cyanex-923 dissolves 6 mass% of water and regeneration will be performed using a heat strip [47]. Butanol can be regenerated from the adsorbent or extractant phase using an evaporation procedure. Butanol removal from fermentation broths in current industrial practice is performed using distillation but this is not an integrated process.

6.2.4. Phenol

Phenol removal from aqueous phases is discussed in [48]. Due to the severe toxicity of phenol, only low product concentrations are in the aqueous fermentative phase. The low concentrations, in combination with the relative low vapor pressure of phenol [49], will make pervaporation based recovery from a overall process perspective non-feasible. Adsorption of phenol is possible [50–53]. Activated carbon, which was reported by Costa and Rodriguez [54] will be used here for adsorption based calculations. Costa and Rodriguez [54] reported an expression for loading time for multiple experimental runs of a fixed bed, depending on liquid flow-rate through the column. Regeneration of the sorbate will be performed using ethanol. For L–L extraction/pertraction, again, an organic extractant such as Cyanex-923 will probably work best and is used in this paper due to phenol's partition coefficient of 1100 coupled to a modest water uptake of 6mass%. A base wash with subsequent acid neutralization will be used for both extractive phase regeneration.

6.3. Methods: definitions, assumptions and boundaries

The integrated system, shown in Fig. 1, can be described in various degrees of detail. The system is defined as consisting of two coupled unit operations, the fermentation and the integrated product recovery. The main goal is to show the general economic behavior of such an integrated system. Therefore, the economic performance has been divided into two main costs, the capital expenditure (CAPEX) and operational expenditure (OPEX). Both fermentation and product recovery influence the CAPEX and OPEX. This paper reduces the complexity of the optimization problem of integrated systems, by linking all four cost factors to one main process variable, the product concentration in the fermentor, as will be shown in the next section. General assumptions, simplifying the analyses, are used in this paper: the production amount is 100,000 tons annually; the fermentation and integrated product recovery are continuous operations; the microorganisms are retained in the fermentation unit and do not grow significantly; an annual production time of 8000 h is assumed for sizing of the fermentation equipment. Furthermore, literature values of product fluxes, loading capacities, volume-specific productivities and carbon yields have been obtained to allow modeling of the behavior of the unit operations. A mass balance of the product over the unit operations, shown in Fig. 1, shows the system to operate in a steady state as long the amount produced in the fermentation equals the amount of product removed during product recovery. This assumption is valid as long as a possible bleed or

purge is neglected. The productivity of the fermentation (Q_{fer}) and the product flow (F_{rec}) are then equal to:

$$Q_{fer} = F_{rec} \text{ (kg/h)} \quad (1)$$

Cost optimizations of the system shown in Fig. 1 are thus possible for any production amount, if both Q_{fer} and F_{rec} are used to size the process equipment. The specific method applied to calculate the unit operations are detailed per recovery operation for each product and can be found in Section 6.4, while using the details given in Section 6.2.

6.3.1. CAPEX fermentation

The capital expenditure required for the production of biochemicals depends on the size of the fermentation vessel. In order to evaluate the annual capital costs on the fermentation side for a required productivity (kg/h), estimations should be made on the volume-specific productivity of the fermentor ((kg/m^3)/h).

6.3.2. OPEX fermentation

In the fermentation, the feedstock is converted into a bio-chemical. The dominant operational expenditure during fermentation is assumed to be determined by the feedstock cost. The OPEX of the fermentation can thus be expressed as a (cost) function of the product yield on substrate depending on the product concentration in the fermentation.

6.3.3. CAPEX product recovery

The capital expenditure is determined by the individual costs of the product recovery unit operations. Most mass transfer operations can be expressed per area of transfer equipment. Then the costs depends on the product flux of recovery option. The flux can be calculated using equations presented in Section 6.4.

6.3.4. OPEX product recovery

The operational expenditure during the product recovery is determined by the energy costs and the costs of any auxiliary material used (such as acid/base). The energy requirement, as function of the product concentration entering the capture step, is needed for the calculation of the OPEX. The energy requirement during recovery is dependent on the amount of product and auxiliary phase, and the process conditions. The auxiliary phase is the phase

facilitating separation of the product compound from the aqueous feed phase. Key parameter is the selectivity of recovery as it details the mass amounts involved in the recovery operation [43].

6.3.5. Overview costs functions

Combining the previous Sections 6.3.1–6.3.4, it can be generally stated that main cost considerations in the production of biochemicals arise from the four parameters given in Table 3. In Section 6.4 we will detail the modeling and costs per operation.

Table 3 Cost determining parameters for fermentation and product recovery.

	Fermentation	Product recovery
OPEX	Product yield on substrate	Selectivity
CAPEX	Volume-specific productivity	Product mass flow

6.4. Modeling

The modeling of the fermentation and product recovery requires background process data. First, the process specific data are listed, followed by the method for cost calculation. All cost correlations presented in the next sections can be replaced by readers' personal correlations. Therefore, these relations should be used as a general guideline for making cost estimations. In this paper we will discuss the three different cases (phenol, 1-butanol and lactic acid) where the bio-chemicals vary from severely toxic to relatively non-toxic towards the host micro-organism. Furthermore, these products have varying yields on substrate and varying physical properties such as vapor pressure, aqueous solubility and extractability, amongst others.

6.4.1. Volume-specific productivity of fermentation

In order to estimate CAPEX on the fermentation side, volumespecific productivities should be known. However, inhibition kinetics and final product titers are difficult to predict and are organism- and product-specific. When products are removed from the microbes' environment, the yields on substrate and/or volumespecific productivities can increase significantly. Fig. 2 shows a correlation between the aqueous solubility of compounds and the concentration inhibiting the microorganisms producing them, adapted from Straathof [55]. The so-called critical concentration will be set as the final product titer.

Fig. 2 shows critical concentrations for a wide range of products from biological conversions. Critical concentrations are limiting product concentrations in the fermentation unit and are therefore also the final attainable concentration when no product removal is applied. Estimating a priori a volume-specific productivity Q_{max} is not possible since this depends on whether the fermentation product is a primary or secondary metabolite and also on the micro-organism. Therefore, maximum volume-specific productivities found in literature were used as Q_{max} (see Table 2). To estimate the productivities, Eq. (2) from Luong et al. [36] is used, which is a simplified representation of real product inhibition kinetics.

$$Q = Q_{max}\left[1-\left(\frac{C_{ferm}}{C_{crit}}\right)^{\beta}\right] \qquad ((kg/m^3/h) \qquad (2)$$

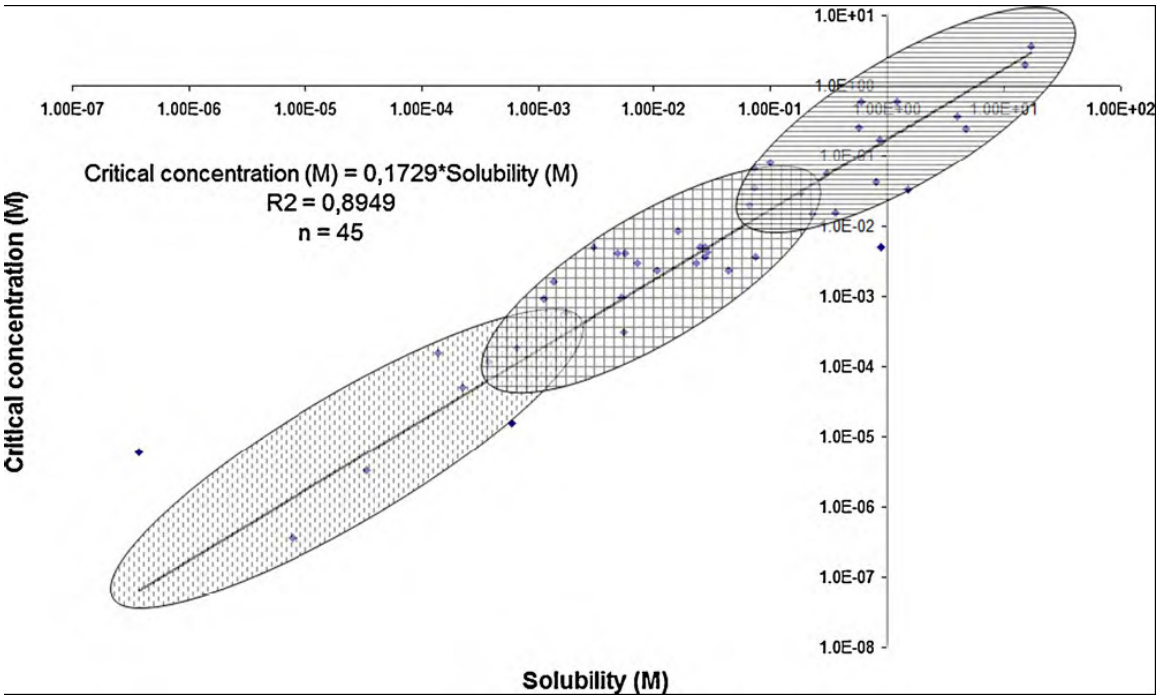

Fig. 2. Least squares fit between solubility and critical concentration of biological conversion products. The vertical stripe containing ellipsoid contains severely inhibiting compounds such as alkaloids/pharmaceuticals; the squares containing ellipsoid represents highly inhibiting molecules which are mostly fine-chemicals; the ellipse with horizontal lines contains relatively non-inhibiting molecules and mainly consists of typical bulk chemicals.

