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# Separation technology - Making a difference in biorefineries

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**Keywords:** Separation technology, Biomass conversion, Process intensification, Biorefinery

## Highlights

- Separation and purification accountable for largest part of costs in biorefineries
- Hybrid technologies based on process intensification ready to make a big difference
- Energy efficient separation technologies that require low CapEx and OpEx

## Abstract

In the quest for a sustainable bio-based economy, biorefineries play a central role as they involve the sustainable processing of biomass into marketable products and energy. This paper aims to provide a perspective on applications of separations that can make a great difference in biorefineries, by significantly reducing the costs and thus making the processes competitive without subsidies. A parallel is drawn between bio-refinery and petro-refinery, to highlight the specific separation challenges encountered in biorefineries and point out the impact of separations on the total costs. Existing and foreseen separations in biorefineries are reviewed, and the upcoming challenges in the bio-domain (additional to current fossil) are identified. Relevant industrial examples are provided to illustrate the tremendous eco-efficiency benefits of well-designed separation processes based on process intensification principles (e.g. reactive separations, dividing-wall column, affinity and trigger-enhanced separations). These examples also illustrate the low sustainability of several bio-separations currently practiced, in terms of high relative energy requirements, large amounts of gypsum co-production and/or excess use of caustic.

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## 1 **1. Introduction**

2 Biomass is nature's way of storing solar energy and is considered a renewable alternative to  
3 fossil resources. Biorefineries involve the sustainable processing of bioresources into a  
4 spectrum of marketable products and energy (IEA Bioenergy Task 42). However, this is not  
5 an entirely new concept, as biomass converting technologies (sugar, starch, pulp & paper)  
6 have been around for a long time and these can be partly considered as biorefineries. As the  
7 biorefinery concept evolved, a variety of criteria is used now for the taxonomy: technological  
8 implementation status, type of raw material used, main intermediate produced, conversion  
9 process applied, or a combination of these features (de Jong and Jungmeier, 2015).

10 Remarkably, the nature is fully able to operate efficiently with a mix of reactants that lead to a  
11 mix of products. Hence Mother Nature does not offer pure chemicals to the humankind. The  
12 chemical industry, on the other hand, developed along the line of using almost pure raw  
13 materials (obtained in pre-treatment steps) that are converted into a mix of products which are  
14 separated afterwards into pure components/intermediates. These are then combined to make  
15 materials with well-tuned and controlled structures and properties. Thus, purity is (so far) the  
16 key to control these processes.

17 A comparison between the oil refineries and biorefineries will help to put things into context  
18 and show the role of separation technology in both cases. Figure 1 illustrates this analogy. A  
19 classical refinery transforms fossil sources (oil & gas) into energy, fuels, and chemicals. The  
20 raw materials are converted first into building blocks, from which more valuable  
21 intermediates and end-user products are obtained. The separation and purification steps in oil  
22 refineries typically use distillation technologies (along with liquid extraction, crystallization,  
23 absorption, adsorption, membranes) that can account for 40-50% of the total costs (Kiss,  
24 2013). A biorefinery has quite similar functions to a classic refinery, but in this case the  
25 feedstock used is biomass instead of oil. In addition to the production of energy, fuels and  
26 chemicals, a biorefinery may also produce bioproducts such as food for humans and livestock.  
27 On the way to chemicals, the biomass is converted to biochemical building blocks, a set of  
28 functional molecules that are more suitable for organic synthesis. It is worth noting that all  
29 separation technologies applied in biorefineries are derivatives from the petro-chemical  
30 industry. As the balance in properties of the streams is different than the ones in petro-  
31 chemical industry, a different balance/emphasis in separation technologies could be expected.  
32 The biomass pre-treatment step (involving mainly phase separations, but also size reduction,  
33 removing dirt/sand, etc.) already leads to some primary products, and it is responsible for 20-  
34 40% of the total costs (Ramaswamy et al., 2013). Afterwards the conditioned biomass is used

1 on dedicated technology platforms where it is converted into products. These platforms are  
2 primarily determined by the chemistry routes and the feedstock composition (de Jong et al.,  
3 2012). Several technology platforms are available, such as: *biogas* (methane from anaerobic  
4 digestion), *syngas* (a mixture of CO and H<sub>2</sub> from gasification for Fischer-Tropsh synthesis),  
5 *hydrogen* (by steam reforming, water electrolysis, or fermentation), *C6 sugars* (hydrolysis of  
6 sucrose, starch, cellulose and hemicellulose), *C5 sugars* (hydrolysis of hemicellulose), *lignin*  
7 (from lignocellulosic biomass processing), *pyrolysis oil* or *bio-crude* (hydrothermal  
8 liquefaction oil, as obtained by a thermo-chemical biomass-to-liquid technology), *oils and*  
9 *fats* (from oil crops, algae and waste oils), *organic juice* (liquid after pressing wet biomass),  
10 *electricity and heat* (internal use or to grid). These platforms produce in most cases liquid or  
11 gas mixtures of components that require expensive separation steps contributing to the largest  
12 part of the total costs (Ramaswamy et al., 2013; de Jong and Jungmeier, 2015).

13  
14 While there are many recent books and reviews tackling the topic of biorefinery – mainly the  
15 pre-treatment and conversion steps (Centi and van Santen, 2007; Kamm et al., 2010;  
16 FitzPatrick et al., 2010; Cherubini, 2010; Naik et al., 2010; Pandey and Kim, 2011;  
17 Bridgwater 2012; Aresta et al., 2012; Stuart and El-Halwagi, 2012; Pandey et al., 2015; and  
18 others) – there are only very few publications dedicated to the (role of) separation technology  
19 in biorefineries (Huang et al., 2008; Ramaswamy et al., 2013). These latter papers give an  
20 overview of available separation technologies and discuss some applications, but no critical  
21 evaluation is made and no boundary conditions are provided for the actual applicability.

22 This perspective paper aims to fill this gap, by identifying the key challenges (caused by  
23 reactivity, polarity, dilution, complex matrix) and foreseen separations in the envisaged  
24 biorefineries, raising some warning signals with regard to several unsustainable separations  
25 that should be avoided, while indicating when certain separations are applicable or not by  
26 using relevant examples. An overview is given with regard to applications of separation  
27 technologies that can make a great difference in biorefineries by simplifying processes (less  
28 equipment) and reducing the operating costs (lower energy requirements), making the  
29 biorefineries more competitive even without any subsidy. The focus of this work is on the  
30 efficient separation (meaning molecular separation, not phase separation) of fluid mixtures  
31 using various technologies (e.g. reactive separations, advanced distillation, affinity and  
32 trigger-enhanced separations, etc). Several showcases are presented to illustrate the impact of  
33 separation on eco-efficiency.

34

## 1 **2. Challenges and opportunities for separations in biorefineries**

2 In addition to biomass conversion steps (including pre-treatment), separation and purification  
3 of biomass converted components into products is of utmost importance for biorefinery  
4 applications. Compared to conventional chemical processes, the separation in biorefineries  
5 may be severely hindered by factors, such as (in case of water-based biorefineries): low feed  
6 concentration, product inhibition issues, and/or low product yield leading to very diluted  
7 (aqueous) streams that resemble more waste water streams than typical chemical reactor  
8 effluents. Note that we assume mainly water-based biorefinery streams throughout this paper.  
9 However, we will occasionally consider other type of biorefinery stream where appropriate,  
10 e.g. streams that consist of pyrolysis or liquefaction oils and lipids.

11 Moreover, the presence of water and oxygenated compounds forming complex matrices and  
12 azeotropes constitutes an additional difficulty as compared to oil refineries. Another key  
13 aspect is the production of high-volume low-value biofuels and/or low-volume high-value  
14 chemicals. The economy of scale in the biorefinery domain is at a different level as compared  
15 to fossil based refineries, as the mass yield of product to feed is typically much worse (with  
16 very few exceptions) thus making the CapEx per kg product even more important. In many  
17 cases the separation part is the crucial factor determining the commercial success of  
18 biorefineries, as it accounts for the largest part of the total costs (Ramaswamy et al., 2013;  
19 Kiss et al., 2015).

20 To summarize, the challenges in separation technology for biorefineries relate to the presence  
21 of reactive mixtures, often temperature restricted to 150 °C, polarity of components present in  
22 the mixture, often much diluted aqueous solutions, and a complex matrix of organics that  
23 often contains also inorganic compounds with a detrimental effect on extraction. Examples of  
24 separation challenges foreseen in the biorefineries include among others:

- 25 • Concentration of oxygenates from water (aqueous streams), as for example acids (e.g.  
26 acetic, lactic, succinic, levulinic) and/or their corresponding salts; light oxygenates  
27 (e.g. alcohols, carbonyls); heavy oxygenates (e.g. sugars)
- 28 • Removal of sugars from a mix of phenols (e.g. from pyrolysis oil)
- 29 • Separation of lights from heavies, with similar molecular structure (e.g. bio-oil)
- 30 • Decontamination of sugar (e.g. removal of furanics/phenolics for fermentation, and  
31 removal of amino acids/ash for chemo catalysis)
- 32 • Fractionating (algal/microbial) biomass in lipids, proteins, carbohydrate rich fractions

33 With the risk of oversimplification, the novelty of many separation challenges relies on two

1 main characteristics of the streams, namely their thermal instability and high dilution. These  
2 challenges are partly compensated by an important opportunity: bio-based components are  
3 generally highly polar and functional hence offer opportunities for intermolecular affinities.

4 *Thermal instability* is a key issue in biorefineries since it hinders the workhorse of separation  
5 technologies, the classic distillation. Complex and reactive mixtures (prone to fouling) are  
6 obtained from processing of lignocellulose or sugar streams, and they contain hundreds of  
7 components as found in liquefaction and pyrolysis oil, or the sugar product stream from acid  
8 or hydrogenation/hydrogenolysis processes. The thermal instability results mainly from the  
9 presence high functionalized molecules, which contain reactive functionalities such as  
10 hydroxyls, aldehydes, ketones and carboxylic acid groups or furanic rings. The challenge is  
11 further worsened by the fact that biorefinery streams often consist of complex mixtures  
12 containing hundreds of components and often come at low pH (Lange, 2015). Dewatering the  
13 product may worsen the situation by increasing the concentration of reactive components and  
14 contained acids. This makes subsequent separation at high temperature (e.g. by distillation),  
15 unfavorable compared to alternative low-temperature separations (e.g. LLX, permeation). But  
16 a few alternative distillation technologies may still be worth considering, e.g. vacuum  
17 distillation, molecular distillation, short-path distillation, pass-through distillation. Such an  
18 example is the separation of phenolics from bio-oil (Elkasabi et al., 2014).

19 *Diluted (aqueous) solutions* require typically a pre-concentration before the actual separation  
20 and purification. Indeed biomass conversion often proceeds in diluted liquid phase e.g. as  
21 diluted sugar stream (e.g. sugar juice or starch/cellulose hydrolysate) or derivatives from such  
22 stream (e.g. after conversion of the diluted sugars to a variety of oxygenates such as alcohols,  
23 polyols, acids or furanics). High dilution often results in large reaction processing equipment  
24 and expensive separation schemes. The abundant solvent (generally water) is generally lighter  
25 than the desired product hence, re-concentration by solvent evaporation can be an expensive  
26 endeavor (due to the high enthalpy of vaporization of water). Alternative, non-distillative re-  
27 concentration may include precipitation (e.g. of acid salts), extraction (e.g. of furanics and  
28 phenolics) or ultrafiltration (e.g. of bio-oils and other high molecular weight products).

