



# Comparative early stage assessment of multiproduct biorefinery systems: An application to the isobutanol platform



Jonathan Moncada<sup>a,\*</sup>, John A. Posada<sup>b</sup>, Andrea Ramírez<sup>a,c</sup>

<sup>a</sup> Energy & Resources, Copernicus Institute of Sustainable Development, Utrecht University, The Netherlands

<sup>b</sup> Department of Biotechnology, Faculty of Applied Sciences, Delft University of Technology, The Netherlands

<sup>c</sup> Energy & Industry, Faculty of Technology, Policy and Management, Delft University of Technology, The Netherlands

## HIGHLIGHTS

- An early stage assessment method was applied to bio-isobutanol production.
- An early stage assessment method was applied to multiproduct biorefineries.
- Isobutyl acetate, GTBE, ketones and alkanes were considered as isobutanol products.
- Bio-based isobutanol has advantages over fossil-based isobutanol.
- Bio-based multiproduct systems have advantages over equivalent counterparts.

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## ABSTRACT

An early stage assessment method is applied to the production of isobutanol from lignocellulosic biomass, and to three multiproduct portfolios from the conversion of isobutanol: Case 1: production of isobutyl acetate and glycerol tert-butyl ether (GTBE), Case 2: production of isobutyl acetate and ketones, and Case 3: production of isobutyl acetate alkanes. The method screens and compares each route with its equivalent petrochemical counterpart. The method is composed by different indicators involving economic and environmental aspects. Sensitivity analyses were carried out to account for variation in prices, weighting factors and distribution of isobutanol to isobutyl acetate (in multiproduct portfolios). Results show that bio-based isobutanol has advantages over fossil-based isobutanol. In multiproduct systems, case 1 performs better, followed by cases 2 and 3. Screening using economic or environmental aspects show to have a significant effect on the results, where bio-based systems tend to perform better when environmental aspects are included.

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## 1. Introduction

Isobutanol is an important building block with broad applications in markets such as solvents, coatings, paints, fuels and as precursor for the production of commodity chemicals (Erickson et al., 2012). Traditionally, isobutanol has been produced from the hydroformylation of propylene (oxo process) (Hahn et al., 2000). In recent years, there has been great interest in producing isobutanol from sugars (Lan and Liao, 2013). Gevo Inc. and Butamax Advance Biofuels-LCC are two companies producing bio-based isobutanol, and recently confirmed a global cross-license and set-

tlement agreements to open clear paths on the development of markets for bio-based isobutanol (Butamax, 2016).

There are several pathways to obtain fuels and chemicals from isobutanol. Isobutanol can be dehydrated into isobutylene, which is a feedstock for products such as tertiary butyl ethers for fuel additives (e.g., glycerol tertiary butyl ether (GTBE)) (Sutter et al., 2015), p-xylene (Lin et al., 2014), isooctane (Goortani et al., 2015) and polymers (Davidson et al., 2015). Other application of isobutanol is its cross condensation with acetone to produce ketones (C7–C11), which can further be converted into alkanes/alkenes, amines as fuel and fuel additives (Breitkreuz et al., 2014; West et al., 2008). Isobutanol is also used in esterification and transesterification reactions for producing isobutyl acetate which has broad applications in inks, coatings and adhesives, among others (Muñoz et al., 2006).

\* Corresponding author at: Energy & Resources, Copernicus Institute of Sustainable Development, Utrecht University, Heidelberglaan 2, 3584 CS Utrecht, The Netherlands.

E-mail address: [J.MoncadaBotero@uu.nl](mailto:J.MoncadaBotero@uu.nl) (J. Moncada).

Given the several options for isobutanol applications, there appear many alternatives to develop process schemes. An important element on designing new processes is the integrated assessment of technical, economic and environmental aspects. The classical approach for assessing and selecting the most promising routes involves the full process design followed by economic analysis and ex-ante environmental assessment. Nevertheless, depending on the stage of development, availability of data (e.g., downstream processing configuration, utilities consumption, equipment sizing) can be limited to perform a comprehensive analysis. Alternatively, early stage assessment methods (i.e., including technical, economic and environmental aspects) have been used in previous works for screening bio-based derivatives (Moncada et al., 2015; Patel et al., 2012). On top of this, most of literature on bio-based isobutanol production focuses on experimental work (e.g., (Lan and Liao, 2013; Minty et al., 2013)) and literature is scarce on isobutanol production from a systems analysis perspective. The major contribution is from (Tao et al., 2014), who carried out a detailed techno-economic and life cycle assessments on isobutanol production, and its comparison to ethanol and butanol. Nevertheless, conversion of isobutanol into prospective products was not covered. Literature is also scarce on early techno-economic and environmental assessment of multiproduct biorefinery systems using isobutanol as feedstock. In this study, the early assessment is applied for both the production of isobutanol from lignocellulosic biomass, and the conversion of isobutanol into isobutyl acetate, Glycerol tert-butyl ether and C7–C11-ketones and alkanes following a multiproduct biorefinery approach. Both isobutanol production and its conversion of value-added products are novel processes. The goal of this study is threefold: i) to assess the early performance of bio-based isobutanol in comparison to its petrochemical counterpart; ii) to screen and compare integrated multiproduct biorefinery systems for the conversion of isobutanol; and iii) to assess to which extent the early assessment method can be applied to integrated portfolios and how the screening based on solely economic or environmental aspects affect the comparisons.

## 2. Materials and methods

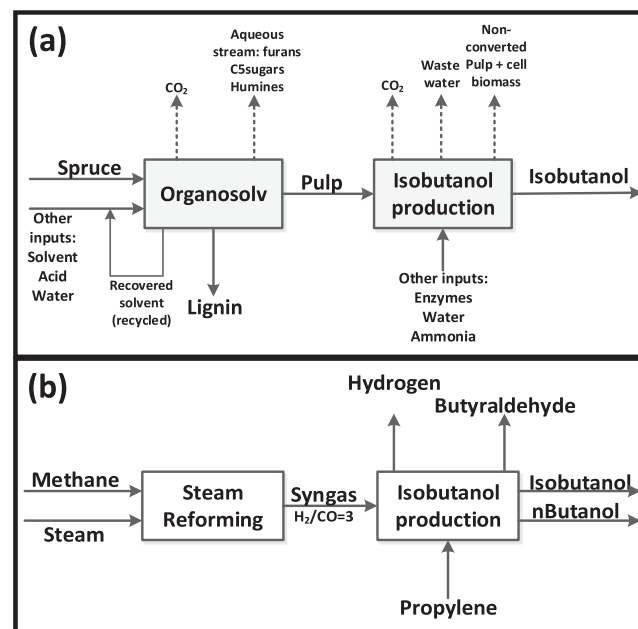
A first level of analysis corresponds to the comparison (early stage) of standalone bio-based isobutanol against standalone fossil-based isobutanol, while a second level focuses on the comparison of multiproduct systems from the conversion of isobutanol (both bio-based and fossil based). For both levels, the approach consisted of 3 main steps: i) basis of design ii) process modelling and iii) early assessment. Each step is explained below.