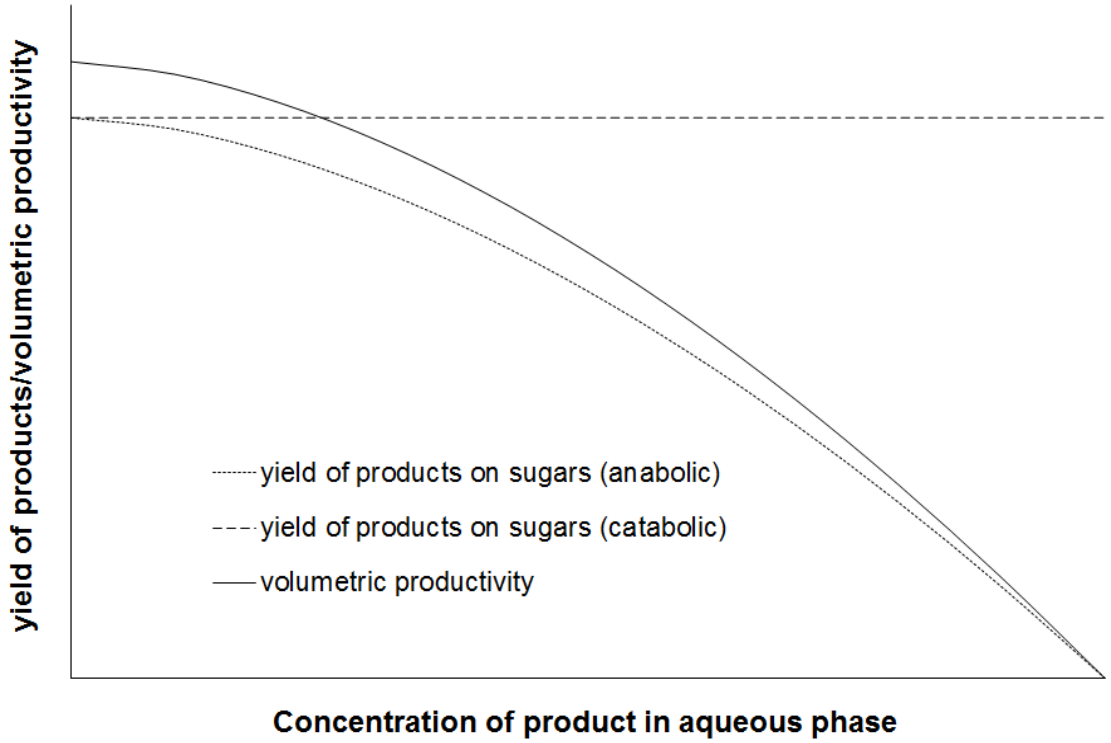

Fig. 3. Assumed influence of product concentration in fermentation broth on volume-specific productivity and yield.

The β is an inhibition constant, which is set to 1.69, like in [56]. The volume-specific productivity provides the relevant process information necessary to estimate the size of the fermentation equipment. The listed volumetric productivities in Table 2 depend on the cell density present. High cell density fermentations can show higher volume-specific productivity. The high cell density fermentation will require the negation of an existing limitation, e.g. mass transfer limitation.

6.4.2. Fermentation yield

Product yields on glucose ($Y_{p/s}$) are directly coupled to the concentration of the product in the aqueous phase in a similar way as the volume-specific productivity equation. Products such as phenol, which are not produced by the microbial catabolism, will have product yields on glucose approaching zero near the critical concentration due to their molecular toxicity. Although product yields depend on type of microbial host and metabolic route, a simple equation is required. Product yield can be calculated using Eq. (3), which is analogous to Eq. (2), but it is outside the scope of this article to support it with data.

$$Y_{p/s} = Y_{p/s\,max}\left[1-\left(\frac{C_{ferm}}{C_{crit}}\right)^{\beta}\right] \quad (-) \qquad (3)$$

In Fig. 3 the yields and volume-specific productivity are plotted as a function of the fermentation broth product concentration. It should be noted that yields of catabolic products are set to a constant of 90% of their maximum theoretical yield since they are produced by the maintenance reaction. The operational costs on the fermentation side are dependent on substrate costs. However, renewable raw materials experiences large price fluctuations, and prices of 2nd generation feedstock derived materials, such as lignocellulosic hydrolysate are not yet known. Therefore, this paper defines one C-6 feedstock, glucose, valued at 0.25 euro/kg, which is done for transparency reasons. Additional calculations using actual feedstock and feedstock prices can optionally be carried out and compared the results shown here. As the glucose costs are set, for the production of 100,000 tons/year the operational expenditure is a function of the product yield on glucose and is shown in Fig. 4.

6.4.3. Product recovery fluxes

The capital expenditure for recovery operations depends strongly on the type of recovery applied and product concentrations in the feed and product recovery phase. The cost of the recovery equipment is directly linked to the costs of the equipment.

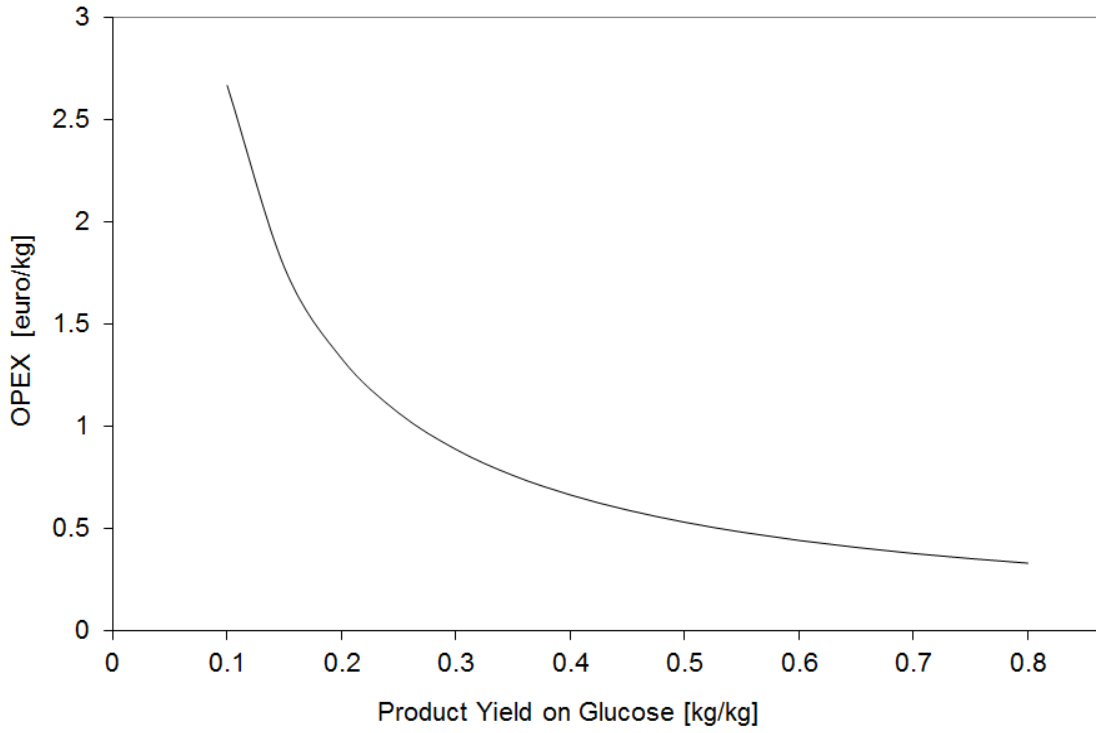

Fig. 4. OPEX of fermentation as function of the product yield on glucose.

Sizing the recovery operation will be based on the mass transfer of the chemicals involved. The mass transfer is a function of the product concentration and will be calculated using Eq. (4).Most process operations require regeneration of the auxiliary phase used to capture the product. Using Eq. (4), the total interfacial area will be calculated assuming that the concentration in the product recovery phase remains zero.

$$F_{rec} = K_{ov} \cdot A_{eff} \cdot \left(c_{ferm} \cdot p\right) \quad \text{(kg/h)} \qquad (4)$$

For the listed recovery techniques, the relations linking the product concentration, via the equipment size, to the expected capital expenditure, are given in the next section and are obtained by comparing scientific literature data. In the next sections different recovery techniques are discussed in terms of initial fluxes and costs associated with the operation. If the same unit is used in both operations, either the capturing step or the recovery step determines the size of the equipment. The unit operations are primarily sized in this paper based on the capturing operation. The process times for any regeneration operation is assumed equal the capturing step if no data is readily available.

6.4.3.1. Adsorption

The adsorption and desorption of the desired product are necessary operations during adsorptive recovery of a bio-chemical. Most adsorption processes are column operations and overall mass transfer coefficients can be derived from numerous correlations and approximations. Transport rates for adsorption process for spherical particles will be approximated by [57]:

$$k = 15 \cdot \frac{D_{aq}}{R_p^{\,2}} \qquad \text{(1/s)} \qquad (5)$$

Eq. (5) is valid for pore diffusion controlled adsorption. The diffusion coefficient (D_{aq}) can be calculated using the Wilke–Chang correlation [58].

$$K_{ov} = k \cdot \frac{R_p}{3} \qquad \text{(m/s)} \qquad (6)$$

Eq. (6) describes overall mass transfer for spherical particles, where pore diffusion is the main rate-determining step. However, it is not the goal of this paper to fully calculate the adsorption and desorption profiles. When K_{ov}, the amount of relative interfacial area and feed concentration are known, initial fluxes can be calculated using Eq. (4).

6.4.3.2. Pervaporation

Pervaporation is carried out with aid of membrane material. A characteristic parameter is the trans-membrane flux. Generally, the flux is expressed as a function of the retentate product concentration and membrane thickness. Literature data expressing the membrane flux can be found for various systems. No data on pervaporation, at fermentation temperatures, were found for lactic acid and phenol since these compounds have a low vapor pressure. Therefore only butanol will be discussed in this paper [59,60]. Trans-membrane flux is mainly dependent on membrane material, temperature and membrane thickness. Many different membrane materials can be used and literature is extensive. An overview of membranes and their performance is given by Vane [3]. When product flux and production amounts are known the required membrane area can be calculated. The CAPEX is calculated from membrane and membrane housing costs. Then, capital expenditure can be estimated using membrane prices and lifespans such as in Appendix B.