29 *Large feed variability* is expected in the feed streams entering the separation or purification  
30 stages in a biorefinery compared to the low variability in a regular oil refinery. This is clearly  
31 the outcome of the large diversity in terms of properties and content that the raw biomass may  
32 possess. Such variability may greatly affect the performance of the separation and purification  
33 processes and would require a very careful design of the processes in order to achieve their

1 targets. As variability may affect some process configurations more than other factors, with a  
2 direct economic impact, this issue has to be considered in the separation process selection.

3 *Feed detoxification* is a peculiar case of separation with diluted feed. Microorganisms used  
4 for sugar fermentation are often sensitive to low concentration of toxins such as acetate,  
5 furanic or phenolics. In contrast, chemical catalysts are more sensitive to either basic minerals  
6 (e.g. for acid-catalysis) and/or N-, S- and Cl-components (e.g. for hydrogenation) contained in  
7 the feed (Lange, 2015). New and inexpensive technologies for feed detoxification will likely  
8 become of prime importance. Owing to the low concentration of toxins, feed detoxification  
9 will likely include ion-exchange, adsorption, extraction or precipitation.

10 These separation challenges are particularly encountered in the front end of the biorefineries.  
11 Once these intermediate streams are upgraded to well-defined and thermally stable platform  
12 molecules, conventional distillation may come back as very effective approach. This does not  
13 mean that separation research ends here as biorefineries offer a wealth of opportunities in  
14 advanced distillations, e.g. azeotropic, extractive or reactive distillations.

15

### 16 **3. Applications of separations in biorefineries**

17 This section gives an overview of the main applications of key separation technologies in  
18 biorefineries, conveniently grouped here according to the separation mechanism. Additional  
19 details about each of these technologies are provided in the books of Seader et al. (2011), de  
20 Haan and Bosch (2013), Kiss (2013) and in particular Ramaswamy et al. (2013) who puts  
21 them in the context of biorefineries.

22

#### 23 **3.1 Phase-change separations**

24 *Distillation* processes are used in biorefineries for the separation and dehydration of alcohols  
25 (bioethanol and biobutanol), purification of biodiesel, isolation of volatile organic compounds  
26 (essential oils) and phytochemicals from biomass (extract), concentration of chemicals in  
27 pyrolysis oil and separation of various fractions (alcohols, aldehydes, ketones, acids,  
28 phenolics and sugars). A particular case is the steam distillation process that is used for the  
29 direct separation of the desirable components from solid (not liquid) biomass feedstock  
30 (Bergeron et al., 2012; Ramaswamy et al., 2013). Distillation is a prime candidate for  
31 purification of final low molecular weight products, but it is not convenient for high-boiling  
32 components, particularly when these are highly functionalized and thus temperature sensitive.

33 *Precipitation and crystallization* applications to biorefineries include: ethanol precipitation  
34 for recovery of hemicelluloses from the pretreated hydrolyzates (pre-hydrolysis liquor) and

1 spent liquors from pulp mills, precipitation by acidification using CO<sub>2</sub> or sulfuric acid applied  
2 to extract lignin from kraft black liquor, separation of succinic acid from fermentation broth  
3 or proteins from aqueous solutions (Huang et al., 2008; Ramaswamy et al., 2013).

4 **Filtration** is an established solid-liquid separation technology (Sparks and Chase, 2015). As  
5 solid biomass is typically the starting feedstock in biorefineries, a number of solid-liquid  
6 separation tasks (including filtration) are involved, such as the separation of prehydrolyzate  
7 and post-distillation slurries. Hence the use of efficient and cost-effective filtration processes  
8 is important for improving the overall process performance (Ramaswamy et al., 2013).

9

### 10 **3.2 Affinity-based separations**

11 **Liquid-liquid extraction** (LLX) plays an important role in biorefineries, being used for  
12 separating biofuels (bioalcohols) and chemicals (carboxylic acids) from dilute mixtures  
13 (fermentation broths), extraction of acetic acid from biomass hydrolysates using mixed  
14 solvents, extraction of 5-hydroxymethylfurfural (HMF) from an aqueous reaction solution  
15 using methyl isobutyl ketone (MIBK) as solvent, removing inhibitors from biomass hydro-  
16 lyzates and various impurities (soap, methanol, and glycerol) from biodiesel, extraction of  
17 chemicals (aqueous extractions, or extraction with hydrophobic-polar solvent and antisolvent)  
18 of fast pyrolysis bio-oils, and extraction of succinic, maleic, lactic, and itaconic acids with  
19 ionic liquids, or by reactive extraction using amines (Huang et al., 2008; Ramaswamy et al.,  
20 2013). The main advantage of using LLX is in the recovery of (diluted) components that are  
21 boiling at higher temperature than the solvent (water) and are thermo-sensitive. Extraction  
22 avoids or minimizes the need to distil out huge amounts of water, which is very energy  
23 intensive. Depending on concentration and nature of the solute, reactive extraction with e.g.  
24 amines could be required due to the low extractability with physical solvents such as MIBK.  
25 Relatively low boiling solutes (e.g. acetic acid) can be stripped readily from such composite  
26 solvents (amines diluted in MIBK, 1-octanol or other diluents). For higher boiling solutes  
27 (e.g. lactic acid), direct thermal regeneration is not feasible due to stability issues of both  
28 solvent and solute. In such cases, extraction – back-extraction is applied (Krzyzaniak et al.,  
29 2014), aiming at concentrating the solution to the max, prior to further thermal purification.

30 **Supercritical fluid extraction** (SFE) using CO<sub>2</sub> is very suitable for extracting hydrophobic  
31 constituents from biomass, e.g. recovery of value added phytochemicals (pigments, phenolics,  
32 carotenoids) and lipids from microalgae (Huang and Ramaswamy, 2012). The advantages of  
33 SFE are speed (no surface tension, low viscosities, fast diffusivity) and selectivity (properties  
34 of a sc-fluid can be altered by varying pressure and temperature). But the requirements for



1 high pressures increases the process costs compared to conventional LLX, so SFE process  
2 should be used only where the advantages are major and offset the drawbacks. In many cases  
3 SFE is used with the intent to avoid water distillation. Notably, the evaporation of water costs  
4 in terms of thermal energy  $2.26 \text{ MJ kg}^{-1}$ , while the  $\text{CO}_2$  re-compression to supercritical  
5 conditions requires electricity up to  $0.54 \text{ MJ kg}^{-1}$  (i.e.  $\sim 1.3 \text{ MJ kg}^{-1}$  equivalent thermal energy  
6 when considering electricity generation).

7 **Solid-liquid extraction** (SLE) technology includes classic solid-liquid extraction, ultrasound-  
8 and microwave-assisted extraction, as well as pressurized subcritical liquid extraction.  
9 Biomass contains value-added co-products such as bioactive compounds and phytochemicals  
10 (phenolics, terpenes, sterols, enzymes, polysaccharides, alkaloids, toxins, and pigments) that  
11 can be extracted using SLE prior to or during conversion (Huang and Ramaswamy, 2012).

12 **Absorption** is used for the removal of acid gases ( $\text{H}_2\text{S}$  and  $\text{CO}_2$ ) from syngas prior to further  
13 conversion into methanol and diesel fuel, or  $\text{CO}_2$  capturing. A particular method is *reactive*  
14 *absorption* that combines the absorption of gases in liquid solutions with simultaneous  
15 chemical reactions. This method is used for gas treatment and purification, removal of  
16 harmful substances, and the production of various industrial chemicals (Yildirim et al., 2012).

17 **Adsorption** can be used in biorefineries for the efficient removal of inhibitors from biomass  
18 hydrolysate, separation and purification of biofuels and chemicals (dehydration of bioalcohols  
19 with molecular sieve), removal of impurities (glycerol, methanol, free fatty acids, soap,  
20 catalyst, metals, water and glycerides) from the raw biodiesel using magnesium silicate  
21 (Magnesol®) or magnesium silicate and bentonite as adsorbent (Ramaswamy et al., 2013).

22 **Simulated moving bed** (SMB) is often used for separation processes by adsorption in the bio-  
23 domain: e.g. purification of glycerol from biodiesel production (using the Ambersep BD50  
24 resin, or gel-type acidic ion-exchange resin beads) where the raffinate stream contains salts  
25 and organic impurities including FFAs, purification of oligosaccharides (made up of xylose  
26 and arabinose units), isolation of lactic acid from acetic acid, separation of sugars (glucose  
27 and xylose) and EmimAc (IL) from the biomass hydrolysate (Ramaswamy et al., 2013).

28

### 29 **3.3 Size/charge-based separations**

30 **Ion exchange** (IEX) can be used in biorefineries for the removal of inhibitors from biomass  
31 hydrolysate (acid, salts), purification of biodiesel to remove impurities (FFA, glycerol,  
32 methanol, and soap using IEX resin Lewatit® GF202), separation of carboxylic acids,  
33 purification of succinic acid (IEXs are used for simultaneous acidification and crystallization)

1 and of xylose from biomass prehydrolyzates (Ramaswamy et al., 2013). Fortunately, IEX also  
2 trap other organics by means of adsorption.

3 **Membrane separations**, such as **microfiltration** (0.050-10  $\mu\text{m}$ ), **ultrafiltration** (1-100 nm),  
4 and **nanofiltration** (< 2 nm) can be used in biorefineries for the separation of biofuels and  
5 chemicals, depending on the molecules to be separated: e.g. removal of inhibitors (acetic  
6 acid), algal biomass harvesting, separation of hemicelluloses from biomass hydrolyzates (or  
7 process water of pulp mills), lignin recovery from pulp mill waste liquors or biomass  
8 prehydrolysis liquor, biodiesel separation and purification (Atadashi et al., 2011), separation  
9 of liquid mixtures (carboxylic acids recovery from dilute solutions), gas separation and  
10 purification (He et al., 2012; Ramaswamy et al., 2013). **Membrane pervaporation/pertraction**  
11 is a particular case – a highly selective, economical, safe, and eco-friendly technology – being  
12 a promising method for liquid-liquid separations in biorefineries, with applications such as the  
13 removal of inhibitory products from fermentation broth (Huang et al. 2008).

14 **Electrodialysis** is used in biorefineries for the separation of organic acids or carboxylic acids  
15 (acetic acid, oxalic acid, citric acid, gluconic acid, and succinic acid) from their fermentation  
16 broths (Huang et al., 2007), recovery of basic components such as mono-ethanol amine (de  
17 Groot et al., 2011), bipolar membrane electrodialysis for the production of organic bases (de  
18 Groot et al., 2011) and of lactic acid by continuous fermentation with an integrated product  
19 recovery process (Strathmann, 2010), as well as recovery of gluconic, ascorbic and succinic  
20 acids from their sodium salts (Wang et al., 2011; Ramaswamy et al., 2013).

21

### 22 **3.4 Reactive separations**

23 Mostly applied to equilibrium reactions (to drive the reaction to complete conversions) and in-  
24 situ product removal (where the products are removed to avoid the bio-/catalyst poisoning),  
25 reactive separation processes make use of process intensification principles to combine the  
26 reaction and separation step in single unit, thus leading to significant advantages in terms of  
27 eco-efficiency: high conversion/yield, enhanced selectivity, high productivity, improved  
28 energy efficiency, and less equipment (Schmidt-Traub and Gorak, 2010; Kiss, 2013).