### 2.1. Basis of design

This section focuses on the data, process steps and assumptions to calculate the mass and energy balances of the reaction system(s) of both standalone isobutanol (bio-based and petrochemical) and integrated multiproduct schemes.

#### 2.1.1. Isobutanol production

**2.1.1.1. Bio-based route.** The system for producing bio-based isobutanol from lignocellulosic biomass is composed of two sections: i) biomass pretreatment and ii) hydrolysis and fermentation (see Fig. 1a). There are different technologies to pretreat lignocellulosic biomass. In this work, organosolv was selected as pretreatment technology due to the interest on producing high quality lignin and the possibility to obtain relatively high purity pulp to further convert it into C6 sugars (Wildschut et al., 2013). The resulting



**Fig. 1.** Simplified flow diagram of the different steps of isobutanol production: a) bio-based isobutanol, b) fossil-based isobutanol. Dotted streams represent waste streams.

C6 sugars are subsequently converted into isobutanol by action of yeasts.

Spruce wood was used as feedstock and acetone as solvent. The organosolv reactor was modeled at 150 °C, acetone concentration 60 wt% in water, sulfuric acid as catalyst with a dosage of 60 mM, a solvent to biomass ratio of 5 L per kg and an operating pressure of 15 bar. Conditions were gathered based on organosolv of spruce (Constant et al., 2016). A pulp yield of 45% (based on initial biomass loading) and a lignin yield of 75% were obtained experimentally (based on initial lignin content). The reactions describing organosolv fractionation were set to match the pulp and lignin yields. After the pretreatment stage, the solvent is recovered and recycled. The cellulose rich pulp is enzymatically hydrolyzed to produce a C6 sugars rich stream assuming a conversion rate of 95% (Pan et al., 2005). Next, the hydrolyzed liquor (rich in C6 sugars) is used as substrate to produce isobutanol assuming 93% of the theoretical yield to account for cell growth and product formation. C6 sugars derived from organosolv fractionation (hemicellulose fraction rich in mannans which are hydrolyzed into C6 sugars, see Tables S1 and S2 in Supplementary information) are also used to feed the fermentation step.

**2.1.1.2. Fossil-based route.** The fossil-based route also comprises two main steps (see Fig. 1b): i) steam reforming of methane and ii) hydroformylation of propylene into butyraldehydes and butanols. Steam reforming of methane produces syngas ( $H_2:CO$  ratio 3:1), which later reacts with propylene to produce butyraldehyde, isobutanol and n-butanol. The excess of hydrogen is assumed as a co-product of the system. Reactions and conversions were calculated based on the work presented by (Sutter, 2007).

#### 2.1.2. Integrated multiproduct biorefinery cases

The downstream conversion of isobutanol considers four end possible products: i) Glycerol Tert-butyl Ether (GTBE), ii) Acetone-isobutanol condensation products, iii) hydrogenated acetone-isobutanol condensation products, and iv) isobutyl acetate. In this paper, three configurations of multiproduct systems are considered. The three multiproduct systems aim to include

two processing lines for obtaining one product with material application (i.e., isobutyl acetate), and one product with fuel or fuel additive application (e.g., GTBE, ketones or alkanes). A multiproduct integrated biorefinery approach was adopted to model the three systems, as this has shown to be beneficial for the overall performance of the integrated concept over standalone decentralize production lines as previously discussed in literature (Moncada et al., 2014; Mountraki et al., 2016). As isobutanol is the initial feedstock for the two processing lines in each case, it needs to be distributed between each one. Explanation of each case is provided below.

**2.1.2.1. Case 1.** This case considers the joint production of isobutyl acetate and GTBE as final products from the conversion of isobutanol, which is assumed to be distributed (either bio-based or fossil-based) in a 50:50 ratio (see Fig. 2a). The production of isobutyl acetate corresponds to the esterification of acetic acid and

isobutanol. This reaction was modeled at equilibrium (Gibbs free energy minimization) at 60 °C and 1 bar, and acetic acid: isobutanol feed ratio of 2:1 (mol basis). Non-converted acetic acid and isobutanol are recycled back to the reaction stage.

In the case of GTBE production, two conversion steps are needed. The first one is the dehydration of isobutanol into isobutylene at 290 °C and 51.5 bar according to (Lin et al., 2014). The second conversion step involves the production of GTBE from glycerol and isobutylene considering an isobutylene to glycerol feed ratio of 2 (mol basis), 90 °C and 15 bar (Di Serio et al., 2010). GTBE is considered a mixture of di- and tri-GTBE, thus mono-GTBE is recycled to the reactor to further be converted into di and tri-GTBE. Butenes obtained in both isobutylene and GTBE stages are considered as co-products. Note that in this paper the integrated production of GTBE and isobutyl acetate is assessed for both bio-based and fossil-based isobutanol.

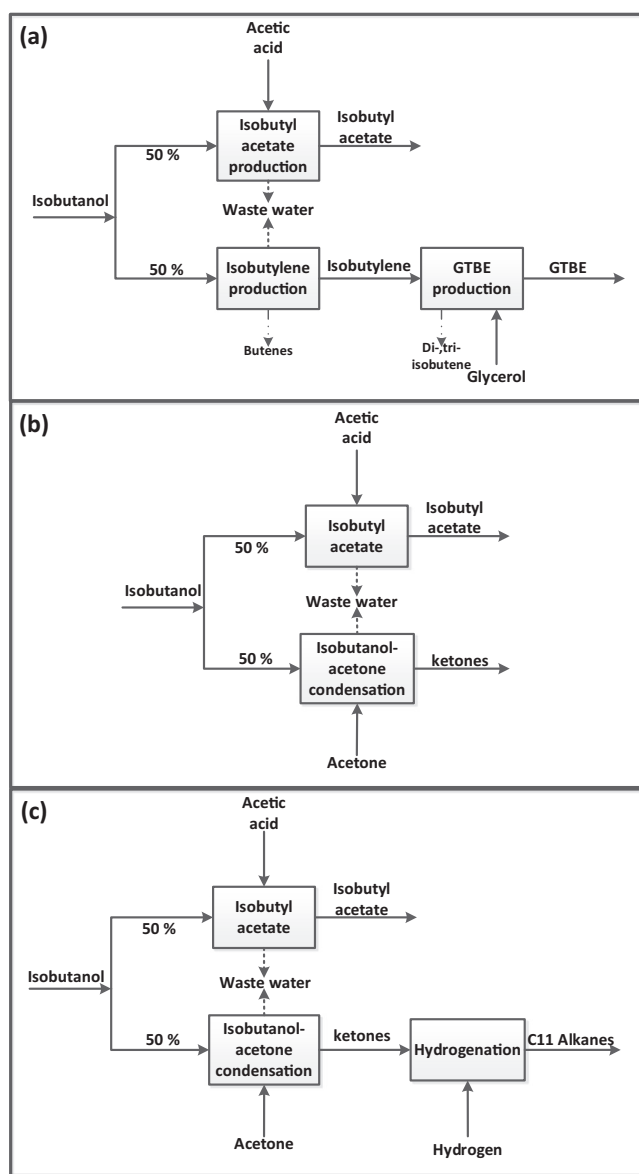
**2.1.2.2. Case 2.** This case considers the production of isobutyl acetate and isobutanol-acetone condensation ketones as final products, also assuming a distribution ratio of 50:50 for isobutanol (see Fig. 2b). The production of isobutyl acetate is analogue to that explained in Case 1. The production of isobutanol-acetone condensation products (C7 & C11 ketones) is carried-out at 330 °C, 5 bar and acetone to alcohol feed ratio of 2:1 (mol basis) according to (Breitkreuz et al., 2014). Both, non-converted isobutanol and acetone are recycled back to the reactor.