6.4.3.3. L–L extraction

Estimation of CAPEX of an in-stream L–L mixer-settler extraction step requires values of the product fluxes into the organic phase. To calculate product fluxes, one needs to know the required amount of interfacial contact area, and molecular diffusivities in aqueous and organic phase. The required amount of interfacial area needed depends on the speed of agitation in the mixer-settler. Paulo et al. [61] found an average Sauter mean droplet diameter over a wide range of Reynolds numbers. Therefore, we apply an average drop diameter (d_{vs}) of 3.4mm in our calculations. It is assumed that the droplets will have an aqueous film layer (Δz) and mass transfer coefficients in this layer will be calculated using Eq. (7).

$$K_{aq} = \frac{D_{aq}}{\Delta z} \quad \text{(m/s)} \qquad (7)$$

These droplets are assumed to be rigid, resulting in a Sherwood number of 6.6. Organic phase molecular diffusivities can be calculated using the Minhas-Hayduk correlation [62]. When N_{sh}, D_{org} and d_{vs} are known, the K_{org} value can be calculated using:

$$(N_{sh})_{ov} = \frac{K_{org} \cdot d_{vs}}{D_{org}} = 6.6 \qquad (8)$$

The overall mass transfer coefficient is calculated using Eq. (9):

$$\frac{1}{K_{ov}} = \frac{1}{K_{org} \cdot p} + \frac{1}{K_{aq}} \quad \text{(s/m)} \qquad (9)$$

When overall mass transfer coefficients are known, the minimum amount of effective interfacial area can be calculated using Eq. (4), assuming the concentration in the loading phase is zero upon contact with the fermentation broth. To size mixer-settlers, the interfacial area per volume of mixer-settler can be calculated using [63]:

$$a = \frac{6 \cdot \Phi_d}{d_{vs}} \quad (\text{m}^2/\text{m}^3) \qquad (10)$$

Φ_d is the solvent phase hold-up and will be set to 0.3.Now sizing and cost-calculations can be performed using cost equations, and can be found in Appendix B.

6.4.3.4. Pertraction

To estimate CAPEX on hollow-fiber pertraction units, mass transfer coefficients and subsequent product fluxes need to be estimated. High organic/water phase partition coefficients result in mass transfer limitations at the aqueous side [64]. Therefore, it is assumed extraction rate is determined by the resistance at the aqueous side [65]. Therefore, flux calculations involving a pertraction unit will be simplified using Eq. (11).

$$\frac{1}{K_{ov}} \cong \frac{1}{K_{aq}} \qquad \text{(s/m)} \qquad (11)$$

Kaq will be calculated using Sherwood numbers, and has been normalized for 1m length-scale:

$$N_{sh} = \frac{K_{aq} \cdot d_i}{D_{aq}} = 1.62 \left(\frac{d_i^{\,2} \cdot \phi_{aq}}{D_{aq}} \right)^{1/3} \qquad (12)$$

Table 4 Phase transition properties of pure bio-based bulk chemicals and water [66].

Property	T_m [◦C]	T_b [◦C]	$\Delta H_{vap}(T_b)$ [kJ/kg]	$\Delta H_{fus}(T_m)$ [kJ/kg]
Lactic acid	53	n.a.	n.a.	n.a.
Phenol	40.5	181.7	614	122
Butanol	−88.6	117.7	585	127
Water	0	100	2258	334
Ethanol	−114.3	78.4	765	108

However, if products have poor organic/water phase partitioning behavior, mass transfer is influenced by membrane and organic phase as well, making it more complex. For these cases, overall mass transfer coefficients are taken from literature. After obtaining overall mass transfer coefficients, product fluxes can be calculated using Eq. (4). Subsequently, sizing of pertraction can be performed.

6.4.4. Product recovery

The regeneration energy penalty of the product recovery can be expressed by the selectivity of the capturing operation. This selectivity is defined as the ratio of the product concentration and the water concentration in the product recovery stream to that of the feed stream (see Eq. (13)).

$$S = \frac{[C_{product}/C_{ferm}]^{perm}}{[C_{product}/C_{ferm}]^{feed}} \qquad (13)$$

Energy input in the product recovery is one of the key parameters when describing its economic feasibility. Based on a steady state flow process, the mass-specific enthalpy flow is given by Eq. (14).

$$\Delta H = Q_h - W \qquad (14)$$

ΔH is the mass-specific enthalpy change, Q_h is the amount of energy added to the system per mass (kJ/kg) and W is mass-specific work (kJ/kg). The process enthalpy of both feed phase and product phase needs to be calculated in order to estimate the energy needed for the recovery operation. This means the mass flows of the species need to be coupled to the enthalpy balance. The nonideality of the product phase in comparison to the feed phase occurs is not considered here. However, the values of Q_h and W applied on and by the system are dependent on the technique used. One important assumption here is that an azeotrope will not be formed during the regeneration of the product recovery phase, resulting in underestimated energy costs. Usually, the product capture by integrated recovery brings the product from a dilute aqueous stream to an enriched stream containing concentrations of up to 50 mass% product. When starting with 20 g/l of product this means that 49 out of 50 water molecules are removed in the concentration step (relative to a product molecule). Most of the energy requirements are in the product recovery step. Upgrading diluted aqueous streams up to 50 mass% of product will consume the majority of energy required for product recovery. Subsequent product purifications steps will require significantly less energy input (Table 4). As mentioned the unit operations are primarily sized in this paper based on the capturing operation. The process times and thus required

capital expenditure for any regeneration operation is assumed equal the capturing step if no data is readily available.

6.4.4.1. Adsorption

Desorption of product from the adsorbent can be performed by either heat swing or solvent wash. Organic solvents, e.g. ethanol, are used when products with a low vapor pressure are involved. The loaded solvent will still need to be regenerated using temperature swing. The amount of energy input required, is determined by the solute concentration in the washing solvent phase. It is assumed that the total column volume minus adsorbent backbone volume will be filled with washing solvent. All of the product will be desorbed by the solvent and energy-efficiency calculations can be performed using Eqs. (13) and (14).
For the butanol case, being a typical example of a high vapor pressure product, a heat strip is assumed.

6.4.4.2. Pervaporation

The pervaporation of a product requires the feed phase to partly evaporate and form a separate vapor phase. This can be achieved either by heating the feed or by forming a low pressure (vacuum) at the vapor side of the membrane. The low pressure can be maintained by either pumping or cooling the product side of the
pervaporation unit. Our method calculates the energy involved in the main phase transition of the product phase. The product phase is usually brought from liquid to vapor and back to liquid phase. The total energy requirement is calculated by applying Eq. (14) to the known separation selectivity of the pervaporation operation and the chemical properties shown in Table 3. Butanol is the only case where pervaporation is calculated and selectivity and fluxes are taken from Hickey et al. [67].

6.4.4.3. Extraction and pertraction

The main OPEX costs for extraction and pertraction consist of solvent purchase and regeneration costs. The solvent purchase costs depend on type of solvent. Removal of hydrophilic products needs so-called reactive solvents (such as tertiary amines or phosphine oxides) to reach high product concentrations in the organic phase. However, these reactive solvents also dissolve significant amounts of water, resulting in an expensive regeneration. It was stated in Section 6.4.4 that the selectivity of the organic phase towards the product will determine the regeneration costs. The selectivity can be calculated when the water

solubility into the organic phase is known, together with the product partition coefficient. Solvent losses due to their aqueous solubility do not occur in the simplified process scheme of Fig. 1. The amount of solvent needed can be calculated from the total amount of interfacial area needed is known, which can be calculated using Eq. (10).

6.4.5. Costs

All the individual chemical and process equipment prices are compiled in Appendices B and C. Total manufacturing cost (TMC) is calculated by adding the OPEX and CAPEX of both the fermentation and capturing operation. A factor of 4.93 is used to convert purchased equipment costs (PCE) into fixed capital, allowing calculation of the CAPEX of the two defined unit operations [68]. The reader might replace this CAPEX/OPEX calculation by other reasonable ones [69,70]. A linear depreciation over 12 years was applied when calculating cost functions. The resulting cost functions taken for the individual operations are detailed in Appendix B.

6.5. Results and discussion

The subsequent figures show the cost lines that predict the capital expenditure and the operational expenditure for both fermentation and recovery operation as a function of product concentration in the fermentation broth.

6.5.1. Lactic acid

In Figs. 5–7 a comparison is shown of L–L extraction, pertraction and adsorption for product recovery techniques. It can be observed that extraction has the lowest total manufacturing cost (TMC). The low TMC is a result of the relatively low CAPEX costs of the mixer-settlers units and relatively low regeneration costs. Pertraction has a higher CAPEX demand as it includes large membrane area costs. The CAPEX demand of the membrane operation is close to the TMC and the other cost contributions are almost on the base-line in Fig. 7. Extraction and pertraction require a base-wash and acid neutralization step costing about ~20% of the TMC. Running the fermentation at concentrations lower than ~18 kg/m3 shows a steep increase in TMC for adsorption and pertraction. The concentration of lactic acid in the adsorbent material will be low, resulting in low concentrations in the washing solvent and subsequently low regeneration efficiency. Similarly, the pertraction operation is strongly affected by operating at low product concentrations. An increase in product concentration will increase the costs of the fermentation. This can be seen most clearly in the TMC profile for the extraction system in

Fig. 6. Also, looking only at operational costs, TMC is affected strongly by glucose price. Doubling the price of glucose would increase the TMC by approximately 43% of the integrated recovery using extraction. The caption to be used in Figs. 5–14 can be found in Fig. 5.