29 **Reactive distillation** (RD) is applied in biorefineries to the production of succinate esters,  
30 fatty esters & biodiesel (Kiss, 2014), upgrade of flash pyrolysis oil, esterification of succinic  
31 and acetic acid from fermentation of biomass carbohydrates (Orjuela et al., 2011),  
32 esterification of glycerol to produce triacetin (Ramaswamy et al., 2013).

33 **Reaction-membrane separations** include membrane (bio)reactors, bioreactor-membrane per-  
34 vaporation/distillation. Membrane reactors can be used for biodiesel production (Kiss, 2014),

1 while fermentation-membrane pervaporation systems are used in butanol production (in situ  
2 product-recovery technology). For succinic acid production a fermentation-bipolar membrane  
3 electro dialysis system can be used (Ramaswamy et al., 2013).

4 **Extractive fermentation** applications in biorefineries include for example the extraction of  
5 butanol from the fermentation broth (Dhamole et al., 2012). Proposed configurations consist  
6 of fermentation integrated with in-situ product removal, as well as external product removal  
7 in an extraction column with a recycle of product-lean broth. Membrane-assisted solvent  
8 extraction can also be used for recovery and separation of organic acids, biofuels, and other  
9 chemicals (Ramaswamy et al., 2013).

10

### 11 **3.5 Technology selection**

12 Based on our (industrial) experience we can draw the following recommendation of selecting  
13 separation technologies and give the following initial rules of thumb.

14 → Distillation is a strong option under the following conditions:

- 15 ○ The temperature of thermal degradation of all components largely needs to  
16 exceed the reachable boiling point for distillates (at atmospheric or vacuum  
17 conditions).
- 18 ○ The difference in boiling point of products to separate needs to exceed 5 °C.
- 19 ○ The concentration of the distillate needs to exceed 10 %wt of the feed stream.

20 → Affinity separation is usable as an economical separation or pre-concentration method  
21 under specific conditions:

- 22 ○ Product and medium need to show significant differences in chemical affinity  
23 on at least one specific scale, e.g. acidity/basicity, polarity, H-bonding, etc.
- 24 ○ Low concentration of solute can be affordable if the affinity gap is sufficiently  
25 large to be exploited in an economical way.
- 26 ○ The extractant needs to provide a moderate level of bonding, i.e. not too weak  
27 to ensure efficient extraction but at the same time not too strong to allow  
28 efficient regeneration (Jongmans et al., 2012).
- 29 ○ Interactions of impurities (trace compounds) in the feed and the extractant need  
30 to be minimized.
- 31 ○ Very critical is an affordable sorbent recovery concept. This can be distillation  
32 (for extraction), thermal desorption (for adsorption), depressurization (for  
33 adsorption), or back extraction with a medium that is convenient for  
34 downstream processing.

1 → Permeation is a viable option for separation when the right materials are available

- 2 ○ The product and medium need to show large difference in diffusivity. This is
- 3 often related to molecular weight. However it can also imply difference in
- 4 chemical affinity, when the diffusion proceeds via selective ‘dissolution’ in
- 5 polymeric membrane, or in charge, i.e. in size of the solvated ion.
- 6 ○ The permeable materials should be able to cope with the large feed variability.
- 7 ○ The availability of affordable permeable materials (able to operate at extreme
- 8 conditions) is critical to such processes and must be evaluated at early stages.

#### 10 4. Evaluation of separation processes

11 Among others, process systems engineering (PSE) can contribute with shortcut methods that  
12 allow the techno-economic evaluations of separation processes. This section briefly provides  
13 some short cut methods to evaluate the cost of distillation and sustainability of separations. It  
14 is worth mentioning that mainly distillation and extraction, as well as micro/ultra/nano-  
15 filtration are used on large scale production in biorefineries, while other separation methods  
16 are still in research and development stage. However, in case of extraction the costs of  
17 recovery (often by distillation) determine the overall costs, while the cost of filtration largely  
18 depends on the cost of membranes (i.e. designated membrane area and type of material).

##### 20 4.1 Evaluation of distillation processes

21 The cost of process segments, including complex distillation trains, was reported to be largely  
22 dictated by the duty of their major equipment (Lange et al., 1996, Lange, 2001). Indeed, the  
23 investment cost (inside battery limit) of process segments of fuel and chemical plants was  
24 shown to correlate with their overall energy transfer duty according to the following equation  
25 (cost updated to 2014):

$$26 \text{ Investment cost (ISBL, \$M 2014)} = 4.7 * (\text{exchange duty [MW]})^{0.55} \quad (1)$$

27 Process flow modeling programs, which are now common tools for engineers, easily provide  
28 the equipment duties required by this equation. However, a well-converged and optimized  
29 process flow model may already be too demanding for a preliminary cost estimate. Simpler  
30 though cruder estimates may then become handy. A few decades ago, Rudd et al. (1973)  
31 eluded on such crude estimate by proposing to use the ratio ‘*feed flow / boiling-point*  
32 *difference*’ as indicator for distillation cost, e.g. for selecting the cheapest sequence of  
33 distillation columns for complex systems. However, they did not provide the support for this  
34 indicator, or any specific factor for converting this ratio into distillation cost. Building on this

1 concept, the new concept of *distillation resistance* ( $R_d$ ) – detailed in another dedicated paper  
 2 (Lange, 2016) – can be taken as good proxy for the overall duty of a complex distillation and  
 3 the overall distillation costs. This concept assumes that the thermal duty is determined by the  
 4 fraction of the top streams (which are vaporized and then condensed), and the difference in  
 5 boiling points of components to separate (which determine the reflux ratios).  $R_d$  is defined as  
 6 the sum of the individual ratio ( $F_i/\Delta T_i$ ) of all condensable distillates, where  $F_i$  is the mass  
 7 fraction [%wt on total feed intake] of each component and  $\Delta T_i$  is the temperature difference  
 8 [°C] between its boiling point and that of the first heavier component in the feed.

$$9 \quad R_d [100/^\circ\text{C}] = \sum F_i [\% \text{wt}] / \Delta T_i [^\circ\text{C}] \quad (2)$$

10 Simple distillations show  $R_d < 1$  and a duty of  $\sim 1 \text{ GJ t}^{-1}$  feed whereas demanding distillations  
 11 show  $R_d = 3-7$  and a duty of  $3-8 \text{ GJ t}^{-1}$  feed. Reasonable linear regressions are proposed to  
 12 relate  $R_d$  with reboiler and total duties, which allow estimating the OpEx and overall CapEx.

$$13 \quad \text{Thermal duty} [\text{GJ t}^{-1} \text{ feed}] = 1.1 \times R_d \quad (3)$$

$$14 \quad \text{Firing duty} [\text{GJ t}^{-1} \text{ feed}] = 0.6 \times R_d \quad (4)$$

$$15 \quad \text{OpEx} [\$ \text{ t}^{-1} \text{ feed}] = 5 [\$ \text{ GJ}^{-1}] * \text{Firing duty} [\text{GJ t}^{-1} \text{ feed}] = 3 \times R_d \quad (5)$$

$$16 \quad \text{CapEx} [10^6 \$, 2014] = 4.7 * (\text{Thermal duty} [\text{MW}])^{0.55} \quad (6)$$

17 The concept of distillation resistance is based on an average distillation quality. Such  
 18 assumption is reasonable when evaluating complex distillation trains that separate more than  
 19 5 streams. But care should be taken when stringent requirements are made on product purity  
 20 or product recovery, particularly when the evaluation is limited to a single and demanding  
 21 distillation. Also, when process intensification methods are employed (e.g. DWC technology)  
 22 the capital and operating expenditures should be reduced by about 25% (Kiss, 2013).

23 Besides the cost estimation of distillation, the energy efficiency of such processes can be also  
 24 estimated. Pleşu et al. (2015) proposed a simple equation that is easily usable in calculations  
 25 to evaluate the distillation sequence energy efficiency (DSE) for any alternative. DSE is  
 26 calculated as the sum of feed molar fractions ( $x_i$ ) multiplied by the product of column  
 27 efficiencies – which are equal to the Carnot efficiency for distillates, 100% for bottoms  
 28 product. In case of side stream products with boiling point higher than that of the feed, the  
 29 efficiency is 100% - otherwise it corresponds to the Carnot efficiency of the column.

$$30 \quad DSE = \sum_{i=1}^O \left( x_i \prod_{C=1}^N \eta_C \right) \quad (\text{maximize}) \quad (7)$$

31 where  $\eta_C$  is the Carnot efficiency of the column:  $\eta_C = (T_{\text{bottom}} - T_{\text{distillate}}) / T_{\text{bottom}}$ . Once DSE  
 32 is calculated, all the alternative solutions can be sorted from higher to lower efficiency.

1 Another simple criterion used especially when comparing various distillation alternatives with  
 2 each other is the  $N_S \times (RR+1)$  which is directly proportional to the total annual costs (Kiss,  
 3 2013). This product includes the number of stages ( $N_S$ ) that is proportional to the column  
 4 height  $h_c$ , and the reflux ratio + distillate ( $RR+1$ ) factor that is proportional to the column  
 5 diameter  $d_c$ . Furthermore,  $d_c$  is proportional to the production rate, while the reflux ratio +  
 6 distillate ( $RR+1$ ) multiplied with the distillate rate ( $D$ ) and the heat of vaporization ( $\Delta H^{\text{vap}}$ )  
 7 gives the energy requirements of the distillation column:

$$8 \quad C_{\text{shell}} = f_p (M\&S/280) d_c^{1.066} h_c^{0.802} \quad (8)$$

$$9 \quad C_{\text{hex (reboiler/condenser)}} = (M\&S/280) c_x A^{0.65} \quad (9)$$

$$10 \quad C_{\text{energy}} = (RR+1) D \Delta H^{\text{vap}} \text{ hours/year} \quad (10)$$

11 where  $f_p$  and  $c_x$  are cost factors, M&S is the Marshall & Swift equipment cost index, A is the  
 12 heat exchange area. Note that in contrast to the previous methods, such analysis requires a  
 13 short-cut or detailed modeling of the column, but is presumably more accurate.

14

## 15 **4.2 Evaluation of alternative separation processes**

16 The correlation between energy exchange duty and CapEx discussed above is not limited to  
 17 distillation but can be extended to other separation technologies that are energy intensive, i.e.  
 18 that require more than 10 MW energy exchange. Large-scale extraction likely meets these  
 19 requirements when the solvent is regenerated by means of distillation. Indeed, the solvent  
 20 distillation column is likely to dominate the cost of the whole extraction train. The cost  
 21 contribution of the extraction may then be accounted for by addition of a modest cost penalty  
 22 of up to 25%. By extension, the concept of distillation resistance  $R_d$  may also be of value for a  
 23 first estimate of CapEx. However, the accuracy might become questionable as only two  
 24 components are separated.

25 In cases of separation train based on extraction and back extraction, the correlation between  
 26 exchange duty and CapEx might not apply. The same is expected for other, more energy-lean  
 27 separation technologies e.g. based on crystallization, precipitation, membrane permeation or  
 28 ion-exchange. Other indicators need to be developed for such applications. One alternative  
 29 indicator could be the mass transfer flux involved in the separation. This approach was  
 30 proposed for evaluating the recovery of butanol, lactic acid and phenol from fermentation  
 31 broth by means of adsorption, pervaporation, extraction and pertraction (Oudshoorn et al.,  
 32 2010). The mass transfer flux was used to estimate the interfacial area and the vessel volume  
 33 required for separation. Various equations are then used to derive CapEx and OpEx from the  
 34 estimated separation volume. When applicable, the regeneration of the auxiliary phase was

1 accounted for by doubling the CapEx and OpEx, with the assumption that regeneration  
2 follows the same limitations (e.g. same time constant) as the separation itself.