**2.1.2.3. Case 3.** This case considers the production of isobutyl acetate and hydrogenated isobutanol-acetone condensation products (C11 Alkanes), assuming an isobutanol distribution in a 50:50 ratio (see Fig. 2c). The production of isobutyl acetate is analogue to that explained in Cases 1 and 2. The production of condensation products (C7 & C11 ketones) is analogous to that explained in Case 2. However, non-converted isobutanol and acetone, and C7 ketones are recycled to shift the reaction to C11-ketones. After this, the C11-ketones are hydrogenated into C11-Alkanes.

## 2.2. Process modelling

Given the early stage of development, block diagrams displayed in Figs. 1 and 2 were modeled in Aspen Plus v8.4 (Aspen Technology, Inc., USA) to generate their overall mass balances, which are the basis for the early assessment. Each conversion step (process) considers the ideal separation of solvents, products, co-products and non-converted reactants, which are recycled back to complete conversion. This assumption is in accordance to the level of detail of the early assessment method (Moncada et al., 2015; Patel et al., 2012). The plant capacity was set to 1000 ktonne/year of spruce wood chips (dry basis) for the bio-based routes (water content assumed as 10 wt%). This capacity is fixed in order to obtain high volume of products (benefiting from the economies of scale) for a biorefinery located in Rotterdam, the Netherlands. The chemical composition of spruce wood used to model spruce in Aspen Plus was gathered from the work of (Constant et al., 2016). The size of the petrochemical route was set to match the isobutanol capacity produced in the bio-based route.

Physicochemical properties for lignin and hemicellulose were manually introduced into Aspen Plus v8.4 property databases and obtained from (Wooley and Putsche, 1996). In other cases, if the molecular structure is known and can be drawn in the compound wizard of Aspen Plus v8.4, it was exported into the properties module which uses experimental data reported by the National Institute of Standards and Technology (NIST). The nonrandom two-liquid (NRTL) thermodynamic model was used to calculate the activity coefficients of the liquid phase and the Hayden O'Connell equation of state was used to describe the vapor phase.



**Fig. 2.** Simplified block diagrams of isobutanol conversion into isobutyl acetate, glycerol tert-butyl ether (GTBE), ketones and alkanes: a) integrated production of isobutyl acetate and GTBE, b) integrated production of isobutyl acetate and ketones (acetone-isobutanol condensation products), c) integrated production of isobutyl acetate and C11-alkanes.

### 2.3. Early stage assessment

Three early assessment indicators compose the method: economic constraint (EC), energy related impacts of raw materials (EIRM) and process complexity (PC) (Moncada et al., 2015). The indicator economic constraint (EC) represents the ratio of raw material costs to the value of marketable products and co-products, which is a simplified approach to evaluate the economic potential of a process alternative (nevertheless incomplete since it only accounts the raw material contribution in the cost section (Moncada et al., 2015; Posada et al., 2013)). A ratio lower than “1” indicates a potential economic benefit (Moncada et al., 2015; Posada et al., 2013).

The indicator energy related impacts of raw materials (EIRM) is composed by the cradle-to-gate cumulative energy demand (CED, MJ per functional unit) and greenhouse gas emissions (GHG, kg of CO<sub>2</sub>-eq per functional unit). For both standalone isobutanol production (see Fig. 1), and multiproduct systems (see Fig. 2) the functional unit is 1 kg of isobutanol. This relies on the fact that isobutanol is not only the main product from the conversion of biomass, but also the intermediate for the multiproduct systems. All systems are multiproduct portfolios (i.e., several products are produced), which implies multi-functionality. There are multiple approaches to address multi-functionality (ISO, 2006). In this case the upstream section of isobutanol production (i.e., standalone isobutanol systems and upstream section of multiproduct systems) was subdivided from the downstream conversion of isobutanol (i.e., multiproduct systems described above). System expansion is also not possible since many of the co-products do not have identical fossil counterparts (e.g., lignin), therefore, including additional functions of the co-products within the system boundaries can be a very difficult task. Allocation of both GHG and CED of the raw materials is therefore necessary among all co-products. Therefore, allocation is applied for the isobutanol production step (i.e., standalone systems and upstream section of multiproduct systems).

According to the ISO guidelines (ISO, 2006), when allocation cannot be avoided, the environmental burdens of a system need to be first partitioned between the functions reflecting the physical relationships between them. In case where physical relationships cannot be established, other approaches for partitioning can be adopted (such as allocation based on the economic value of the functions) (ISO, 2006). Following this reasoning, mass allocation is preferred over economic and energy allocation, since mass flow-rates represent a physical relationship between the functions of the system and exclusively depend on the technology performance. Energy allocation may also be used as it also depends on physical relationships of the functions, however, it is avoided since the products obtained in each system have material functionality rather than energy functionality. Economic allocation is avoided, first following the ISO guidelines (ISO, 2006), and second due to high uncertainty on prices assigned to each product (for instance high uncertainty in lignin price). In the case of downstream conversion of isobutanol allocation is avoided by the selection of the functional unit.

Process complexity provides an indication of the possible extra costs and environmental impacts of processing stage related to one conversion step, by considering 6 categories: i) downstream processing; ii) concentration of main product; iii) inherent reaction mass loss; iv) reaction enthalpy; v) number of co-products; and vi) reaction pressure (Moncada et al., 2015).

The three early assessment indicators were applied to both the bio-based and fossil-based routes. Each indicator was normalized by the maximum (i.e., the worst) score of the two processes that are being compared (bio-based vs. fossil-based). The three

indicators were aggregated into a single score by using the following weighting factors: 40% for EC, 30% for EIRM (15% CED, 15% GHG) and 30% PC (Moncada et al., 2015). These weighting factors are based on expert elicitations according to (Moncada et al., 2015; Posada et al., 2013). These indicators can be grouped into economic and environmental aspects. The indicator PC aims to mimic both costs and environmental impacts of the processing stage, thus 50% of its weighting can be split into economic aspects while the remaining 50% into environmental aspects. By grouping the indicators, the weighting factor would be 55% and 45% for economic and environmental aspects, respectively. The weighting factors reflect economic feasibility as the first requirement to implement a process on a commercial scale and long term sustainability should be complemented by reduction of environmental impacts (Moncada et al., 2015).

The single scores of the bio-based and fossil-based routes are related through an index ratio, defined as the score of the bio-based route over the score of the fossil-based route. Index ratios lower than 1 indicates a better performance of the bio-based system in comparison to the petrochemical system. Index ratios higher than 1 indicates better performance of the petrochemical system in comparison to the bio-based system.