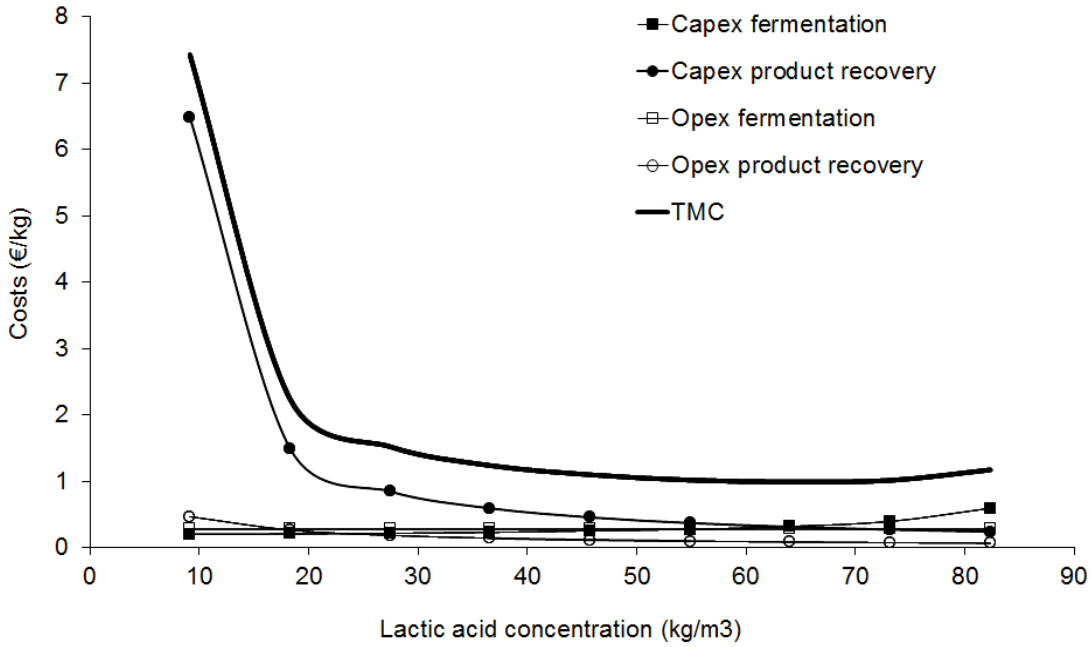

Fig. 5. Recovery of lactic acid by adsorption as function of the concentration in the fermentor.

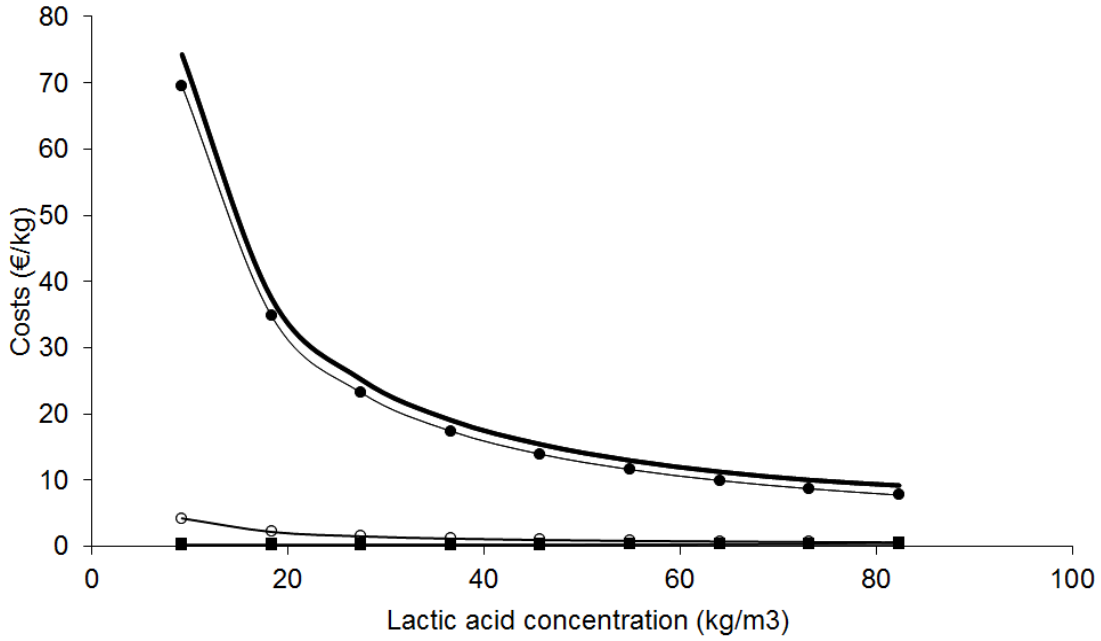

Fig. 6. Recovery of lactic acid by pertraction as function of the concentration in the fermentor.

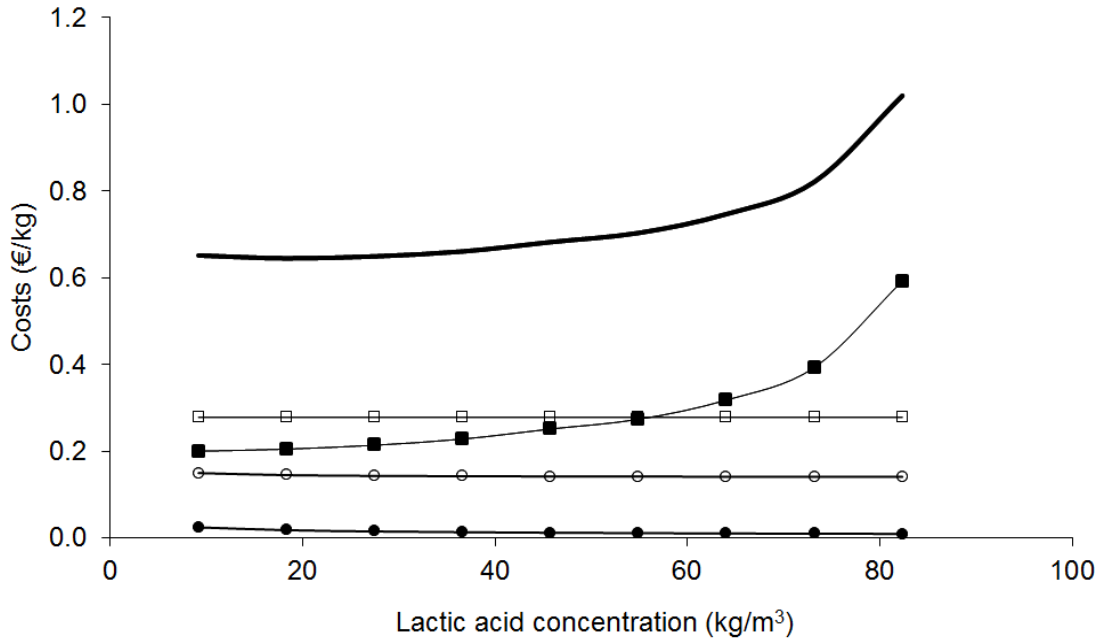

Fig. 7. Recovery of lactic acid by extraction as function of the concentration in the fermentor.

6.5.2. Butanol

A comparison of adsorption, pervaporation, L–L extraction and pertraction for product recovery is shown in Figs. 8–11. Due to the product inhibition of butanol, lower volume-

specific productivities require larger fermentation vessel volumes, resulting in higher CAPEX. The fermentative production of butanol using integrated recovery by pervaporation has an overall minimum, when operating the fermentation at approximately 14.8 kg/m^3 butanol. At lower butanol concentrations the product flux through the membrane is relatively low. The low product flux leads to an increase in membrane area and the relatively low butanol concentration in feed phase results in a subsequently high energy demand for regeneration. The TMC increases strongly at low butanol concentrations. The butanol trans-membrane flux remains mostly below 1 kg/(m^2 h). An increase in butanol concentration will negatively influence the fermentation productivity, shifting more costs towards the fermentative operation. The lowest TMC is predicted for an adsorptive based recovery at 3.33 kg/m3 butanol in the fermentor. The amount of water adsorbed relative to butanol, dictates the energy efficiency of the overall process and energy costs dramatically increase when more water is adsorbed. The operational cost of this integrated product removal dominates the TMC for extraction. The result is a relatively high price even at low fermentation concentrations. It should be noted that the lowest TMC is at a higher butanol concentration for extraction than for adsorption. The predicted TMC values of the butanol removal techniques area relatively close to each other, explaining the amount and diversity of research that has been performed on the subject of butanol recovery [43].

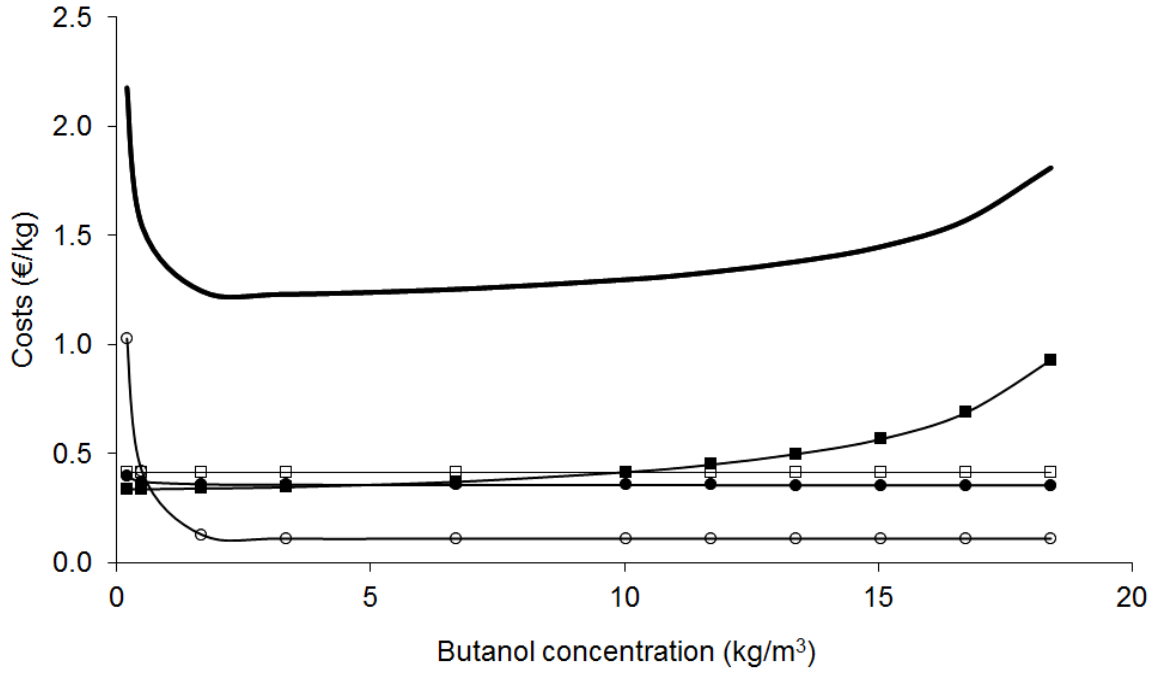

Fig. 8. Recovery of butanol by adsorption as function of the concentration in the fermentor.