3 In case of membrane filtration, Pilutti and Nemeth (2003) reported capital costs of membrane  
4 systems starting at 198-462 \$ m<sup>-3</sup> (0.75-1.75 \$ gal<sup>-1</sup>) for a permeate capacity of 157-315 m<sup>3</sup> h<sup>-1</sup>  
5 (1-2 MGD, million gallons per day), but dropping fast to about 105 \$ m<sup>-3</sup> (0.4 \$ gal<sup>-1</sup>) at 788  
6 m<sup>3</sup> h<sup>-1</sup> (5 MGD) and even 53-106 \$ m<sup>-3</sup> (0.2-0.4 \$ gal<sup>-1</sup>) at capacities of 1577-6309 m<sup>3</sup> h<sup>-1</sup> (10-  
7 40 MGD). The capital costs include membranes, skids, racks, compressors, blowers, pumps,  
8 piping, instrumentation, controls, and other components needed for a complete and operable  
9 system. However, the operating costs are more difficult to estimate as they depend on many  
10 factors including water quality, flux, recovery, pretreatment, and cost of consumables.

11 In a more recent study, Movahed (2010) estimated MF/UF capital costs in the range of 160-  
12 320 \$ per m<sup>3</sup> day<sup>-1</sup> (0.6-1.2 \$ per GPD) permeate capacity, and operating & maintenance costs  
13 (O&M) costs of 0.08-0.1 \$ m<sup>-3</sup> (0.3-0.4 \$ Kgal<sup>-1</sup>) with overall water costs of 0.1-0.16 \$ m<sup>-3</sup>  
14 (0.4-0.6 \$ Kgal<sup>-1</sup>). These costs include equipment, piping, controls, membrane replacement,  
15 chemicals and power but do not include building, site work, and finished water pumping.

16

### 17 **4.3 Critical evaluation of sustainability**

18 Sustainability of processes can be evaluated based on various metrics, such as the life-cycle  
19 analysis (LCA), eco-cost value (EVR) ratio, (socio-)eco-efficiency analysis, or the AIChE  
20 sustainability index (Dimian et al., 2014). It should be realized here that all separation must be  
21 economically and environmentally sensible. For instance, one needs to ensure that the value  
22 of the targeted product exceeds the recovery cost. This may imply that the energy required for  
23 recovering and purifying a bio-fuel component needs to remain a modest fraction of the  
24 heating value of the product itself.

25 One specific example of a bio-fuel is n-butanol, a fuel with an energy content of 36 MJ kg<sup>-1</sup>.  
26 Garcia-Chavez et al. (2012) calculated that a traditional thermal separation (two-distillation  
27 columns with a decanter after the first column to pass the heterogeneous azeotrope) uses  
28 about 21.3 MJ kg<sup>-1</sup> to concentrate the n-butanol out of a 1 wt% solution, which is almost 60%  
29 of the energy content of butanol. In contrast, a process based on liquid extraction would only  
30 cost about 15% of the energy content, of which the majority was spent on evaporation of co-  
31 extracted water. Even less energy consuming (3.76 MJ kg<sup>-1</sup>, 10.4% of the energy content of n-  
32 butanol at a comparable feed concentration range of 0.4-1.2 wt%) is the dual extraction  
33 process proposed by Kurkijärvi et al (2014), which benefits from one more hydrophilic  
34 solvent and one more hydrophobic solvent to reduce the losses of solvent to the raffinate and

1 simultaneously reduces the heat required to evaporate co-extracted water. The efficiency of  
2 extraction processes is thus highly dependent on the selectivity of the solvent and the more  
3 selective, the less energy spent on evaporation of water. A similar conclusion can be drawn  
4 for a wider spectrum of separation technologies based on the overview papers of Oudshoorn  
5 et al. (2009) and Huang et al. (2014). Oudshoorn et al. (2009) considered a variety of  
6 technologies to recover n-butanol from fermentation broth and developed short-cuts for  
7 estimating their energy requirement. Not surprisingly, the separation selectivity appeared to  
8 largely dictate the energy efficiency of separation across all technologies. In fact, few  
9 technologies appeared to have an energy requirement that is lower than ~10% of the heating  
10 value of n-butanol ( $36 \text{ MJ kg}^{-1}$ ). Figure 2 – based on the work of Oudshoorn et al. (2009) –  
11 gives an overview of these technologies for butanol recovery.

12 Next to biofuels, also production of chemicals using fermentation is hindered by the typically  
13 low concentrations. To illustrate the effect of the concentration of the solute in the ferment-  
14 ation broth on energy demand of the recovery, Figure 3 plots the steam costs as function of  
15 the broth concentration when a traditional distillation would be used to separate the binary  
16 acetic acid / water mixture. When the steam cost is higher or equal to the product price then  
17 the process is obviously not economically feasible. A typical value aimed for is to have  
18 energy costs that are about or even less than 10% of the product price. It clearly follows that it  
19 is economically infeasible and unsustainable to recover acetic acid by distillation from the  
20 various fermentation processes, e.g. from a glucose fermentation to produce acetic acid in 5  
21 wt% concentration, or from a fermented wastewater with only 1 wt%. In traditional liquid  
22 extraction processes so called physical solvents are used, for example using ethyl acetate as in  
23 the text book example of Seader et al. (2011). With these solvents, distributions below unity  
24 are observed (IJmker et al. 2014), and the reduction in heat duty of approximately a factor of  
25 three is mainly due to the easier recovery by distillation than the initial process. For example,  
26 Seader et al. (2011) make advantageous use from a heterogeneous azeotrope. However,  
27 Figure 3 clearly shows that these physical solvents will not enable economic processes to  
28 recover acids from fermented wastewater, as the energy costs are higher than 10% of the  
29 product price. Chemically active solvents contain an extractant that complexes the acid,  
30 resulting in much higher distribution coefficients (Krzyzaniak et al., 2013; IJmker et al. 2014;  
31 Reyhanitash et al., 2015), but recovery of the acids from these complex-forming solvents is  
32 not as easy as from a physical solvent and typically involves a back-extraction after which  
33 further treatment is required. This is a nice example of the dilemma mentioned earlier of  
34 selecting an extractant that is neither too weak nor too strong. For the future developments in



1 this field, there is a clear need for innovative process concepts, e.g. in the direction of CO<sub>2</sub>-  
2 enhanced extractions (Reyhanitash et al., 2015), that make a step reduction in the energy  
3 demand such that the recovery costs become much lower than the product price.

4 New developments on the liquid-liquid extraction of organic acids are not only important for  
5 the reduction of the energy usage during the recovery of the solvent, but also with respect to  
6 the co-generation of large amounts of gypsum as byproduct from fermentation-based acid  
7 productions. In the traditional approach the fermentation is treated with Ca(OH)<sub>2</sub> to maintain  
8 microbial activity also at higher acid concentrations, while the extraction is favored at low  
9 pH. Hence the treatment with H<sub>2</sub>SO<sub>4</sub> boosts the extraction efficiency, but co-generates large  
10 amounts of gypsum, e.g. for the industrial fermentative production of lactic acid this is about  
11 one ton of gypsum per ton of lactic acid, which is obviously unsustainable.

12 Although the focus in this section was limited to a single biofuel (n-butanol) and a single  
13 chemicals category (organic acids), the presented challenges in sustainable separations are  
14 certainly valid for a wide range of biorefineries, that typically deal with highly diluted streams  
15 and large amounts of water.

## 16 17 **5. Case studies of separations**

18 This section provides a selection of showcases, applicable to biofuels and chemicals, which  
19 illustrate the great impact of innovative separations in biorefineries.

### 20 21 **5.1 Advanced distillation**

22 Distillation remains a powerful separation technology, particularly at the high-value end of  
23 the biorefinery for the separation and purification of thermally stable and well defined  
24 components. New developments show much promises. Kiss (2013) illustrated the beneficial  
25 use of dividing-wall column (DWC) technology in the production of biofuels, leading to  
26 significant capital and energy savings. Of particular interest is bioethanol, a renewable fuel  
27 produced by various routes (corn-to-ethanol, sugarcane-to-ethanol, integrated lignocellulosic  
28 biomass-to-ethanol) in which the raw materials undergo several pre-treatment steps before  
29 entering the fermentation stage. All these technologies produce diluted bioethanol (typically  
30 5-12 %wt ethanol) that is further concentrated to reach the requirements of the international  
31 bioethanol standards. To reach the purity targets, an energy demanding separation is needed in  
32 practice, in order to overcome the presence of the binary azeotrope ethanol-water (95.63 %wt  
33 ethanol). The separation is typically carried out by distillation, the first step being a pre-  
34 concentration distillation column (PDC) that increases the ethanol content from 5-12% up to

1 91-94 %wt. The second step consists of the ethanol dehydration, up to concentrations  
2 exceeding the azeotropic composition. Quite a number of separation alternatives are available  
3 as described in the literature: pervaporation, adsorption, pressure-swing distillation, extractive  
4 distillation, azeotropic distillation, and hybrid methods combining these options (Vane, 2008).  
5 Among them, extractive distillation (ED) is still the option of choice in case of large scale  
6 production of bioethanol fuel. Typically, ED is performed in a sequence of two columns, one  
7 being the extractive distillation column (EDC) which separates ethanol, while the other one is  
8 the solvent recovery column (SRC) that recovers the mass separating agent that is recycled  
9 back in the process. Further improvements to the extractive distillation process were  
10 proposed, with the aim to increase the energy efficiency of bioethanol purification. One that  
11 stands out is a novel heat pump assisted extractive distillation process, based on mechanically  
12 driven heat pumps (Kiss and Infante Ferreira, 2016). This process efficiently combines vapor  
13 recompression (VRC) with dividing-wall column technology that allows the combination of  
14 all functions (three classic columns) into just one column – flowsheet shown in Figure 4 (Luo  
15 et al., 2015). Table 1 provides more details about the key performance indicators, including  
16 the total investment, operating and annual costs (Luo et al., 2015). Due to the use of a  
17 compressor and a larger side-reboiler required by the VRC system, the total investment cost  
18 of this VRC E-DWC process is about 29% higher than for the classical process, but this is  
19 compensated by the significant energy savings, which exceed 60% at a direct comparison.  
20 The specific energy requirements are only 4.46 MJ kg<sup>-1</sup> (1.24 kWh kg<sup>-1</sup>) ethanol for the novel  
21 VRC assisted E-DWC, thus energy savings of over 50% are possible as compared to other  
22 classic alternatives described in literature (Baeyens et al., 2015).

23

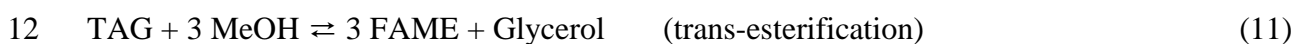
## 24 **5.2 Reactive separations**

25 Another opportunity of a bio-separation is reactive separation, being reactive distillation or  
26 reactive extraction, to circumvent difficulties in separation or in reaction (e.g. thermodynamic  
27 equilibrium or secondary product degradation).