For multiproduct systems and following the multiproduct biorefinery approach, all indicators are calculated for the integrated cases rather than the standalone processing lines. Thus, the EC and EIRM indicator reflect the influence of each processing line and the distribution of isobutanol on the multiproduct system. The calculation of EC and EIRM indicators are based on information supplied in Tables S11–S13. For instance, the EC indicator of case 1, is calculated using revenues of products and raw material costs from the isobutyl acetate, GTBE processes, and the upstream section (e.g., lignin revenues in the case of bio-based isobutanol). In consequence, in case that the distribution of isobutanol changes, and accounting for the difference in prices between GTBE and isobutyl acetate, the EC indicator can also change. Same reasoning is followed for the EIRM indicator where all raw materials of all processes contribute to this indicator. For instance, glycerol used in GTBE production and acetic acid used in the isobutyl acetate process contribute to the EIRM indicator, together with the upstream EIRM of isobutanol production. In consequence, in case that the isobutanol distribution changes, the contribution of glycerol or acetic acid on the overall EIRM can also change and a different proxy can be obtained. However, since the fossil route and the bio-based route consider identical downstream conversion processes, and because the index ratio is used as proxy to relate both the fossil and bio-based routes, the difference in EIRM can only be reflected in the difference in feedstock to produce isobutanol (i.e., lignocellulosic biomass, or propylene and methane). The PC indicator can be used for processes with more than one conversion step by adding the PC indicator of each conversion step into one global PC indicator for each multiproduct biorefinery structure. For the multiproduct systems, aggregation of the indicators followed the same approach as described above.

### 2.4. Prices and energy related impacts of raw materials

Two types of data inputs are used in the current study. The first one corresponds to data on the process level (process modeling). The second type of inputs corresponds to prices, and energy related impacts of the raw materials, which are required to calculate the assessment indicators. Table 1 displays the cumulative energy demand (CED) and greenhouse emissions (GHG) of the raw materials involved in each scheme. Table 2 shows the input prices for both raw materials and products.

**Table 1**

CED and GHG data of raw materials. Input data for calculation of early stage assessment indicators.

Raw Material	CED MJ/kg	GHG kgCO <sub>2</sub> eq/kg	Remark	Source
Biomass	0.72	0.03	Spruce chips at mill	Ecoinvent (2010)
Sulfuric Acid	2.12	0.12	At plant in Europe	Ecoinvent (2010)
Enzyme	2.10	0.12	Assumed as protein	Ecoinvent (2010)
Ammonia	39.90	1.91	At plant in Europe	Ecoinvent (2010)
Propylene	68.50	1.43	At plant in Europe	Ecoinvent (2010)
Natural gas	42.80	0.33	At pipeline in The Netherlands	Ecoinvent (2010)
Steam <sup>a</sup>	3.19	0.18	At plant in Europe, fuel: natural gas	Ecoinvent (2010)
Hydrogen	72.50	1.70	At plant in Europe: from steam reforming of methane	Ecoinvent (2010)
Acetic acid	53.40	1.54	At plant in Europe	Ecoinvent (2010)
Glycerol	22.81	0.81	At biodiesel plant in Europe	Updated from Moncada et al. (2015)
Acetone	67.40	2.23	At plant in Europe	Ecoinvent (2010)

<sup>a</sup> Latent heat: 2.80 MJ/kg.**Table 2**

Summary of input prices used to calculate the economic constraint calculator.

Feature	Value	Unit	Source
Biomass	100	€/tonne dry	Based on Skogsstyrelsen (2013)
Sulfuric acid	220	€/tonne	Average from Alibaba (2015)
Cellulase enzyme cocktail	2000	€/tonne	Nitzsche et al. (2016)
Ammonia	308	Average price	Average from Alibaba (2015)
Lignin	630	€/tonne	Nitzsche et al. (2016)
Propylene	600	€/tonne	Estimated production costs, from refinery
Natural gas	11	€/GJ	IEA (2014)
Steam <sup>a</sup>	44	€/tonne	Based on Ulrich and Vasudevan (2006) and updated to 2014 price
Isobutanol	1200	€/tonne	Average from Alibaba (2015)
n-Butanol	680	€/tonne	Moncada et al. (2015)
Butyraldehyde	3000	€/tonne	Assumed based on Platts (2015b)
Hydrogen	1700	€/tonne	Moncada et al. (2015)
Acetic acid	540	€/tonne	Average from Alibaba (2015)
Glycerol	200	€/tonne	Updated from Moncada et al. (2015)
Acetone	780	€/tonne	Moncada et al. (2015)
Isobutyl acetate	1400	€/tonne	Average from Alibaba (2015)
GTBE	900	€/tonne	Assumed, based on fuel prices
C7/C11 ketone	1000	€/tonne	Assumed, based on fuel prices
Alkanes	1000	€/tonne	Assumed, based on fuel prices

<sup>a</sup> Latent heat: 2.80 MJ/kg.

## 2.5. Sensitivity analysis

The early assessment of the routes is highly affected by input parameters. To assess this influence, several sensitivity analyses are taken into account. The first accounts for sensitivity on prices due to possible volatility and uncertainty considering changes up to 100% below and above the reference values (see Table 2). Afterwards we assessed the influence of isobutanol distribution varying it from 0 to 100% going to isobutyl acetate. This will allow accounting the effect on the index ratio for a distribution of isobutanol that leads to standalone GTBE and condensation products (0% isobutanol distributed to isobutyl acetate), and also accounting for a distribution of isobutanol leading to standalone isobutyl acetate production (100% isobutanol distributed to isobutyl acetate). Finally, the potential impact of weighting of economic and environmental aspects was assessed. One could argue that the comparison of two processes can be carried out by means of economic aspects excluding environmental aspects, or by means of environmental aspect excluding the economic aspects. The sensitivity analysis considers the effect on the index ratio up to 100% contribution of economic aspects is considered, and in the case of up to 100% contribution of environmental aspects. The latter implies

sensitivity analysis of the weighting factor used for aggregating each indicator in a single score.

## 3. Results and discussion

### 3.1. Mass balances

#### 3.1.1. Standalone systems

The early indicators build on the overall mass balances of each system. In the case of standalone bio-based isobutanol production, the main products are isobutanol and lignin with yields of 0.23 and 0.20 kg per kg of dry biomass processed, respectively. These yields are used to calculate mass allocation factors which later are used in the calculation of both CED and GHG indicators (46% for isobutanol). Regarding input streams, acetone is required at a rate of 2.87 kg per kg of dry biomass, however, it is 100% recovered within the system boundaries. Additional inputs account for water for dilution (3.12 kg/kg dry biomass), sulfuric acid (0.03 kg/kg dry biomass), enzyme (0.10 kg/kg dry biomass), and ammonia (0.02 kg/kg dry biomass). Additional outputs (assumed as waste) consists of CO<sub>2</sub> (0.24 kg/kg dry biomass), waste water containing humines, furans and C5 sugars (0.73 kg/kg dry biomass), waste water (2.81 kg/kg dry biomass) and non-converted pulp (0.09 kg/kg dry biomass). The high rate of solvent and water for dilution suggest that prospective separation stages could be difficult and required significant amounts of energy, and thus high process complexity indicator may be expected.