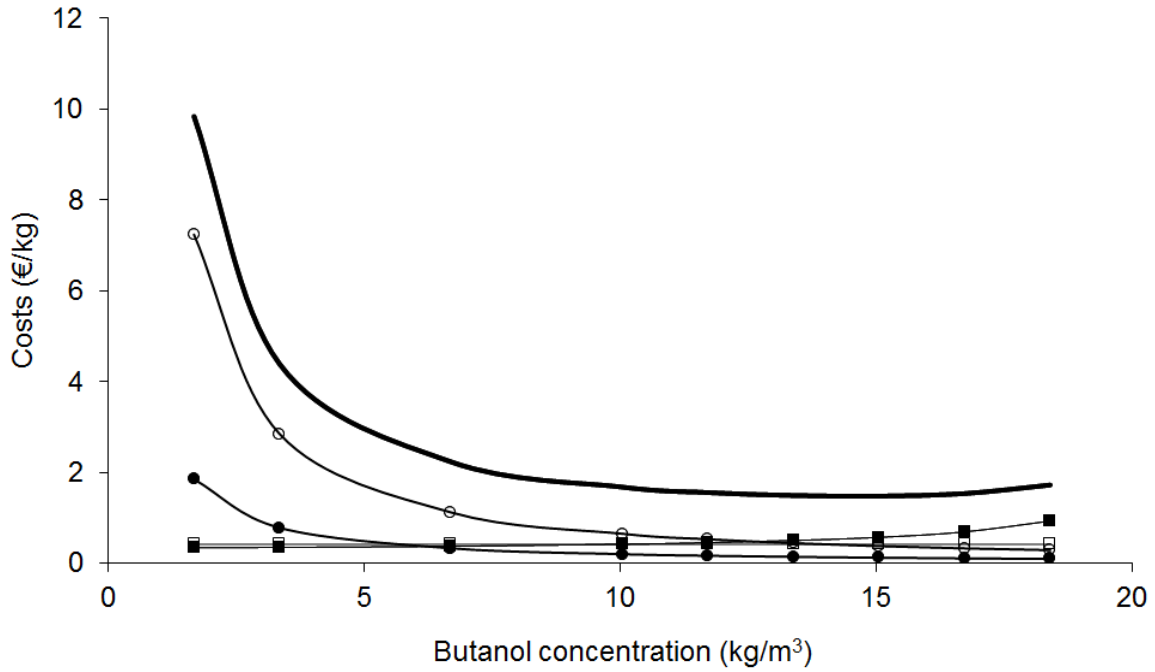

Fig. 9. Recovery of butanol by pervaporation as function of the concentration in the fermentor.

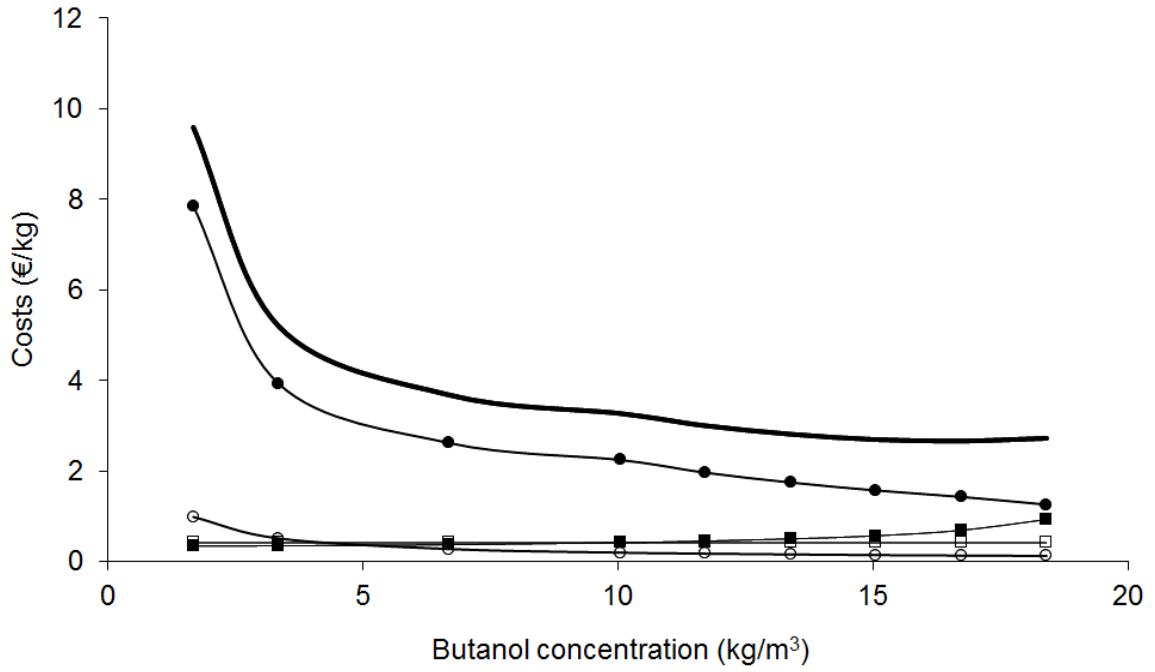

Fig. 10. Recovery of butanol by pertraction as function of the concentration in the fermentor.

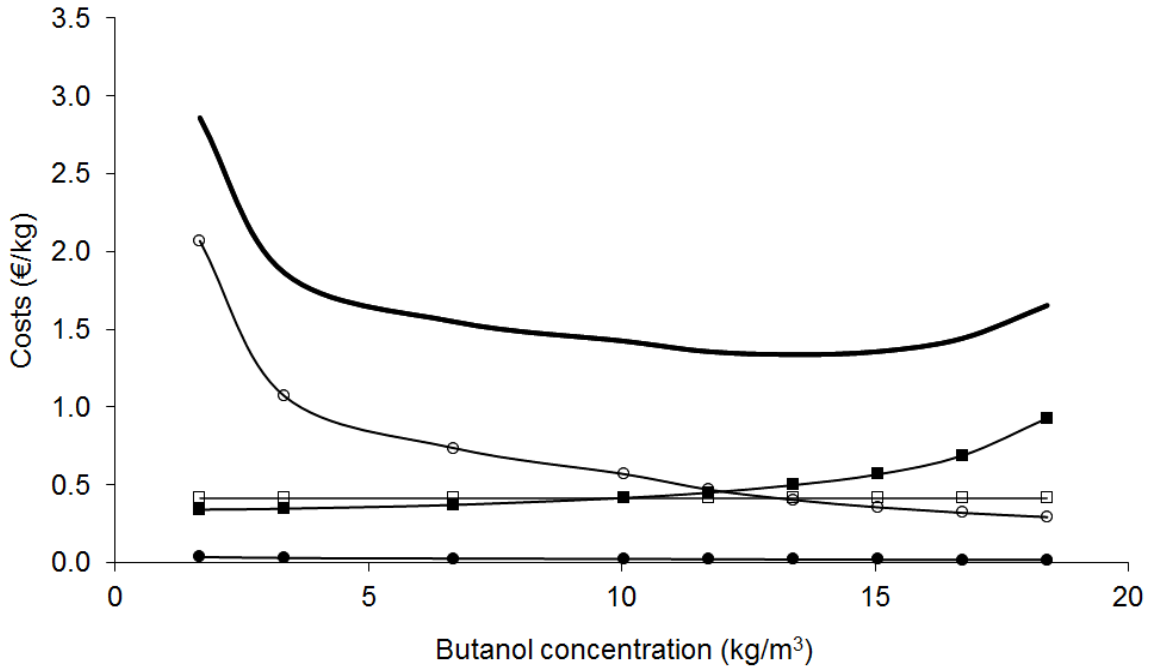

Fig. 11. Recovery of butanol by extraction as function of the concentration in the fermentor.

6.5.3. Phenol

Adsorption, pertraction and extraction recovery of phenol are shown in Figs. 12–14, respectively. The microbial production of phenol does not allow concentrations in the aqueous phase above 0.47 kg/m^3. An efficient system needs to have a high affinity of the auxiliary phase for phenol. All fermentation costs show a steep increase in TMC when product toxicity in the fermentation becomes the dominant factor since yields on glucose decrease. For adsorption, the OPEX of this integrated recovery is the main cost factor. This implies that the phenol concentration and the corresponding adsorption equilibrium are too low for efficient desorption of the adsorbent material with ethanol. Pertraction has a lower TMC for the recovery of phenol concentrations. However, the best technique for integrated processing seems to be extraction since this technique lacks the membrane investment compared to pertraction. TMC for phenol production with extractive recovery is relatively low for the phenol concentration range 0.05–0.28 kg/m^3. Due to the relatively low volumetric productivity during fermentation and the high selectivity of extraction the fermentation costs dominate the costs profile of extractive recovery. When phenol productivity significantly decreases, the TMC increases due to higher fermentation CAPEX.