28 **Reactive distillation** is an established technology, used for example in the recovery of acetic  
29 acid from aqueous liquors. Since acetic acid (normal boiling point of 118°C) is higher boiling  
30 than water, recovering acetic acid by traditional distillation from dilute streams is not  
31 economical due to the large amount of water that needs to be removed overhead. One method  
32 relies on recovering the acetic acid in a valuable form, such as acetate. When a reactive  
33 distillation process is carried out, in which the acetic acid reacts with methanol, the formed  
34 methyl acetate (n.b.p. 57 °C) is then recovered and easily separated over the top (Agregda and

1 Zoeller, 1993). More recently, Le et al. (2015) described a heterogeneous azeotropic  
2 distillation schemes in a DWC for a feed mixture of water, acetic acid and an organic  
3 component (isobutyl acetate) that acts as an entrainer. Remarkable, the proposed Petlyuk  
4 DWC system proposed achieves energy savings of about 20%.

5 Biodiesel production by reactive separations received significant attention during the past  
6 decade (Kiss, 2014). Being a mixture of fatty acid methyl esters (FAME), biodiesel is a  
7 renewable fuel used complementary to petro-diesel fuel. Its main synthesis routes are by  
8 either trans-esterification of tri-alkyl glycerides (TAG) or esterification of free fatty acids  
9 (FFA). Both routes use catalysts (homogeneous or solid acid / base catalysts) and can be  
10 applied in many types of industrial production processes (e.g. batch, continuous, supercritical,  
11 enzymatic, multi-step, reactive separations).



14 The trans-esterification is mainly base catalyzed, while the esterification is catalyzed by acids  
15 – although alternative acid/base catalysts could be used but at prohibitive reaction rates. The  
16 reaction time can be dramatically shortened by increasing the liquid-liquid interfacial area by  
17 various process intensification techniques – e.g. static mixers, micro-channels reactors,  
18 microwaves assisted reactors, ultrasound assisted reactors, rotating / spinning tube reactors  
19 and centrifugal contactors (Qui et al., 2010) – or by integrating the reaction and separations  
20 steps to pull the equilibrium to full conversions, e.g. reactive distillation (Kiss and Bildea,  
21 2012), reactive absorption, reactive extraction, reactive membrane separators (Kiss, 2014),  
22 and centrifugal contactors (Kraai et al., 2008). After the FAME synthesis stage, there are  
23 several down-stream processing steps required for catalyst neutralization and salt removal,  
24 alcohol recovery and recycle, as well as glycerol and biodiesel purification. Among the  
25 process intensification alternatives investigated, reactive distillation is the most promising  
26 option. Figure 5 illustrates a heat integrated reactive distillation process for fatty acids  
27 esterification, and a simpler one similar to reactive absorption (reactive column without  
28 reboiler and condenser). Table 2 provides the process parameters, whereas Figure 6 (Kiss and  
29 Bildea, 2012) compares the energy requirements for a classic two-step process based on pre-  
30 treatment of free fatty acids and trans-esterification of glycerides versus reported reactive  
31 separation processes based on esterification of waste oils with high FFA content (Kiss, 2014).  
32 The figures are worth noting, especially considering the on-going quest on increasing the eco-  
33 efficiency of biodiesel production. The specific energy use in reactive separation processes is

1 significantly lower than the FAME purification step alone in the conventional process. On top  
2 of the energy savings, the reactive separation processes benefit from lower investment costs  
3 and reduced plant footprint due to less equipment being used (Kiss and Bildea, 2012).

4 Levulinic acid can be converted to nylon intermediates adipic acid or caprolactam. Key  
5 processing steps include the hydrogenation to  $\gamma$ -valerolactone (gVL), transesterification to  
6 alkyl pentenoate and e.g. methoxy carbonylation to methyl adipate. The transesterification can  
7 be performed under reactive distillation conditions. The concept was demonstrated to achieve  
8 >95 mol% yield using various homogeneous and heterogeneous acids immersed in gVL with  
9 continuous feed of MeOH and stripping of Me-pentenoate entrained with MeOH vapor – as  
10 shown in Figure 7 (Lange et al., 2007).

11 Reactive distillation comes very handy for coupling levulinate ester with furfural to produce  
12 C<sub>10</sub> oxygenates that can be subsequently converted to C<sub>10</sub> hydrocarbons by hydro-  
13 deoxygenation (Lange et al., 2012). The coupling step is typically performed with an excess  
14 base (e.g. NaHCO<sub>3</sub>) and is followed by an acidification step to generate the acid form of the  
15 furfurylidene-levulinic acid intermediate. However, reactive distillation allows the use of a  
16 catalytic amount of base, e.g. solid base, by stripping water out of the medium and thereby  
17 avoiding hydrolysis of the ester and subsequent neutralization of the basic catalyst.

18 **Reactive extraction** is a very promising technology for the conversion of bio-based feedstock.  
19 Reactive extraction of cellulose-derived levulinic and formic acids with butene was proposed  
20 by Gürbüz et al. (2011) to obtain levulinate and formate esters, thereby allowing for recovery  
21 and recycle of sulfuric acid. The esters were converted over a dual-catalyst-bed system to  
22 GVL and 2-butanol, followed by production of butene to be recycled for reactive extraction  
23 and to be converted to liquid fuels by oligomerization.

24 Another example of reactive extraction can be found in the conversion of sugars to furans. For  
25 instance, bi-phasic systems were explored for the conversion of fructose to HMF, as reviewed  
26 by Kuster (1990). Similarly, Moreau et al. (1998) converted xylose to furfural using HY and  
27 HMOR zeolites at 170°C using biphasic systems (water/toluene or the less effective  
28 water/MIBK). Beyond improved yield, biphasic operation also allows to recover the diluted  
29 furfural by solvent extraction rather than by distillation of the water-rich furfural/water  
30 azeotrope. Bi-phasic systems were further developed for both furfural and HMF by the group  
31 of Dumesic who proposed an integrated process based on sugar dehydration, furanics  
32 recovery and furanics upgrading (Roman-Leshkov et al., 2006). It is worth noting the recent  
33 identification of alkylphenols, which were reported to be effective extractant for furfural even

1 at low extractant/water ratio and could be regenerated by simple distillation of furfural (Azadi  
2 et al., 2012). Such solvent could be produced from the lignin waste-product of the biorefinery.

### 4 **5.3 Triggered affinity separations**

5 The emphasis of this section is not so much on the extraction part that is typically the focus of  
6 most studies, but rather on the subsequent ‘non-distillative’ separation.

7 **Extractions with operational swings.** Following the reasoning above, the usefulness of  
8 thermal separations in biorefineries is limited to situations where reasonable concentrations of  
9 the desired products are obtained, e.g. bio-ethanol productions with yields of 5-12%. For  
10 more diluted systems, it is generally better to apply affinity separation, such as (reactive)  
11 liquid-liquid extraction. Often, and especially when the distribution ratios – defined as  
12  $[\text{solute}]_{\text{extract}} / [\text{solute}]_{\text{raffinate}}$  – are low, the concentration in the extract phase is low and the  
13 heat duty for direct thermal recovery from the solvent extremely high. Therefore, extraction –  
14 back-extraction cycles are commonly used, in which achieving a high concentration factor is  
15 aimed for in order to facilitate further purification, e.g. by crystallization. The traditional  
16 approach to increase the ratio between the distribution ratio in the back-extraction stage and  
17 the distribution ratio in the extraction stage is to apply a temperature swing, but also diluent  
18 swings may be applied (Krzyzaniak et al., 2013). The drawback of applying a diluent swing is  
19 the need for an additional recovery step, in which the preferably low boiling diluent is  
20 evaporated before the solvent is sent back to the primary extraction process. More recently,  
21 the use of CO<sub>2</sub> was reported to boost the distribution of acetic acid in an extraction from very  
22 dilute (1 wt%) aqueous solutions resembling fermented aqueous wastewater (Reyhanitash et  
23 al., 2015). Using this approach, distribution ratios could be increased up to 7-fold, and the  
24 ratio of the acetic acid to co-extracted water increased from 1wt% to 34wt%. In addition to  
25 the large concentration factor, a second benefit of using CO<sub>2</sub> instead of a volatile organic  
26 diluent is that instead of a distillation, the added CO<sub>2</sub> is simply removed from the system by  
27 depressurization which has a lower cost penalty than water evaporation.

28 **Extractions with temperature induced phase splitting.** It is also possible to induce a phase  
29 split in a homogeneous system by applying a trigger. Temperature induced phase splitting is a  
30 concept that makes use of changes in miscibility with temperature. Due to a temperature  
31 change, the miscibility reduces, resulting in a phase split creating two liquid phases. Two  
32 temperature-dependent phase splitting events are known, one achieved when exceeding the  
33 lower critical solution temperature (LCST), and the other when cooling below the upper  
34 critical solution temperature (UCST). Both LCST-behavior and UCST behavior may be

1 exploited in combination with liquid extraction. LCST behavior is mostly utilized in aqueous  
2 two-phase systems (ATPS) – see Figure 8 and Wohlfarth (2004) for more examples. ATPS  
3 systems have been applied for a range of applications interesting for biorefineries, e.g. for  
4 fractionation of salts (Milosevic et al., 2014), proteins (Grilo et al., 2016) and alkaloids (Freire  
5 et al. 2012). After the extraction, the solvent recovery is achieved by an induced phase split  
6 due to a mild temperature increase. Especially in biorefineries, the mildness of this technique  
7 valuable due to the sensitivity of many molecules (e.g. proteins), which in such ATPS may be  
8 isolated without losing their functionality. Examples of ATPS application include extraction  
9 of fatty acids (Glembin et al., 2014), and proteins (Desai et al., 2014) in algae biorefineries.  
10 Monteillet et al. (2014) showed another application of LCST behavior, where they combined  
11 LCST with a magnetoresponse to create multiresponsive ionic liquid emulsions capable of  
12 extracting  $\beta$ -carothene.

13 A very recent application of UCST behavior was recently reported by Kumar et al. (2015),  
14 who applied the induced phase splitting upon cooling in the fractionation of a complex bio-oil  
15 stream generated by thermal liquefaction of lignocellulosic biomass. This approach was then  
16 applied to recover the light fraction of the bio-oil for recycling as liquefaction medium – see  
17 Figure 9 (Kumar et al., 2015). This approach is based on hot extraction ( $T \sim 70$  °C) of the light  
18 fraction of the oil with a suitable extraction solvent followed by cold ( $T \sim 25$  °C) de-mixing of  
19 the light fraction and the extraction solvent. The study illustrated the selection of the  
20 extraction solvent and definition of required solvent properties, showed the potential of  
21 multistage extraction / regeneration for the bio-oil produced by direct thermal liquefaction,  
22 extended the concept to fractionate a petroleum crude oil, discussed the theoretical basis of  
23 the fractionation using polymer solution theory, and showed a low energy requirement of the  
24 extraction process by means of process simulation, i.e., an equivalent of  $\sim 1\%$  of the biomass  
25 intake (Kumar et al., 2015).

26 ***Extractions with CO<sub>2</sub>-induced phase splitting.*** The concept of splitting phases by bubbling  
27 CO<sub>2</sub> through a homogeneous system was first reported by Jessop et al (2005), and following  
28 this seminal paper, many publications appeared on extraction of lipids from natural sources  
29 such as soy bean (Phan et al., 2009) and microalgae (Boyd et al., 2012).