In the case of fossil-based production isobutanol, n-butanol, butyraldehyde and hydrogen are obtained as products with yields of 0.11, 1.39, 0.25 and 0.06 kg per kg of propylene feed. The mass allocation factor for isobutanol corresponds to 6%. Additional inputs are natural gas and steam at rates of 0.38 and 0.43 kg per kg of propylene feed. This system does not show waste streams (at the level of detail assumed for the early assessment), which suggest that the process complexity indicator may be lower than that of the bio-based system. Other important factor is the difference in allocation factors where the contribution of isobutanol in the bio-based process is factor 7 higher than that of the fossil-based process. For both the bio and fossil processes, the overall capacity of isobutanol production is equivalent to 197 ktonne/y.

#### 3.1.2. Multiproduct portfolios

The downstream conversion of isobutanol is analogous for both the bio-based and fossil-based routes. For case 1, isobutyl acetate is produced at a rate of 1.57 kg per kg of isobutanol. At the base case distribution (50% of isobutanol going to this process, 98 ktonne/y), 154 ktonne of isobutyl acetate are produced yearly. Waste water is also obtained in this process (0.27 kg/kg isobutanol). Acetic acid is consumed at a rate of 0.84 kg/kg isobutanol. In the GTBE process (including the isobutylene production step), GTBE is obtained as

main product (86 wt% di-GTBE, 14 wt% tri-GTBE) at a rate of 1.28 kg per kg of isobutanol (98 ktonne/y of isobutanol feed to GTBE process), which yields a yearly production of 126 ktonne. Other butylene isomers (0.02 kg/kg isobutanol) and Di-,Tri-isobutylene (0.01 kg/kg isobutanol) are obtained as co-products. Waste water is obtained as additional output (0.24 kg/kg isobutanol) and glycerol an additional input, consumed at a rate of 0.56 kg/kg isobutanol.

For case 2, yields of the isobutyl acetate process are analogous to those explained for case 1. For the condensation products process, C7 and C11 ketones is the main product (31 wt% C7, 69 wt% C11) obtained at a rate of 1.25 kg/kg isobutanol (isobutanol feed flowrate of 98 ktonne/y), yielding 123 ktonne per year. Waste water is obtained as additional output (0.26 kg/kg isobutanol). Acetone is consumed at a rate of 0.5 kg per kg of isobutanol used in the condensation process.

In case 3, yields of the isobutyl acetate process is also analogous to those of cases 1 and 2. However, the condensation process involves an additional hydrogenation step to produce C11-alkanes as main product at a yield of 1.05 kg per kg of isobutanol (98 ktonne/y of isobutanol feed, base case). The annual production of C11-alkanes is equivalent to 104 ktonne. In this process, waste water is produced at a higher rate (0.38 kg/kg isobutanol) than that shown for case 2. Acetone is consumed at a rate of 0.4 kg/kg isobutanol, and hydrogen at a rate of 0.03 kg/kg of isobutanol. Inputs such as hydrogen and acetone are traditionally produced from fossil-sources, thus, higher GHG and CED of raw materials can be expected for the ketone/alkane systems (cases 2 and 3) than those of GTBE where glycerol is the additional input (case 1).

## 3.2. Early stage assessment

### 3.2.1. Isobutanol production

Table 3 shows the results for the early assessment indicators. For both bio and fossil routes the EC indicators is below 1, which reflects that the income by revenues is higher than the costs of raw materials. However, the EC of the bio-based route is lower (better) than that of the fossil route by 17%. Note however that the bio-based route highly relies on the income by isobutanol sales with a share of 62% (62% isobutanol, 38% lignin) while in the case of the fossil route isobutanol sales accounts for 7% of the total revenues (7% isobutanol, 49% n-butanol, 5% hydrogen, 39% butyraldehyde). This reflects the big difference in the two systems in terms of co-product distribution. In the case of EIRM, both CED and GHG emissions of the raw materials are lower (better) for the bio-based route than those of the fossil route. In the case of CED, the bio-based is 90% lower than the petrochemical counterpart. The main difference is due to the high contribution of propylene on the total CED of the fossil route (76%). In the case of GHG emissions, the bio-based route is 73% lower than the petrochemical counterpart. By comparing the PC indicator, the bio-based route has a score 44% higher (worse) than the petrochemical counterpart. The main difference is due to higher complexity of the bio-based route to con-

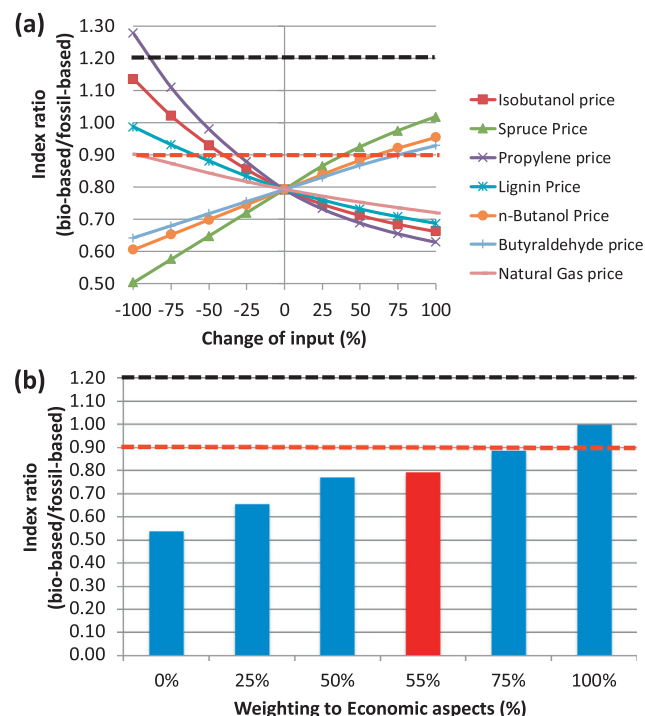
vert lignocellulosic biomass into fermentable sugars, which requires the use of a solvent and high dilution rates as described in the mass balances.

The aggregated score of the bio-based route is lower (better) than that of the petrochemical route by 21%. This difference drives to an index ratio (bio-based score/fossil-based score) of 0.79. A derivative can be classified as favorable if its index ratio is below 0.9, promising if its index ratio is between 0.9 and 1.2, and unfavorable if its index ratio is above 1.2 (Moncada et al., 2015). According to this classification, bio-based isobutanol falls within the group of favorable derivatives, which reflects the advantages of the bio-based route in comparison to the fossil counterpart at base case conditions.

Fig. 3a shows the results on sensitivity analysis on prices, showing that propylene price affects the index ratio the most. A decrease of its price over 30%, leads to index ratios above 0.9 (isobutanol classified as promising). The index ratio starts to be above 1.2 with a decrease of propylene price by 90%. Nevertheless, this is unlikely to happen since the price of propylene used in the base case (600 €/tonne) is relatively close to the price reported by Platts in January 2015 (786 USD/tonne, approx. 690 €/tonne) (Platts, 2015a). On the other hand, an increase of 100% of propylene price leads to an index ratio of 0.63, which would be the case if propylene price rises as high as values reported for 2014 (Platts, 2015a). Isobutanol price is the second price parameter that affects the index ratio the most. A decrease on isobutanol price over 40% of the reference value, results in index ratios above 0.9. An increase on isobutanol price has a similar effect than the case of propylene price, leading the index ratio to 0.66. If lignin is considered a non-valuable product (0 €/tonne) the system has an index ratio above 0.9 (approx. 1). The latter confirms the importance of lignin val-

**Table 3**  
Early stage assessment indicators for standalone isobutanol. Normalized scores in brackets. Weighting factors: EC = 0.4, CED = 0.15, GHG = 0.15, PC = 0.3. Allocation to isobutanol based on mass.