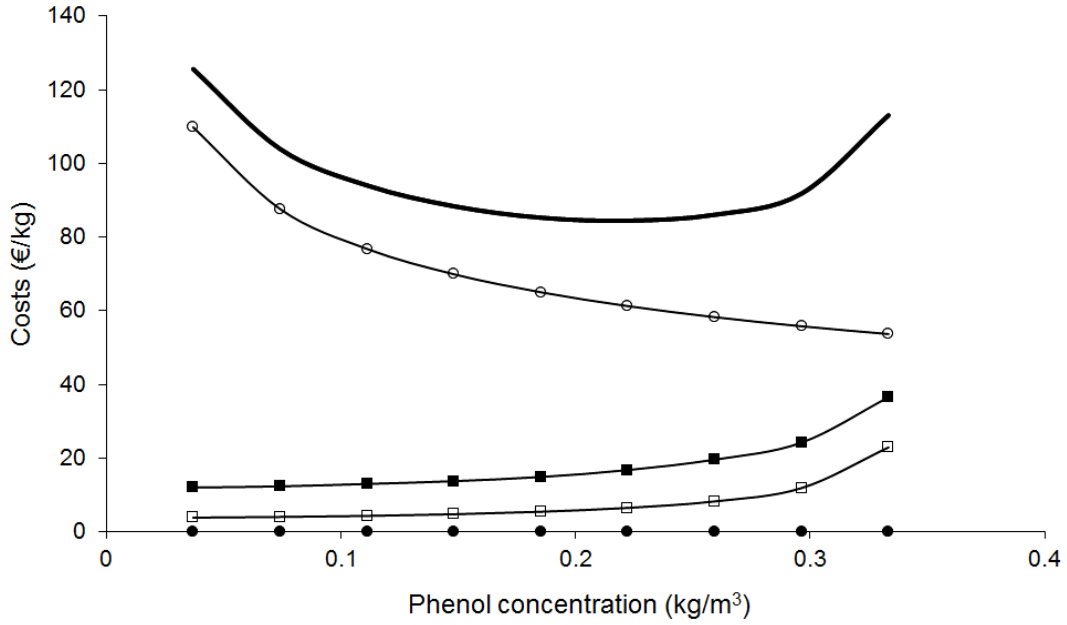

Fig. 12. Recovery of phenol by adsorption as function of the concentration in the fermentor.

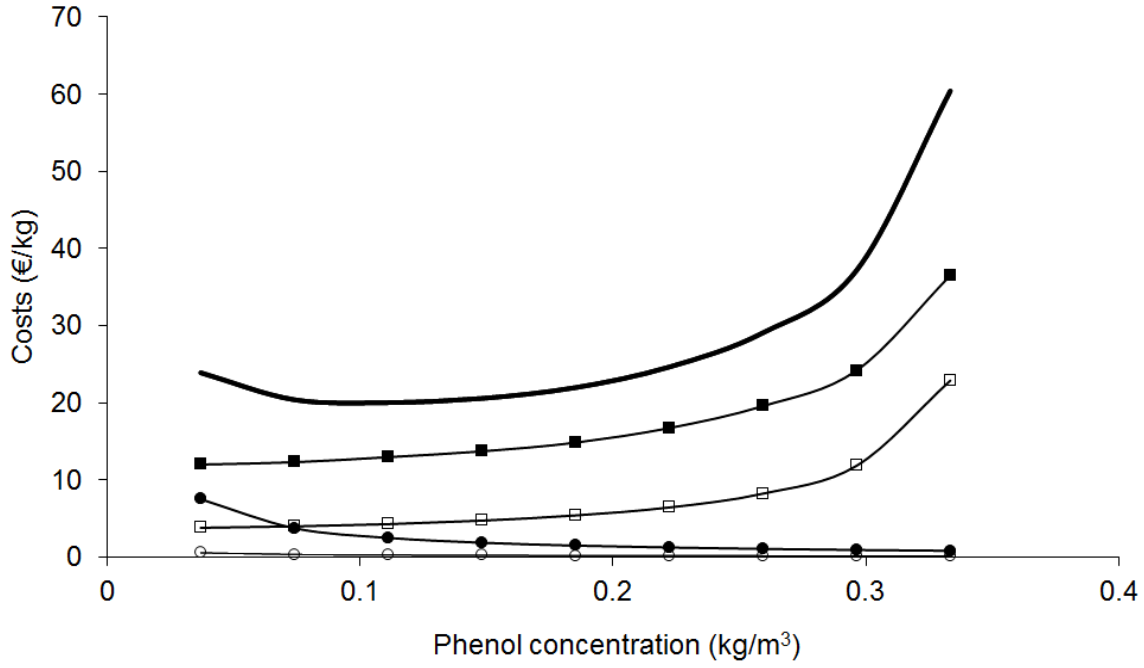

Fig. 13. Recovery of phenol by pertraction as function of the concentration in the fermentor.

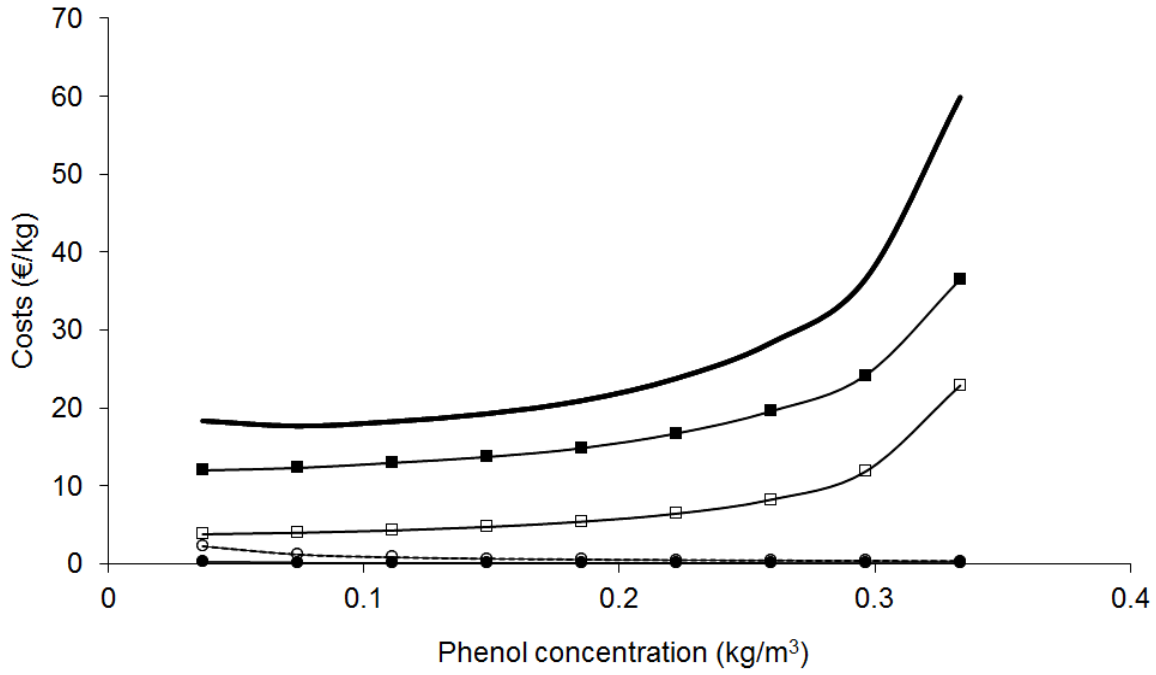

Fig. 14. Recovery of phenol by extraction as function of the concentration in the fermentor.

6.6. Conclusions

Cost predictions for the biological production of lactic acid, butanol and phenol, using integrated product recovery techniques, have been constructed. The cost predictions are a result of the application of the shortcut methods derived in this paper, as shown in Sections 6.3 and 6.4.We believe the accuracy of the methods to be such that the behavior of cost trends in Section 6.5 is correct. However, the absolute cost values are still rough approximations. Therefore, the shortcut method may be used to quickly select the process option to be developed further and to be analyzed in much more detail according to conventional methods. The three chemicals show a wide range of physical properties and fermentation parameters resulting in different cost contributions. Whenever the product recovery operation is efficient at low concentrations or inexpensive, the production by fermentation can take place at lower product concentration. Both the operational and capital expenditure can be the dominant cost factors. Specifically, one can conclude that lactic acid production should benefit the most from integrated recovery by extraction. However, in this manuscript no comparison has been made with other configurations such as batch fermentations with a coupled recovery. According to the current analysis, recovery of butanol should be performed using adsorption, although it should be noted that extraction and pervaporation have TMC values relatively close to those of adsorption. The scale of the

process can also have a significant impact on relative costs of each of the product recovery units. Integrated product recovery can be an important tool when a lower TMC need to be reached for phenol and should be performed using extraction. Phenol yields on glucose decrease with increasing phenol concentrations, resulting in an additional beneficial effect of integrated product recovery.

6.7. Recommendations for model refinement

The costs calculations of the DSP have an accuracy dictated by the applied method and do not take auxiliary phase regeneration in specific detail into account.

A method to estimate CAPEX costs for DSP regeneration operations is to link the overall heat duty of the regeneration step to CAPEX requirements [70]. By adding the specific CAPEX for regeneration operation to the already calculated CAPEX, as describe in this paper, the regeneration of the auxiliaries, e.g. the solvent phase or adsorption material, can be taken into account.

Regeneration can be in the form of back-extraction, temperature based regeneration or distillation. This refinement will further require the calculation of specific heat duties during regeneration and so product and process dependant properties need to be taken into account for each separation technique. E.g. butanol recovery from an organic solvent can be done by distillation and one would operate the distillation column making use of the existence of an azeotropic point in butanol/water mixtures. Furthermore the OPEX of the DSP can now be recalculated as more detailed energy requirements are available.