30 Du et al. (2013) have worked out a conceptual process scheme (Figure 10) for the extraction  
31 of lipids from microalgae using CO<sub>2</sub> switchable secondary amines. It was shown that with the  
32 secondary amines it was actually possible to extract the lipids from wet algae. However, to  
33 make the benchmark hexane extraction efficient, drying of the algae prior to extraction was  
34 needed for good extraction efficiency. This type of process with its ability to extract from wet

1 algae was further examined and compared with other technologies to extract lipids from algae  
2 (Du et al., 2015). Although to date the research on this topic is ongoing, and detailed aspects  
3 of process elements like solvent recovery are still under investigation, the study showed that  
4 among the other technologies investigated (such as hexane extraction and extraction with  
5 supercritical CO<sub>2</sub>), using CO<sub>2</sub>-switchable solvents was the only approach to yield more  
6 energy (37.8 MJ kg<sup>-1</sup> lipids) than the separation costs (19.8 MJ kg<sup>-1</sup> lipids).

## 7 8 **6. Conclusions**

9 Separations in biorefineries are responsible for the largest part of the total costs and hence any  
10 major improvements in separations can make the difference between a commercial success  
11 and failure. By reviewing the existing and foreseen separations in biorefineries, identifying  
12 and discussing the additional challenges in the bio-domain, and providing an overview of  
13 applications of separation technologies in biorefineries, this perspective paper concludes that  
14 there are many opportunities to improve separations in biorefineries. A selection of relevant  
15 examples related to biofuels and chemicals proved that separation technology can make a big  
16 difference in biorefineries, by considerably reducing the overall energy requirements and the  
17 production costs, thus increasing competitiveness of bio-based fuels and chemicals.

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22 *Related Processes*, 27 Sep - 2 Oct 2015, Chania, Crete, Greece) are gratefully acknowledged.

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- 9  
10

1 **Tables**

2

3 **Table 1.** Bioethanol dehydration process comparison in terms of key performance indicators

<b>Key performance indicator</b>	<b>Classic process</b>	<b>E-DWC process</b>	<b>VRC E-DWC process</b>	<b>Difference vs. classic (%)</b>
Equipment cost breakdown (k\$)				
– column shells (incl. internals)	1,103	1,111	912	
– condensers (heat exchangers)	1,335	1,073	71	
– reboilers (heat exchangers)	885	1,442	356	
– process-process heat exchangers	137	–	1,503	
– compressor (VRC)	–	–	1,632	
Total investment costs, TIC (k\$)	3,462	3,626	4,477	+29.3
Total operating costs, TOC (k\$ yr <sup>-1</sup> )	5,784	5,355	4,221	–27.0
Total annual costs, TAC (k\$ yr <sup>-1</sup> )	6,130	5,718	4,668	–23.8
CO <sub>2</sub> emissions (kg CO <sub>2</sub> t <sup>-1</sup> product)	288.94	288.31	173.04 (112.35)	–40.1 (–61.1)
Thermal energy use (MJ kg <sup>-1</sup> product)	7.45	7.45	2.88	–61.1
Electrical energy use (MJ kg <sup>-1</sup> product)	n/a	n/a	0.50	n/a
Equivalent energy requirements (MJ kg <sup>-1</sup> )	7.45	7.45	4.46	–40.1

4 \* Values given in parenthesis are for the case when electricity is generated from renewable sources.

5

1  
2 **Table 2.** Comparison between integrated reactive-absorption vs reactive-distillation processes  
3 (at a plant capacity of 1250 kg h<sup>-1</sup> fatty esters)

Equipment / Parameter / Units	RD	HI-RD	RA	HI-RA
Reactive column – reboiler duty (heater), kJ s <sup>-1</sup>	136	136	n/a	n/a
HEX-1 heat duty (fatty acid heater), kJ s <sup>-1</sup>	95	0	108	27
HEX-2 heat duty (methanol heater), kJ s <sup>-1</sup>	8	0	65	0
Reactive column – condenser duty (cooler), kJ s <sup>-1</sup>	- 72	- 72	n/a	n/a
HEX-3 water cooler/decanter, kJ s <sup>-1</sup>	- 6	- 6	- 77	0
COOLER heat duty (biodiesel cooler), kJ s <sup>-1</sup>	- 141	- 38	- 78	- 14
FLASH heat duty (methanol recovery), kJ s <sup>-1</sup>	0	0	0	0
Compressor power (electricity), kJ s <sup>-1</sup>	0.6	0.6	0.6	0.6
Reactive column, number of reactive stages	10	10	10	10
Feed stage number, for acid / alcohol streams	3 / 10	3 / 10	1 / 15	1 / 15
Reactive column diameter, m	0.4	0.4	0.4	0.4
Reflux ratio (mass ratio R/D), kg kg <sup>-1</sup>	0.10	0.10	n/a	n/a
Boil-up ratio (mass ratio V/B), kg kg <sup>-1</sup>	0.12	0.12	n/a	n/a
Productivity, kg ester kg <sup>-1</sup> catalyst h <sup>-1</sup>	20.4	20.4	19.2	19.2
Energy requirements per ton biodiesel, MJ t <sup>-1</sup> FAME	688.3	391.6	498.2	77.7
Steam consumption, kg steam t <sup>-1</sup> FAME	295	168	214	34

4

5



1 **Figure captions** (auto-updated)

2

3 **Figure 1.** Analogy between petroleum refinery (left) and biorefinery (right)

4

5 **Figure 2.** Estimated energy requirements (as percent of heating value of butanol) and  
6 selectivity (defined as  $(X_{BuOH}/X_{H_2O})_{prod} / (X_{BuOH}/X_{H_2O})_{feed}$ ) for the recovery of 2  
7 %wt 1-butanol from aqueous solution. The numbers  $x/y$  °C represent the temperature for  
8 recovery and regeneration (based on the data from Oudshoorn et al., 2009).

9

10 **Figure 3.** Steam costs for distillation of acetic acid and water as function of the molar fraction  
11 of acetic acid in the feed (a reflux ratio of 3 and a steam price of 6 €/GJ were assumed)

12

13 **Figure 4.** Vapor recompression (VRC) assisted extractive dividing-wall column (E-DWC) for  
14 bioethanol concentration and dehydration

15

16 **Figure 5.** Heat integrated reactive distillation (top) and reactive absorption (bottom) processes  
17 for biodiesel production

18

19 **Figure 6.** Energy requirements for a conventional two-step process based on FFA pre-  
20 treatment and trans-esterification (top) versus reactive separation processes (bottom)

21

22 **Figure 7.** Trans-esterification of  $\gamma$ - $\omega$ αλερολαχτονε with methanol to methyl pentenoates  
23 (200 °C, lactone : pTSA = 50:1 molar ratio, MeOH feed rate = 11 mol mol<sup>pTSA</sup>-1 h<sup>-1</sup>)

24

25 **Figure 8.** Lower critical solution temperature (LCST) phase diagram for glycol ethers (based  
26 on data from Christensen et al., 2005). Squares: water + diethylene glycol 2-methyl-1-butyl  
27 ether, circles: water + diethylene glycol n-pentyl ether, triangles: water + triethylene glycol n-  
28 heptyl ether

29

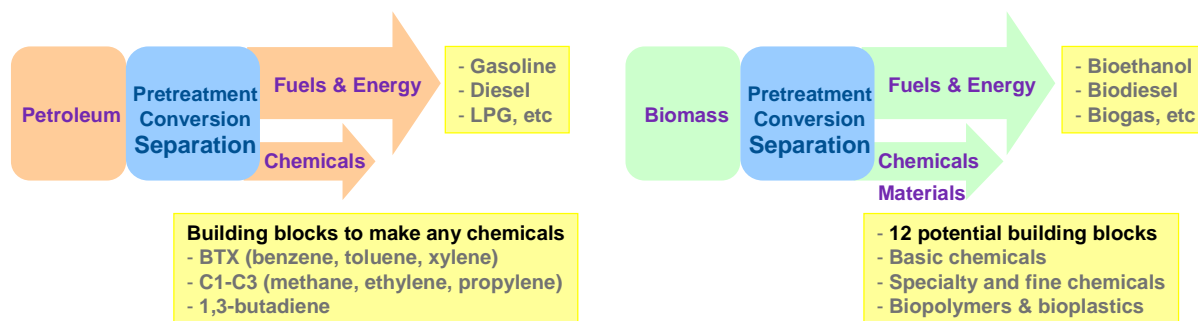
30 **Figure 9.** Process block diagram of direct liquefaction followed by extraction of the light oil  
31 and subsequent recovery of the extraction solvent

32

33 **Figure 10.** Conceptual process for extraction of lipids from microalgae with a secondary  
34 amine solvent. After the extraction stage, a CO<sub>2</sub>-induced phase splitting stage allows recovery  
35 of the oil from the solvent, after which the solvent is regenerated by bubbling nitrogen.

36

1



- Extensive experience & technological developments
  - Rather uniform & constant raw material composition
  - Feedstock relatively homogeneous
  - High hydrogen / low oxygen content (O/C ratio < 0.1)
  - High energy content, not much water to be removed
  - Chemical processes: small to large molecules
  - Separation accounts for 40-50% of total costs
- Ongoing conceptual & technological developments
  - Variable composition of raw materials
  - Feedstock relatively heterogeneous
  - High oxygen content (O/C ratio > 0.4)
  - High water content (energy intensive removal)
  - Combined processes: large to smaller molecules
  - Separation accounts for 60-80% of costs

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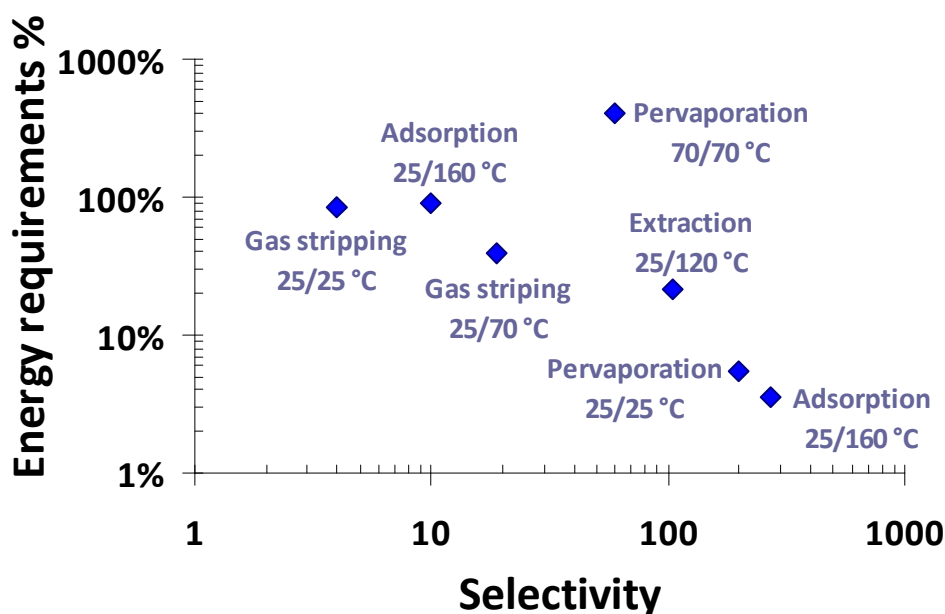
Figure 1. Analogy between petroleum refinery (left) and biorefinery (right)