Indicators	Bio-based	Fossil-based
Economic constraint	0.35 (0.83)	0.42 (1.00)
CED (MJ/kg iBuOH) (allocated)	4.93 (0.10)	49.89 (1.00)
GHG (kg CO <sub>2</sub> -eq/kg iBuOH) (allocated)	0.25 (0.27)	0.92 (1.00)
Process complexity	5.44 (1.00)	3.05 (0.56)
<b>Single aggregated score (after normalization)</b>	<b>0.69</b>	<b>0.87</b>
<b>Index ratio</b>	<b>0.79</b>	



**Fig. 3.** a) Sensitivity analysis of price inputs of isobutanol case: bio-based vs. fossil-based. Index ratio = 0.79 (change of input 0%). For index ratios below 0.9 the bio-based system is favorable (red dotted line). For index ratios between 0.9 and 1.2, the bio-based system is promising. For index ratios above 1.2 the bio-based system is unfavorable (black dotted line). b) Sensitivity analysis of weighting factors of isobutanol production Red bar: base case. Blue bars: sensitivity cases. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

orization on the overall performance of lignocellulosic based biorefineries (Ragauskas et al., 2014). Biomass price should also be considered as a key aspect on the performance of the bio-based route in contrast to the fossil-based alternative. Increases on its price above 40% of the reference, leads to index ratios above 0.9. Contrary, if biomass price is decreased the lowest index ratios can be reached. Even at drastic changes, the system is likely to be in between the favorable and promising groups. The latter suggest that in general, the system is robust to change in prices when comparing the bio-based route against the petrochemical counterpart.

The outcome of the early assessment highly depends on the distribution of economic and environmental aspects (base case 55% to economic aspects). In the case in which economic aspects are accounted as 100% (thus leaving out the effect of environmental aspects), the index ratio increases from 0.79 (base case) to 1 (see Fig. 3b). In contrast, for 100% contribution of environmental aspects, the index ratio decreases from 0.79 to 0.54. In the first case (screening based on economic aspects) the index ratio shifted from being favorable to being promising. In the case of screening using environmental aspects, the index ratio fall within the limit value of 0.9 classifying it as favorable. Overall, changes in weighting factors remain isobutanol within the favorable and promising region, suggesting robustness. Nevertheless, this may not always be the case and will exclusively be dependent on the case studied and the conditions related to each. Imagine the case in which lignin price drops to 100 €/tonne (leaving other parameters fixed at base case values), the index ratio at base case weighting (55% to economic aspects) is 0.95 which classifies bio-based isobutanol as favorable. However, when only economic aspects are considered the index ratio increases up to 1.34, which classifies bio-based isobutanol as unfavorable. On the other hand, when only environmental aspects are considered (100%), the index ratio is 0.54, which classifies isobutanol as favorable. The latter reflects how conflictive would be deciding whether bio-based isobutanol offer advantages over fossil-based isobutanol when lignin is sold at 100 €/tonne. From an economic perspective the system is still classified as unfavorable, which would imply special attention on developing lignin markets which may hold the system competitive in contrast to the conventional technology. In terms of environmental aspects, the advantages are clearer for the bio-based route in contrast to the fossil based route.

When comparing bio-based isobutanol with other derivatives from lignocellulosic biomass (assessed using the same method, and derived from sugars from lignocellulosic biomass (Moncada

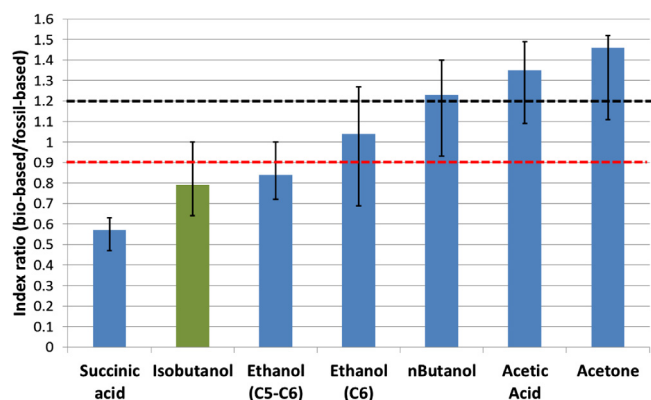
et al., 2015)), isobutanol stands behind succinic acid in the ranking of derivatives, and before ethanol (see Fig. 4). This highlights the potential of bio-based isobutanol production and its potential capacity to replace a fraction of the current petrochemical counterpart.

### 3.2.2. Multiproduct systems

Table 4 shows the results of the early assessment indicators for the multiproduct systems. By comparing the EC indicator, in the three cases, the values are below 1 indicating potential economic benefits for all bio-based and fossil routes in cases 1, 2 and 3. For all cases the EC indicator is similar, however, only in case 1 it is lower (better) by 6% for the bio-based route in comparison to the fossil route. In cases 2 and 3, the fossil route shows lower (better) EC indicators than the bio-based route by 4 and 9%, respectively. By comparing the CED indicator, in all cases, the bio-based routes are lower (better) than the fossil routes by 56, 49 and 49%, respectively. The GHG indicator shows a similar trend than the CED indicator, where in all cases the bio-based routes are lower (better) than the fossil routes by 37, 31 and 31%, respectively. The main difference between the fossil routes and bio-based routes in the CED and GHG indicators, is related to the difference in upstream impacts of the initial raw materials (i.e., biomass and propylene). When aggregating the PC indicator of the different conversion steps, in all cases, the fossil routes show lower values (better) than the bio-based routes by 27, 28 and 26%, respectively. The main difference is reflected in the upstream section before the isobutanol conversion step as explained for standalone isobutanol.

When comparing the aggregated scores, in all cases the bio-based routes show lower (better) values than the fossil routes. When combining the single scores through the index ratio, case 1 shows the lower value (0.91), followed by case 2 (0.98) and case 3 (0.99). In the three cases, the differences of the bio-based routes and fossil routes are not that significant as in the case of standalone isobutanol production. The three cases show index ratios above 0.9 but below 1.2, which classify them as promising schemes. In the three cases, the isobutyl acetate process is analogue, however, case 1 converts isobutanol into GTBE, case 2 into ketones and case 3 into alkanes. The differences in index ratios thus suggests that the most promising option is the combination of isobutyl acetate and GTBE (case 1), followed by isobutyl acetate and ketones (case 2) and lastly isobutyl acetate and alkanes (case 3). This highlights the advantage of GTBE over ketones and alkanes systems due to the fact that glycerol (auxiliary raw material) shows lower price, CED and GHG indicators than acetone and hydrogen which are the auxiliary raw materials for ketones and alkanes production.