6.8. References

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Appendix A. Nomenclature

A	area	(m^2)
a	volume-specific area	(m^2/m^3)
C	concentration	($kmol/m^3$)
Capex	capital expenditure	(*Euro/year*)
CT	costs	(*Euro/kg*)
d	diameter	(*m*)
D	diffusion coefficient	(m^2/s)
EC	equipment or material costs	(*Euro/unit*)
ΔH	mass-specific enthalpy change	(*kJ/kg*)
F	product flow	(*kg/h*)
J_0	initial flux	($kg/(m^{2\cdot}h)$)
K_{ov}	mass transfer coefficient	(*m/s*)
k	mass transfer rate	(*1/s*)
L	length of hollow fiber	(m^3)
Opex	operational expenditure	(*Euro/year*)
M	mass	(*kg*)
N	number	(-)
p	partition coefficient	(-)
q	adsorbed concentration	(*g/g*)
Q_h	mass-specific heat	(k*J/kg*)
Q	volumetric-specific productivity	($kg/(m^3/h)$)
Q_{fer}	productivity fermentation	(*kgl/h*)
R	particle size	(*m*)
S	selectivity	(-)
T	temperature	(*K*)
X	mole fraction	(-)
Y	yield	(*kg/kg*)
V	volume	(m^3)
W	mass-specific work	(kJ/kg)

Greek

β	inhibition constant	(-)
Δz	axial distance	(*m*)
ε	porosity	(-)
η	energy efficiency	(-)
Φd	solvent phase hold-up	(-)
ν	flow-rate	(m^3/s)
φ	volume flow rate	(m^3/h)

Superscript

perm	permeate phase	(-)
feed	feed phase	(-)

Subscript

aq	water phase
b	boiling
c	crystal
crit	critical
eff	effective
Ferm	fermentation
Fus	fusion
i	internal diameter of hollow fiber
m	melting
max	theoretical maximum
mem	membrane
mix_set	mixer settler
pervap	pervaporation
org	organic phase
ov	overall
p	product
p/s	product on substrate
rec	recycle
SH	Sherwood
Vap	vaporization
Vs	Sauter mean drop-size

Appendix B. Cost-relations for recovery[a] and fermentation

$$\text{Fermentation vessel CAPEX} = (a \cdot V_{ferm}^{b} + c) \cdot 4.93/12 \quad [72]$$

a = 10035 [euro/m3]

b = 0.608

c = 54840 [euro]

$$\text{L–L extraction CAPEX}_{mix\_set} = (a \cdot V_{mix\_set}^{b}) \cdot \frac{4.93}{12} \quad [73]$$

a = 161194 [euro/m3]

b = 0.448

$$\text{Adsorption CAPEX}_{adsorp} = M_{zeolite} \cdot EC_{zeolite} + (a \cdot V^{b} + c) \cdot \frac{4.93}{12} \quad [74]$$

a = 7650 [euro/m3]

b = 0.347 [due to packing relatively size insensitive]

c = −11525.6 [euro]

$$\text{Pervaporation and pertraction CAPEX}_{pervap} = A_{mem} \cdot EC_{mem} + N_{units} \cdot EC_{unit} \cdot \frac{4.93}{12} \quad [74]$$

[a] Capex functions for regeneration of auxiliary phase is assumed in the costs calculations to have the same process time-constants as the initial dsp operation; to take regeneration into account the calculated dsp capex is doubled if a regeneration step is involved.

Lang-factor breakdown [Ref 75]

1 Major equipment, total purchase cost (PCE)		
f1	equipment erection	0.4
f2	piping	0.7
f3	instrumentation	0.2
f4	electrical	0.1
f5	Buildings, process	0.15
f6	utilities	0.5
f7	storages	0.15
f8	site development	0.05
f9	ancillary buildings	0.15
2. Total physical plant costs (PPC)		
PPC = PCE x (1 + f1 +…+ f9)		
f10	design and engineering	0.3
f11	contractor's fee	0.05
f12	contingency	0.1
Fixed capital = PPC x (1 + f10 + f11 +f12)		
Total fixed capital is:		PCE x 3.4 x 1.45 = PCE x 4.93

Appendix C. Cost table

Property	Unit	Costs euro /unit
Glucose	kg	0.25
Electricity	kWh	0.05
Solvent	kg	1.5
Adsorbent material	kg	25
Membrane area	m^2	250
Membrane housing	$900m^2$	1333
Zeolite	kg	30
Calcium hydroxide	kg	0.110
Hydrochloric acid	kg	0.347

Chapter 7: Outlook to bio-based butanol recovery

7.1. Renewable bio-based butanol

1-Butanol has usage as not only a fuel, but also as organic chemical. The world chemicals consumption is at least 10 times smaller than the world fuel consumption. The strong focus in society on renewable production of fuels and of bulk chemicals coincides for butanol and explains the high interest for this compound, as not just an alternative biofuel.

7.2. Butanol from carbohydrates or hydrocarbon

When looking to the future it can be worthwhile to note the past. In the past century, for commercial production of butanol a competition took place between microbial production using carbohydrate feedstocks and the newly arising hydrocarbon based petrochemical industry. This competition was impressively won by the petrochemical industry, becoming completely market dominant. Multiple market reasons determined the outcome, but the main factor was the abundance of low priced feedstock, oil. This oil dominance led to the further development and optimization of oil refineries. When developing new (or old) bio-based butanol production processes, one should realize the shear amount of research, infrastructure and investment made into petrochemical processes. Direct competition will be hard to almost impossible, as long as the boundary conditions do not change. The most dramatic boundary condition is the availability of fossil fuels, which will inevitably run out, but as long as fossil fuels are available their usage will continue.

Major differences exist between petrochemical and microbial based production systems, the more dramatic being the living nature of microbes. This difference translates into a phase difference to exist in the production processes, where the microbial systems have a need for aqueous production vessels (fermentors), and where most conversions in the petrochemical industry occur in an organic environment, with water being mostly used for heating and cooling in the form of steam. The aqueous fermentation systems will be predominantly water with relatively low amounts of organic product. In the case of butanol this can be up to 30 g/L of butanol product [1]. For less inhibiting biochemicals this can excess 100 g/L. Crude oil can contain a small water mass fraction, but the organic product content in petrochemical streams far exceeds fermentation stream product content and can approach 100 %. Due to the volatile nature of most important petrochemical products and the possibility to separate them based on difference in boiling point, distillation has grown into the downstream processing method of choice. Distillation requires energy input to enable

the phase change of liquid phase organic compounds to gaseous phase purified products and is therefore energy intensive. Heat exchange equipment and heat integration methods allow recovery of substantial amounts of heat at the cost of capital investment. The frequent use and state of development of distillation as recovery method means that the shear amount of investments made in distillation and the already existing equipment makes distillation a logical choice for the recovery of butanol. However, one should realize that the original design for distillation (excluding liquor production, as it is a added value consumer commodity) is based primarily on organic feed phase handling. The short term solution for most butanol recovery problems will be distillation, but the scientific development of alternative future separation methods is required, as, most definitely, the basis of the production systems have changed.

7.3. Microbial production of butanol: feedstock

Microbial production of butanol requires feedstock and microbes to convert the feedstock into desired product, making the matching between feedstock and microbe important. Feed sugars or so called first generation feedstocks are seen as directly competing with human food market. Direct usage of these feedstocks is unethical as long as food shortage or high food prices exist and non-food lignocellulosic material is thus the future feedstock of choice. As can be seen from the amount of focus on feedstock utilization, feedstocks have different forms and composition [2,3], and various methods of converting the feedstocks into substrates for later microbial or chemical conversion [4]. If possible, one would want to introduce the concentrated raw feedstock without purification into the fermentation process. The fermentation stability and thus the duration of the fermentation can be significantly impacted by the presence of inhibiting compounds [5,6]. For most fermentations a coupling exist between 1) the feedstock and thus feedstock composition 2) microbial production yield and 3) microbial productivity. The downstream processing can also be significantly impacted by components present in the feed material, but this has not been systematically studied yet. Due to these factors, the economic value of butanol production is a complex function of feedstock properties and therefore local conditions and geographic considerations determine when and where butanol can be produced economically.

7.4. Microbial 1-butanol production: optimization

Butanol can be produced by bacteria [7] and even yeasts [8]. Besides 1-butanol, 2-butanol or iso-butanol can be produced. Classic fermentation is by clostridium based Acetone-Butanol-Ethanol (ABE) fermentation. Metabolic engineering has focussed on obtaining a production strain with enhanced solvent tolerance to allow higher titers [9] or enhanced product yield, e.g. maximizing the amount of butanol produced [1,10]. Production of the cell material itself limits the overall butanol yield on substrate. Operation close to maintenance conditions can limit growth and maximize the product yield, as long as butanol formation leads to net ATP production. By using a cell free synthesis approach, immobilized enzymes needed for desired conversions are used and thus further biomass production is avoided; of course such a system can no longer be seen as a fermentative process [11], but it may be less sensitive to butanol toxicity.

Butanol production (by clostridia) is often associated with butyric acid production, preceding butanol formation. Producing butanol almost exclusively, avoiding an acidic production phase altogether, has been achieved using *E. coli* [1]. However, reaching unlimited product titers is an unlikely feat for any micro-organism [6] and most probably for butanol fermentations the actual total solvent concentration will always be below 50 g/L. From a downstream processing perspective it is always beneficial to enhance the butanol concentration, especially for thermal based recovery methods like distillation. The largest benefit in reducing downstream processing costs is gained when going from low concentrations to slightly higher concentrations. Later rates of returns of increases in concentrations are lower.

One way to limit the build-up of inhibiting compounds in the fermentation broth is to convert butanol in-situ to a new product. This is feasible when simultaneously performing an enzymatic reaction in a two phase system between e.g. short chain acid and butanol [Patent van den Berg, Straathof, v.d. wielen 2011, patent application] or by combining two 1-butanol molecules to form dibutyl ether, which is an unlikely reaction in aqueous environment. If 1-butanol is the desired product, reaction-based removal is not an option.

7.5. Microbial 1-butanol production: integrated product recovery

1-Butanol is a fermentation inhibiting product, the removal of which will be beneficial for the fermentation. To that end (continuous) product removal techniques enhance process productivity, since the fermentation can be maintained [12]. If a batch would have to be stopped at 20 g/L butanol, and this concentration would be achieved after 10 h, for example, the downtime of the fermenter might exceed its production time. Only in theory in-situ product removal could allow indefinite continuous operation of the fermentation. To date most fermentations are carried out as extended fed-batch like operations. A large array of similar fermentation units can be scheduled consecutively in such a way that the overall production process works similar to a continuous plug flow reactor type operation [13]. Our analysis in chapter 6 shows 1-butanol fermentations, where the aqueous dissolved products reach modest to low titers, to be a system in which capital investment and operational costs, for both fermentation as downstream processing, to be similar in overall importance. 1-Butanol fermentations thus need to be optimized as an integrated production system in order to obtain true production cost optimization.