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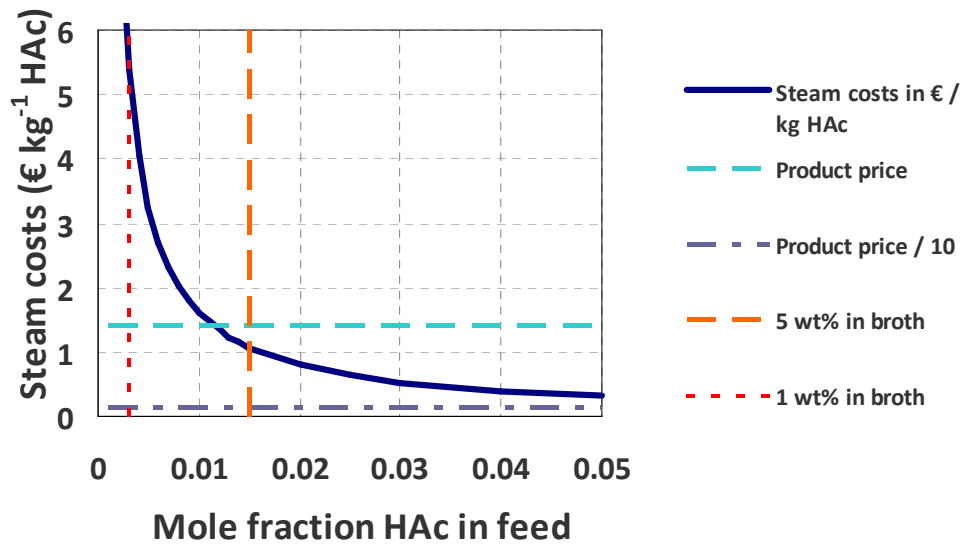
Figure 2. Estimated energy requirements (as percent of heating value of butanol) and selectivity (defined as  $(X_{\text{BuOH}}/X_{\text{H}_2\text{O}})_{\text{prod}} / (X_{\text{BuOH}}/X_{\text{H}_2\text{O}})_{\text{feed}}$ ) for the recovery of 2 % wt 1-butanol from aqueous solution. The numbers x/y °C represent the temperature for recovery and regeneration (based on the data from Oudshoorn et al., 2009).

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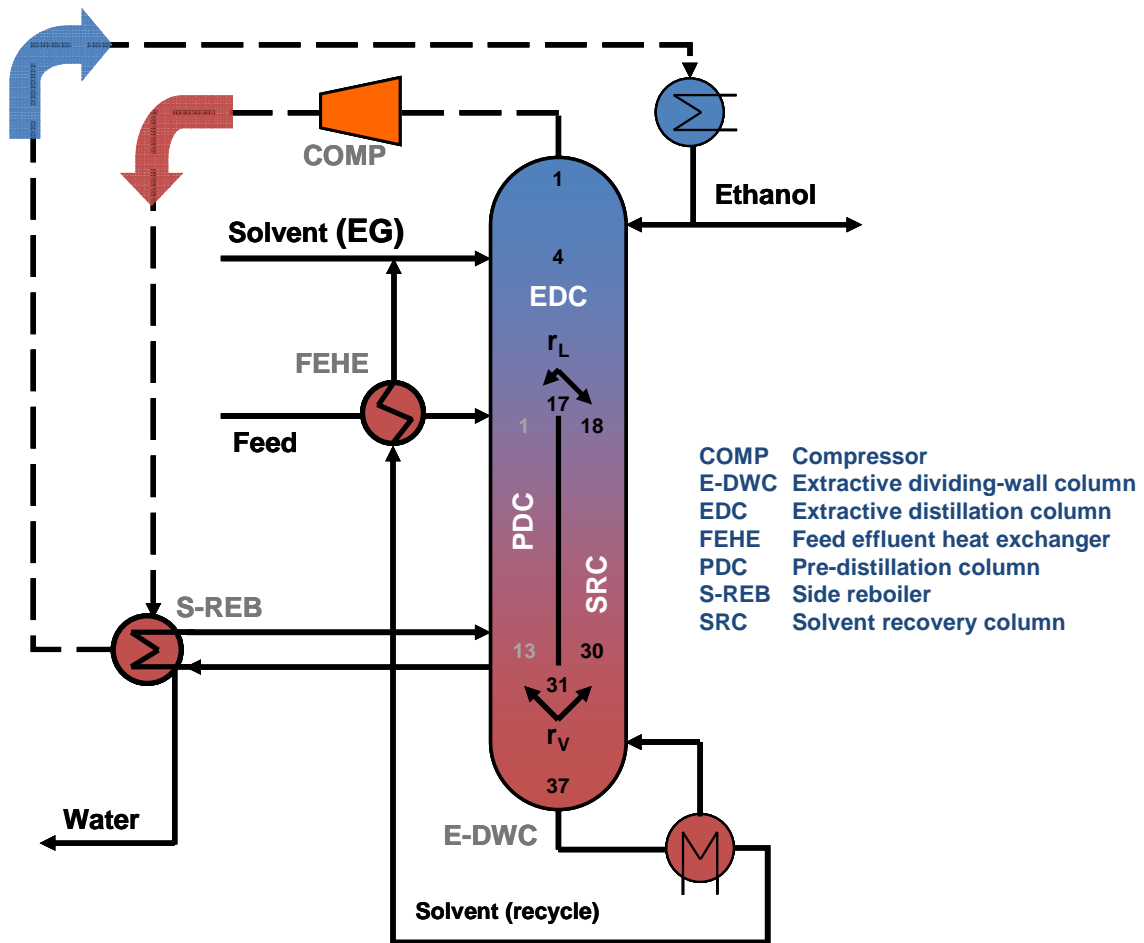
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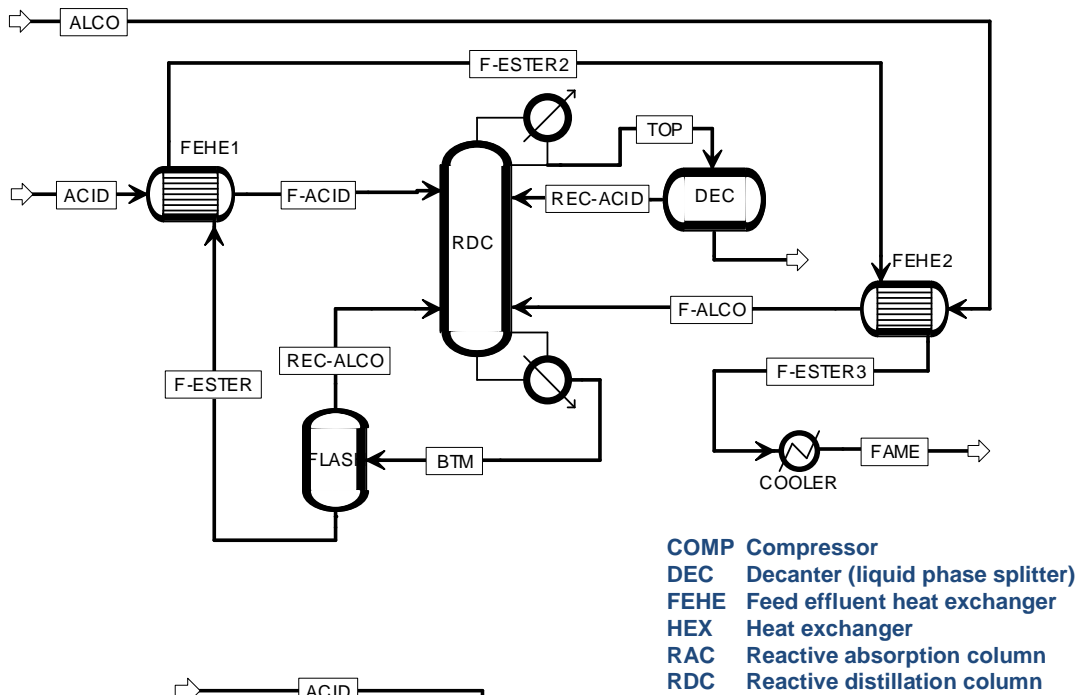


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 2 **Figure 3.** Steam costs for distillation of acetic acid and water as function of the molar fraction  
 3 of acetic acid in the feed (a reflux ratio of 3 and a steam price of 6 €/GJ were assumed)  
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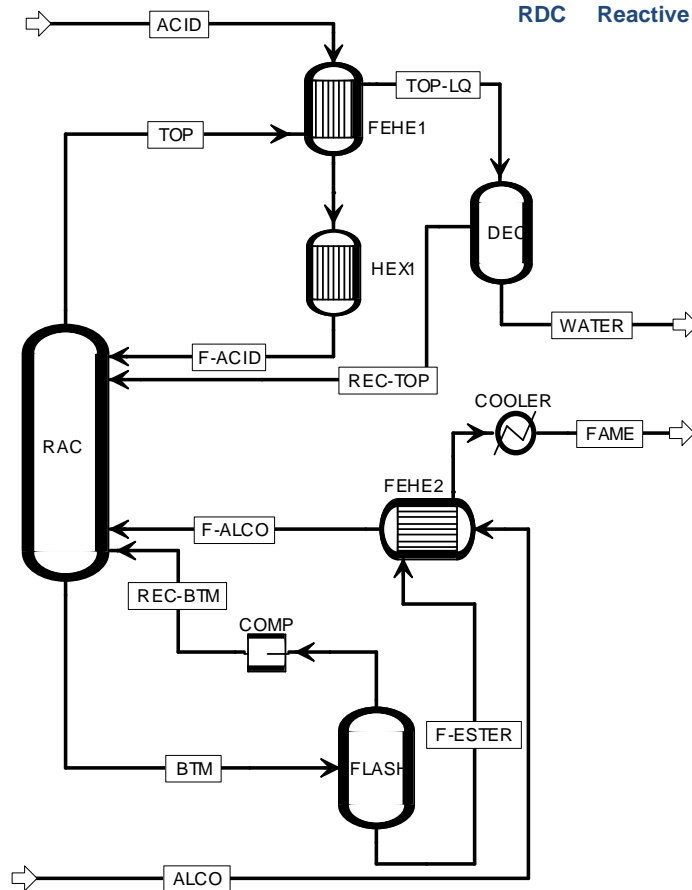
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 6 **Figure 4.** Vapor recompression (VRC) assisted extractive dividing-wall column (E-DWC) for  
 7 bioethanol concentration and dehydration