Fig. 5 shows the sensitivity analysis results for cases 1–3, considering possible variations on prices. For case 1 (see Fig. 5a), propylene price affects the index ratio the most, and decreases above 75% will lead the index ratio to be in the unfavorable region. Nevertheless, this is unlikely to happen since the base case price of propylene (600 €/tonne) is at its low end in comparison to historical prices reported by (Platts, 2015a). In contrast, increases of propylene prices above the base case value will lead the index ratio to be in the favorable classification region. Since the index ratio is on the threshold value of 0.9 for classifying the system as favorable or promising, any increase on prices of isobutyl acetate, lignin, natural gas and GTBE, and decreases in prices of spruce, butanol, butyraldehyde and acetic acid lead the system to be in the favorable region. However, an opposite behavior of these parameters lead the system to be in the promising region. The latter reflects that even at drastic changes in prices, case 1 is still able to be classified between the favorable and promising regions. For case 2, the index is highly affected by propylene price, followed by isobutyl acetate, lignin, butanol and spruce prices. However, for case two changes need to be more drastic to be able to move the index ratio

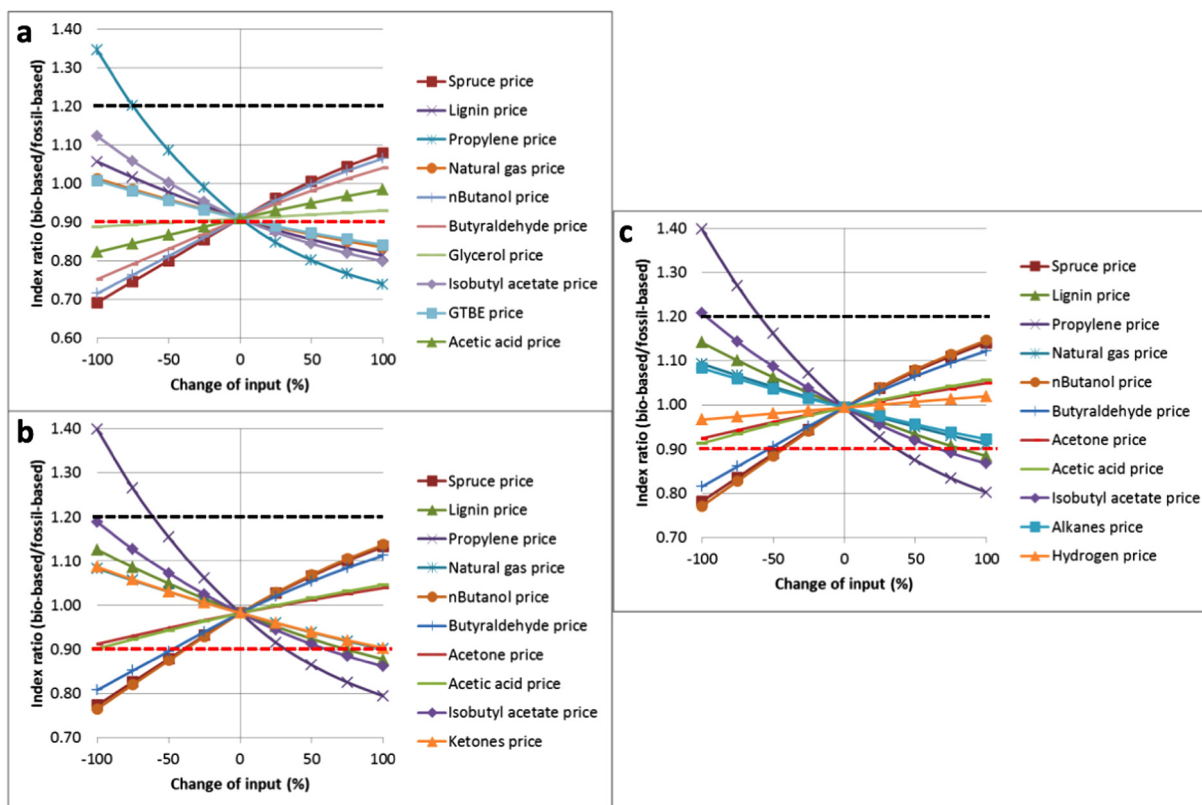


**Fig. 4.** Ranking of isobutanol in comparison to other bio-based derivatives. For index ratios below 0.9 the bio-based system is favorable (red dotted line). For index ratios between 0.9 and 1.2, the bio-based system is promising. For index ratios above 1.2 the bio-based system is unfavorable (black dotted line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Table 4**

Early stage assessment indicators of the multiproduct cases. Normalized scores in brackets. Weighting factors: EC = 0.4, CED = 0.15, GHG = 0.15, PC = 0.3.

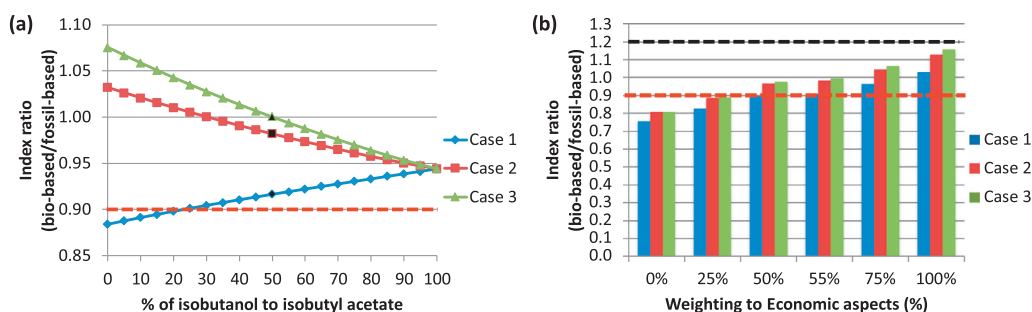
Indicators	Case 1		Case 2		Case 3	
	Bio-based	Fossil-based	Bio-based	Fossil-based	Bio-based	Fossil-based
Economic constraint	0.40 (0.94)	0.42 (1.00)	0.45 (1.00)	0.43 (0.96)	0.47 (1.00)	0.43 (0.91)
CED (MJ/kg iBuOH) (allocated)	33.44 (0.44)	76.32 (1.00)	44.06 (0.51)	86.95 (1.00)	44.51 (0.51)	87.01 (1.00)
GHG (kg CO <sub>2</sub> -eq/kg iBuOH) (allocated)	1.11 (0.63)	1.77 (1.00)	1.45 (0.69)	2.11 (1.00)	1.46(0.69)	2.11 (1.00)
Process complexity	7.71 (1.00)	5.61 (0.73)	7.51 (1.00)	5.41 (0.72)	7.92 (1.00)	5.82 (0.74)
<b>Single aggregated score (after normalization)</b>	<b>0.84</b>	<b>0.92</b>	<b>0.88</b>	<b>0.90</b>	<b>0.88</b>	<b>0.89</b>
<b>Index ratio</b>	<b>0.91</b>		<b>0.98</b>		<b>0.99</b>	

**Fig. 5.** Results of sensitivity analysis on prices of multiproduct cases, a) case 1, b) case 2, c) case 3. Dotted lines represent thresholds for group classification.

to the favorable region (see Fig. 5b) and to most changes the index ratio is robust in the promising group. Case 3 shows a similar behavior than case 2 in which drastic changes in prices are needed to allocate the index ratio as favorable, and for most changes the systems is robust as promising.