7.6. Recovery of bio-based butanol

Butanol needs to be removed from the fermentation broth and a (direct) phase transition is needed. However, many phase transitions are associated with a large enthalpy or entropy change.

The phase transitions shown in chapter 2 show the large (theoretical) list of recovery options. The odd-one-out is liquid to solid phase transitions as the fusion enthalpy is substantially lower in value. Basic guidelines and general engineering rules of thumb unfortunately (the current optimized state of affairs) say solid phase handling is not desirable, as it makes equipment design far more difficult. Also cooling below ambient conditions is associated with more operationally expensive (electrical) cooling by compression, unlike heating which can be done by steam. Not withstanding, freeze crystallization is, on its merits of enthalpy change, preferred over liquid to gas phase transition (distillation).

Compared to distillation other recovery techniques such as adsorption, extraction, and membrane techniques like pervaporation are definitely worthwhile. All listed techniques can be run in a (semi)-continuous like manner, with secondary product or (inert) feed component accumulation and fouling of the system being the last hurdle to be taken. E.g., thermal based recovery is unable to remove non-volatiles, and extractive process can’t

remove components with a low partitioning in the applied extractive phase. Due to the wide range of possible feedstock and possible contaminants, robust 1-butanol fermentation processes will require removal of those specific contaminants when they are (substantially) inhibiting the fermentation. Also membrane operations can be significantly impacted by (microbial) fouling of the membranes, leading to significant increases in pressure drop and an associated increase in operational energy requirement.

Smart choice of the phase manipulation is by constructing the newly formed phase out of product, for 1-butanol this can be done by phase manipulation of water and butanol mixtures, creating a binary liquid-liquid system one of which is an organic product phase. Fermentations that come close to 80 g/L product titers, will be extremely useful when looking at these liquid-liquid phase separations of water-butanol mixtures. Preferably such a phase separation is induced by a readily available low cost compound. For fermentations this can be either carbon dioxide or concentrated feedstock, as feedstock is required anyway. For longer running operations, especially if internal recycles are applied, maintaining volumetric flow profiles is difficult when applying low concentration feed material. Usage of concentrated feed streams thus limits the amount of feed flow into the production process.

Recovery by pervaporation is possible for butanol, and is mostly constrained by the low vapour pressure of butanol. Optimization of membrane structure and matrix to optimize butanol recovery is most often a trade-off between higher product fluxes and lower selectivity [14]. When this trade-off does not appear directly in reported data, this can most often be led back to the operation of the recovery system. By operating the system at higher or lower superficial flow velocities the apparent amount of membrane area can be manipulated, reporting different selectivities for the same membrane. Production at elevated temperature by thermophilic bacteria allows operation at higher temperature, which positively impacts the saturated vapour pressure of butanol. A large downside of fermenting at elevated temperatures is additional energy content of the fermentation broth, although heat can usually be taken from other process steps such as pretreatment, enzymatic hydrolysis and or sterilization operations, which are mostly carried out above 60 ^{o}C.

Adsorptive based recovery of butanol from the liquid fermentative phase with temperature swing regeneration of the sorbent (butanol vaporization) requires the recovery unit to both experience liquid and gas phase and the unit will experience large density difference between both phases, besides the possibility of liquid adhesion to the adsorption material,

which can also increase mass transfer problems. Any operation will need to be designed such a manner that the mechanical operation of having both liquid phase adsorption and gas phase recovery in the same vessel can be performed without damaging the system. Also this density difference in phase can pose significant constrains on the sorbent agent.

Sorbent agent thus needs to be durable for both mechanically and temperature aspects. Adsorptive properties and mass transfer considerations will finally determine the composition of the basic adsorbent, its overall size and matrix (if e.g. a granulation process is applied).

For adsorptive based butanol recovery high-silica zeolite has been shown to be highly selective for butanol compared to water. Also the crystal structure can be chosen in such a manner that adsorption of feed components, like glucose, is avoided. Decreasing the hydrophobic nature of the sorbent agents will positively impact temperature based recovery at the cost of reduced adsorptive properties.

Adsorptive recovery of product from a gas phase auxiliary phase is also possible. This thesis shows the adsorptive liquid recovery of butanol. By first performing a stripping operation, butanol can be recovered from a gas phase, avoiding fouling of adsorbent by non-volatile contaminants and the mechanical stresses of liquid-gas handling in one unit operation. Recovery by adsorption from the gas phase is limited by the vapour phase fraction of butanol in the stripping gas (e.g. CO_2), which is most often low due to the low saturated vapour pressure of butanol. This directly leads to a high volumetric stripping gas requirement. As has also been mentioned for pervaporation, a thermophilic fermentation will change the gas to liquid equilibria conditions favourably. Gas phase adsorption using stripping gas approach is more beneficial when applied to intrinsically more suitable chemicals (defined here as better saturated vapour pressure in most phases), like ethanol.

Currently industrial recovery of bio-butanol is being performed by both Gevo Inc. and Butamax ™ advanced biofuels LLC. The product of interest is iso-butanol, and is used as biofuel or a precursor for chemical synthesis. The applied recovery strategy uses vaporization under vacuum and a combination of vapour phase manipulation with absorption and distillation [15]. Conditions for the vacuum, which vaporizes part of the fermentation liquid, are at a boiling temperature below 30^{o}C, so one can estimate a working pressure of approx. 500 to 3000 Pa. If the vapour phase contains 10 % butanol, energy duty calculations at 3000 Pa for vacuum formation, will give 8 MJ/kg. The vacuum step is followed by distillation also demanding additional energy. Estimates for flash fermentation of 1-butanol provide an overall energy requirement of 17 MJ/kg butanol, with the vacuum

step demanding 36 % of the energy requirement (6.1 MJ/kg) [16]. The overall energy requirement for vacuum based recovery like the Butamax proposed process, is close in range to most of the process options shown in the energy requirement tables 9 and 10 in chapter 2. Also, like for a standard distillation approach, this process involves only gas and liquid phase, but can be applied directly on the fermentation liquid, which simplifies the operation, making the vacuum based recovery a viable industrial recovery method.

7.7. Bio-butanol pricing

To estimate a cost price for bio-based 1-butanol I have increased the detail in the cost price calculations as shown in Chapter 6, outlined in paragraph 7. If one is able to bring down the total energy requirement of the recovery to approximately 3.5 MJ/kg of 1-butanol, the dsp would have a capital expenditure of 0.53 euro/kg and an operational expenditure of approx. 0.05 euro/kg. The fermentation costs are 0.35 and 0.41 euro/kg, respectively. Total 1-butanol cost price is 1.34 euro/kg. Finally, it should be noted that the cost price is directly related to feedstock price and constrained by the butanol concentration during fermentation. Future developments for feedstock price or 1-butanol fermentation conditions will directly influence the butanol cost price to a large extend.

7.8. Conclusions

Bio-based butanol production is achievable, as is currently demonstrated by new or remodelled butanol production facilities in China [17], the U.K. (Gevo Inc.) and the USA (Butamax advanced biofuels LLC, a joint venture of BP and DuPont). The future will see 1-butanol production to be integrated into existing and newly developed productions plants and dedicated facilities for solely 1-butanol production will not exist.

Butanol production strain development was focused on tolerance and product yield and has significantly progressed in recent years. In the coming years the focus will be on fermentation technology, and on usage of impure and mixed 2nd generation feedstocks.

Integrated product removal for 1-butanol is always an optimization problem of fermentative costs versus downstream processing costs, the phase transition of which will be initially via gas phase recovery, using distillation, or stripping combined with adsorption.

Butanol is only one of many green based chemicals and has the distinction to have favourable fuel characteristics and solvent properties. These two product aspects make sure butanol will be one of the chemicals produced in a future bio-based renewable industry. The amount of 1-butanol that inevitably will be produced is dependent on the value associated with butanol.

7.8.

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Propositions accompanying the thesis:
"Recovery of bio-based butanol"
by Arjan Oudshoorn

1) Research without basic questions leads to a lot of publications.

2) Paraphrasing Benjamin Franklin: "the weakness of democracy is the voter" is more relevant now than in his day.

3) In today's specialist society 'informed consent' places responsibility in the hands of the non-specialist.

4) Biofuels should have been named Sustainable Fuels.

5) Humans have great difficulty in coping with probability.

6) Applied Science is a subfield of History.

7) Sustainability in economics leads corporate views to refocus on corporate continuity.

8) Innovation is hampered by conservative business models and risk aversion.

9) A thesis is not a resume.

10) An Engineer should always apply Lefler's law # 36.

These propositions are regarded as opposable and defendable, and have been approved as such by the supervisor, Prof. Dr. Ir. L.A.M. van der Wielen.

Stellingen behorende bij het proefschrift:
"Terugwinning van bio-butanol"
door Arjan Oudshoorn

1) Onderzoek zonder fundamentele vragen levert veel publicaties op.

2) Benjamin Franklin geparafraseerd: "de zwakte van een democratie is de kiezer" is vandaag de dag meer relevant dan in zijn eigen tijd.

3) In de huidige specialistische maatschappij plaatst "toestemming op basis van informatievoorziening" de verantwoordelijkheid bij de niet-specialist.

4) Biobrandstoffen hadden duurzame brandstoffen moeten heten.

5) Mensen hebben moeite om te gaan met waarschijnlijkheid.

6) Natuurwetenschap is een onderdeel van Geschiedenis.

7) Duurzaamheid in economie zorgt ervoor dat bedrijfsvisies zich weer richten op de continuïteit van het bedrijf.

8) Innovatie wordt gehinderd door conservatieve bedrijfsmodellen en risicoaversie.

9) Een proefschrift is geen curriculum vitae.

10) Een ingenieur moet altijd Lefler's Law 36 toepassen.

Deze stellingen worden opponeerbaar en verdedigbaar geacht en zijn zodanig goedgekeurd door de promotor, Prof. dr. ir. L.A.M. van der Wielen.