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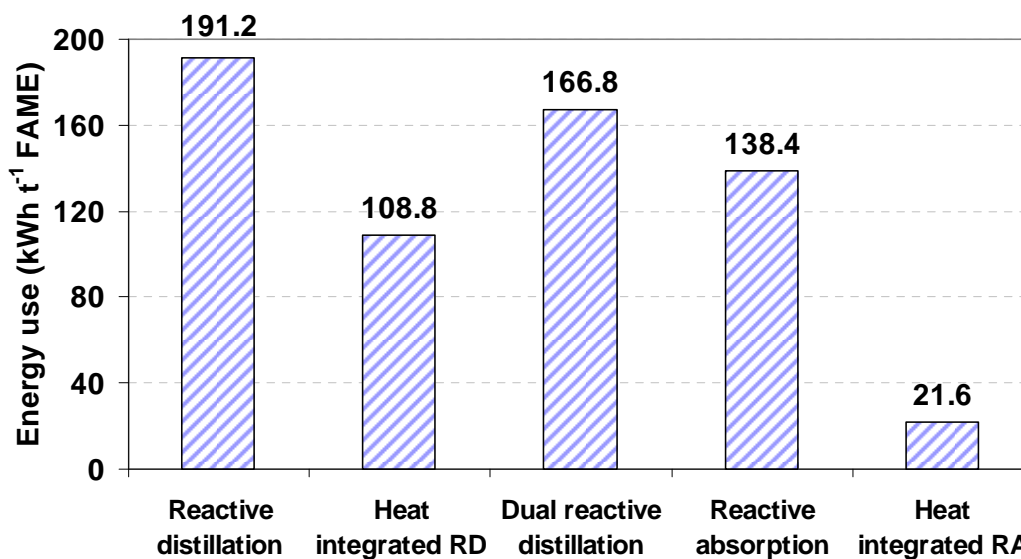
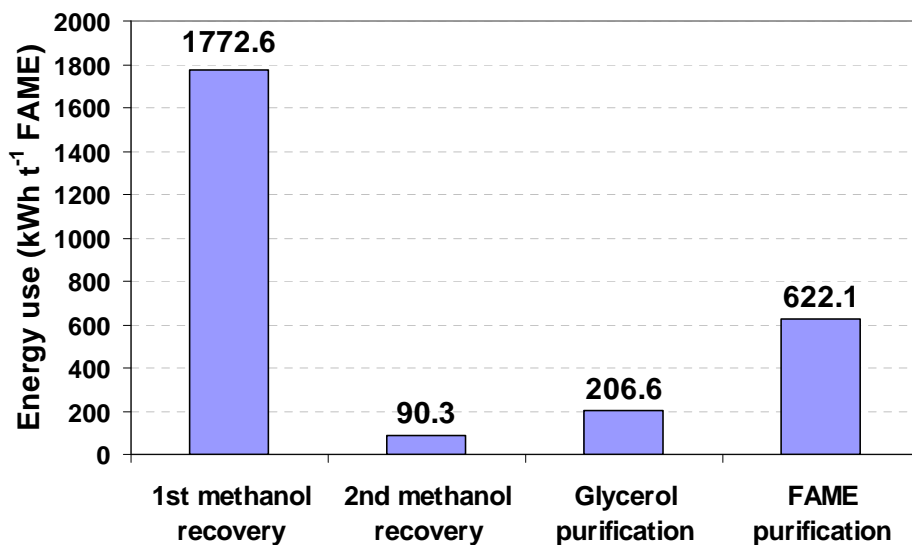
5 **Figure 5.** Heat integrated reactive distillation (top) and reactive absorption (bottom) processes

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for biodiesel production

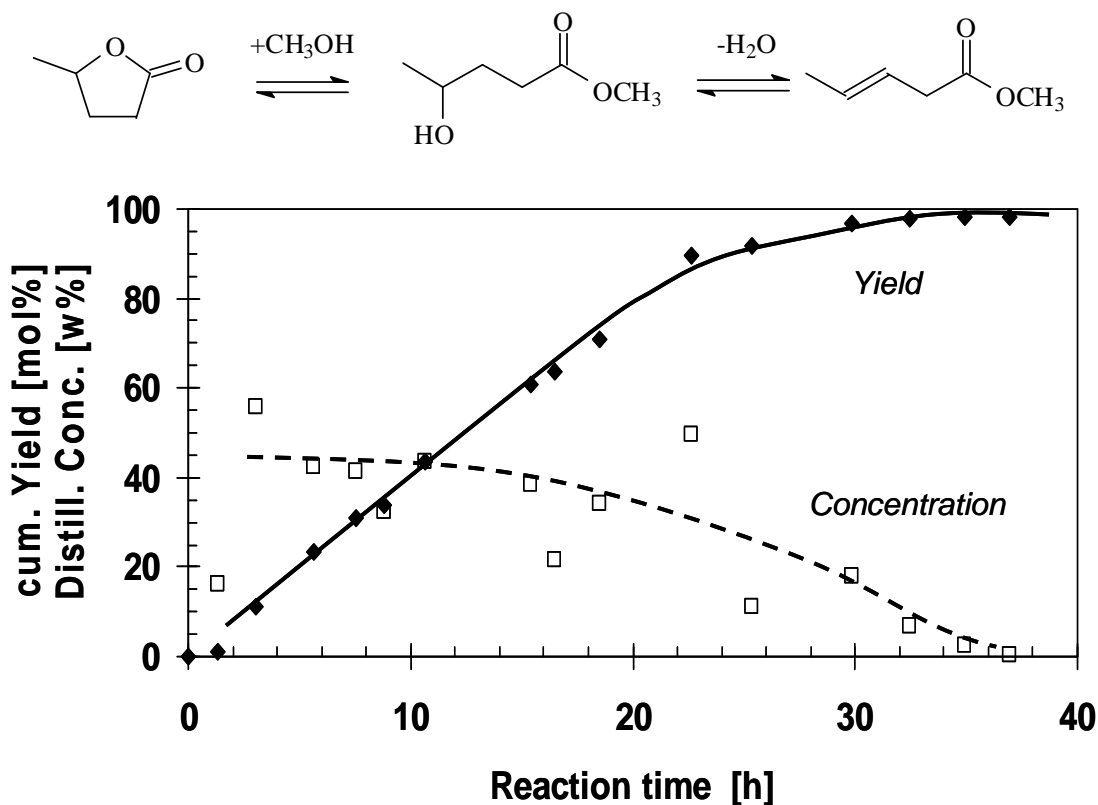
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**Figure 6.** Energy requirements for a conventional two-step process based on FFA pre-treatment and trans-esterification (top) versus reactive separation processes (bottom)

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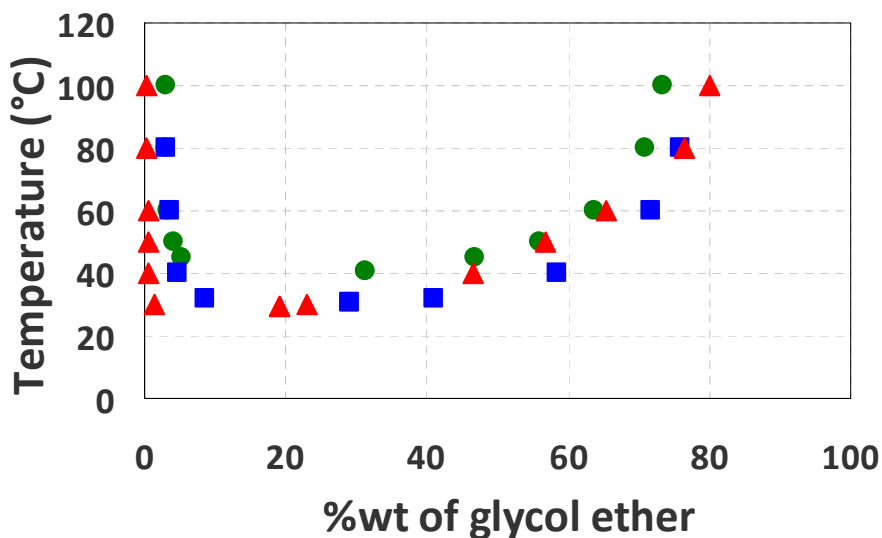
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**Figure 7.** Trans-esterification of  $\gamma$ -valerolactone with methanol to methyl pentenoates (200 °C, lactone : pTSA = 50:1 molar ratio, MeOH feed rate = 11 mol mol<sub>pTSA</sub><sup>-1</sup> h<sup>-1</sup>)

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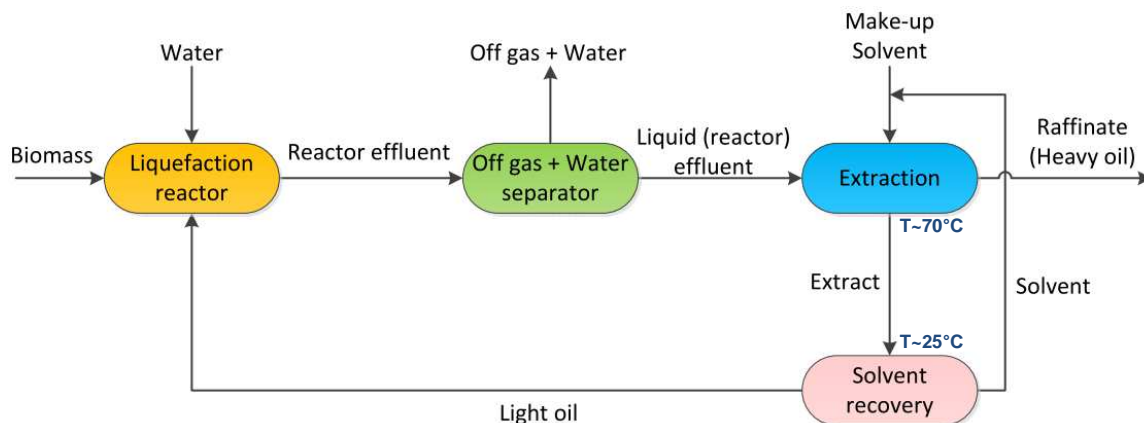
**Figure 8.** Lower critical solution temperature (LCST) phase diagram for glycol ethers (based on data from Christensen et al., 2005). Squares: water + diethylene glycol 2-methyl-1-butyl ether, circles: water + diethylene glycol n-pentyl ether, triangles: water + triethylene glycol n-heptyl ether

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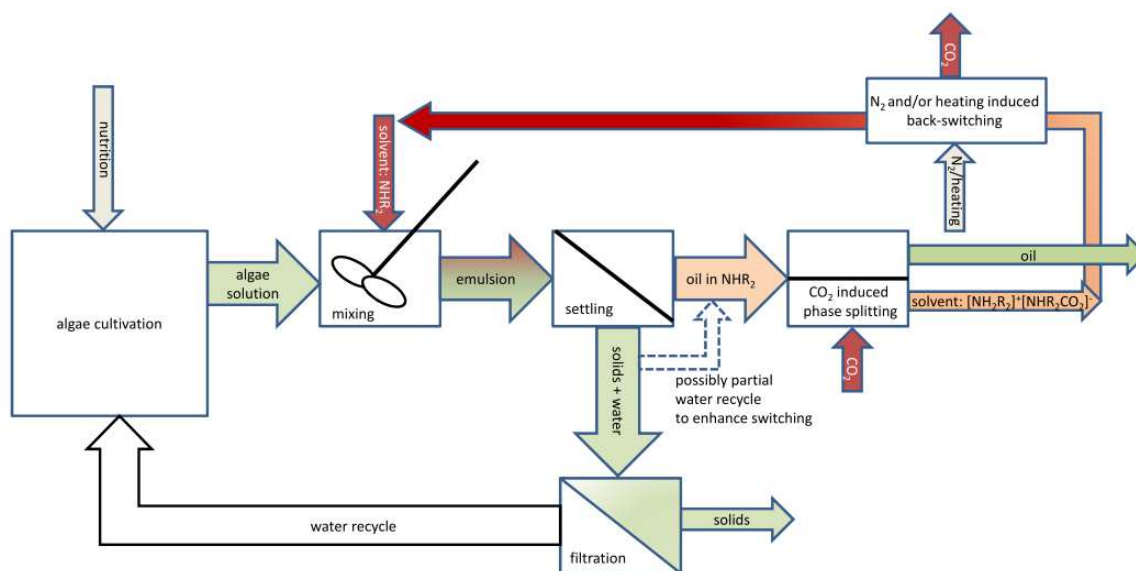
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**Figure 9.** Process block diagram of direct liquefaction followed by extraction of the light oil and subsequent recovery of the extraction solvent



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**Figure 10.** Conceptual process for extraction of lipids from microalgae with a secondary amine solvent. After the extraction stage, a CO<sub>2</sub>-induced phase splitting stage allows recovery of the oil from the solvent, after which the solvent is regenerated by bubbling nitrogen.