Fig. 6a shows the results on sensitivity analysis of the distribution of isobutanol to isobutyl acetate. When the distribution of

isobutanol is equal to each processing line (i.e., isobutanol going to isobutyl acetate production, and isobutanol going to other products), the index ratio for the three cases is classified as promising. However, in case 1, when the distribution of isobutanol starts to be lower for isobutyl acetate (but higher for GTBE), the index ratio tends to be lower (better). For distributions below 20% to isobutyl acetate the system can be classified as favorable. This result sug-

**Fig. 6.** Results of sensitivity analysis of multiproduct systems, a) distribution of isobutanol to isobutyl acetate, base case values in black, b) weighting to economic aspects.

gests that at higher GTBE production rates, the system shows better performance. The index ratio was broken down to understand better which indicator is contributing to this tendency the most. Although revenues and raw material costs changed, the EC indicator remained mostly unchanged. The PC indicator is slightly affected showing higher values when the production of GTBE was increased (considering lower distribution of isobutanol to isobutyl acetate production), since the GTBE process shows higher PC scores than the isobutyl acetate process. The major impact is reflected in both GHG and CED indicators, where the lower values are obtained at lower distributions to isobutyl acetate. The latter is due to lower GHG and CED emissions of glycerol in comparison to those of acetic acid, which are auxiliary raw materials to GTBE and isobutyl acetate, respectively. This results also highlights the importance of the EIRM indicator on the overall behavior of each system, and how it can influence the index ratio. In cases 2 and 3, the behavior of the index ratio is opposite to that described for case 1. In these cases, when the distribution to isobutyl acetate is higher, the index ratios tend to be lower (better). In both cases 2 and 3, the index ratios remain in the promising region, with the highest values when both standalone ketones (case 2) and alkanes (case 3) are considered (0% distribution to isobutyl acetate). When breaking down the index ratios, the EC is significantly affected since at higher distribution to isobutyl acetate revenues are also higher leading to higher values. In contrast to case 1, the EIRM indicator is hardly affected since both CED and GHG impacts related to auxiliary raw materials is similar for cases 2 and 3. The PC indicator starts to be higher (worse) at lower distributions to isobutyl acetate since the individual scores of the acetone condensation step and hydrogenation are higher than that of isobutyl acetate. In contrast to case 1, in cases 2 and 3, when considering different distributions to isobutyl acetate the EC has a large effect. When considering standalone conversion of isobutanol (low and high ends in [Figs. 6a](#)), the ranking (based on index ration) of the conversion alternatives from lower (better) to higher (worse) is GTBE production, isobutyl acetate production, ketones production and alkanes production.

[Fig. 6b](#) shows the results of sensitivity analysis when weighting to economic aspects is changed. At base case conditions (55% to economic aspects), all cases are classified as promising. Nevertheless, when the weighting is more oriented to environmental aspects the systems can shift and classify as favorable (for values higher than 75% to environmental aspects). This highlights the importance of including environmental aspects in the screening of prospective technologies for the conversion of biomass. This will also allow to identify weaknesses and strengths of the screened technologies. When the weighting is only considered to economic aspects (100% in [Fig. 6b](#)), the index ratios are the highest and all above 1, which suggest better economic performance of the petrochemical counterparts than the bio-based systems. However, the index ratios remain in the promising region at base case prices, but as discussed for standalone isobutanol production, it may change if different price scenarios are included such as the case of low lignin price. On one hand, an interesting feature when considering 100% weighting to economic aspects is that the difference in index ratios between the three cases is larger, with cases 2 and 3, 9 and 12% higher than case 1. On the other hand, when 100% weighting is considered to environmental aspects, the difference in index ratios is shorter, where cases 2 and 3 are both 6% higher than case 1. Overall, the influence of weighting is large when deciding whether a route is attractive for further analysis. It should be taken into account that weightings can always be modified and for further analysis the stakeholders can easily modify and adapt them depending on their interests.

One of the limitations of the applied method is the assumption of ideal separation of the mixtures leaving each reactor system. In

some cases, the recovery of products is not always 100% possible due to thermodynamic and equipment limitations. Although the complexity of each process is mimicked by conducting scoring based on heuristics, many details that can influence the overall performance of each technology can be missing. For example, the contribution of utilities in both economics and environmental aspects is expected to be high in any chemical/biochemical process. The use of the CED as an indicator of the environmental impacts of raw materials needs to be carefully revised, since it reports both renewable and non-renewable energy use. Therefore, it can provide a misleading picture depending on the perception of the user. For instance, on one hand, in the case where renewable energy is dominant in the CED indicator, the user can misunderstand the results assuming that all energy is provided from non-renewable sources. On the other hand, the CED can also be very informative on energy resource use independently of its nature. The method is adaptable and it is possible, for instance, to only use the non-renewable energy use component of the CED indicator. Other limitation of the method can be reflected in lack of data of investment costs and additional costs categories, which could be a determining driver to understand the economic feasibility of each system. All in all, these limitations bring with themselves high uncertainty, for instance in the incompleteness of the EC indicator. Nevertheless, it should be taken into account that all options either for the bio-based and fossil-based routes were compared and analyzed at the same level in order to derive a fair assessment. The method also shows that it is possible to be applied in multiproduct portfolios and that it can be useful for applying it for emerging technologies where relevant detailed data is not yet available. The method can be useful to support companies and research institutes interested in screening and selecting novel technology pathways in biorefineries. Something to remark is that we focused our analysis to the scope of a chemical process, specifically oriented to the chemical industry of the bio-based economy and the stakeholders related to it. In this case we considered technical, economic and environmental aspects. However, it should be taken into account that for instance social aspects are not embedded in the current analysis. On one hand, this is an additional limitation of the method, but on the other hand, the level of analysis is still at an early stage, which is considered due to limitations on data availability regarding different aspects of a prospective technology (e.g., social). Following this reasoning, a more comprehensive analysis would always require higher resolution and quality of data inputs, which generally is an issue for systems that are not currently operating at large scales. In this case, the aggregation of economic, technical and environmental aspects helps to visualize, at an early stage, possible hotspots for scaling up the level of analysis of a system. For instance, information provided in this work, may be used to pre-screen technology configurations and later apply a more detailed techno-economic and environmental assessment on the screened options.

#### 4. Conclusions

This study shows that at an early stage, bio-based isobutanol has advantages over petrochemical isobutanol production. All multiproduct cases, show to be promising, with the one combining isobutyl acetate and GTBE having the best performance, followed by the combination of isobutyl acetate and ketones, and combination of isobutyl acetate and alkanes. This study also shows that the screening of possible products is highly affected when considering solely economic and environmental aspects, suggesting that when environmental aspects are included, the systems tend to perform better than the petrochemical counterparts. This highlights the

importance of environmental aspects in the assessment of technologies.

## Acknowledgements

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.biortech.2017.05.074>.

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