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Potential of bioethanol as a chemical building block for biorefineries: Preliminary sustainability assessment of 12 bioethanol-based products

John A. Posada *, Akshay D. Patel, Alexander Roes, Kornelis Blok, André P.C. Faaij, Martin K. Patel

Energy & Resources, Copernicus Institute of Sustainable Development, Utrecht University, Budapestlaan 6, NL-3584 CD Utrecht, The Netherlands

HIGHLIGHTS

- Potential of bioethanol as raw material for biorefineries (to bulk chemicals).
- Multi-criteria early-stage sustainability assessment method for bio-based process.
- Screening and selection of bioethanol derivatives based on sustainability.
- Bioethanol derivatives categorization: favorable, promising and unfavorable.
- Sensitivity, scenarios and uncertainty analyses were performed.

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ABSTRACT

The aim of this study is to present and apply a quick screening method and to identify the most promising bioethanol derivatives using an early-stage sustainability assessment method that compares a bioethanol-based conversion route to its respective petrochemical counterpart. The method combines, by means of a multi-criteria approach, quantitative and qualitative proxy indicators describing economic, environmental, health and safety and operational aspects. Of twelve derivatives considered, five were categorized as favorable (diethyl ether, 1,3-butadiene, ethyl acetate, propylene and ethylene), two as promising (acetaldehyde and ethylene oxide) and five as unfavorable derivatives (acetic acid, *n*-butanol, isobutylene, hydrogen and acetone) for an integrated biorefinery concept.

1. Introduction

Numerous policies supporting the production and use of transport biofuels have globally been established in the last decade (Sorda et al., 2010; Lamers et al., 2011) in order to promote energy independence and mitigate negative environmental impacts caused by the use of conventional fossil fuels (e.g., gasoline, diesel, etc.). As a consequence, bioethanol has become the largest biofuel with an estimated worldwide production of above 100 billion liters in 2011 and with an expected production increase of around 3–7% p.a. in the years 2012–2015 (OECD-FAO, 2012). The rapid development of the bioethanol market has been accompanied by a growing interest in its use as renewable feedstock for the manufacture of bio-based chemicals (Weusthuis et al., 2011; Rass-Hansen et al., 2007). Moreover, bioethanol was recently identified as one of the potential top bio-based raw materials for the chemical industry (Bozell and Petersen, 2010). Significant technological advances have also been achieved on the catalytic conversion of bioethanol (e.g., dehydration, dehydrogenation, oxidation, reforming, gasification, decomposition, coupling, etc. (see Table 1)) and many important chemicals have successfully been synthesized; some examples are: ethylene, propylene, 1,3-butadiene, iso-butylene, hydrogen, acetaldehyde, ethylene oxide, *n*-butanol, acetic acid, ethyl acetate, acetone and dimethyl ether. This outlook of growing production and technological advances for its conversion to bulk chemicals together with the promise of new technologies for cheap cellulosic bioethanol, could work as solid pillars to create competitive biorefining systems based on bioethanol as chemical building block.

Given the large number of options for bioethanol conversion, the identification of its most promising derivatives from a sustainability point of view is by no means a trivial task. This type of research question has traditionally been addressed by in-depth analysis based on conceptual process design (e.g., flowsheeting and process simulation with Aspen Plus and subsequent economic/environmental assessment (Posada et al., 2012)). But such approaches are very time-intensive and require detailed data related to downstream processing which are not available at early design phases (e.g., lab or pilot scale). This is even a more demanding task in the case of integrated biorefineries (i.e., the combined sustainable production of bio-based chemicals, biofuels, bio-based polymers, pharmaceuticals, food and/or feed; adapted from

* Corresponding author. Tel.: +31 30 253 5516; fax: +31 30 253 7601.
E-mail address: J.A.PosadaDuque@uu.nl (J.A. Posada).

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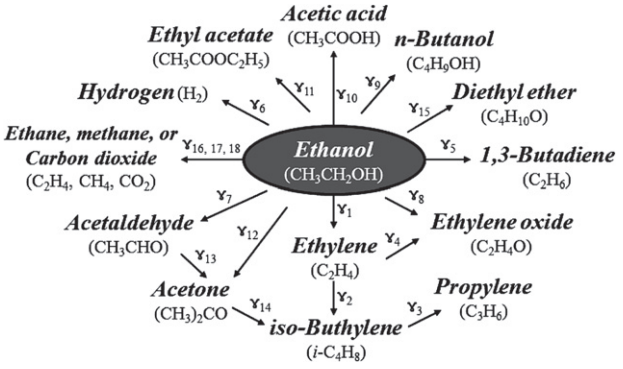
Table 1
Collection data of the considered reactions.

Product	Mass and (molar) yields[a]	Temp (°C)	Involved reactions[a]	Reference	Conventional process	Market (million m.t.)	Main uses	Commercial price (€/tonne)[b]
Ethylene	0.60 (0.99)	450	γ_1, γ_7, γ_{15}, γ_{16}	Bi et al. (2010)	Steam cracking of naphtha	136.2	Raw material	1100–1350
Propylene	0.32 (0.35)	550	γ_1, γ_2, γ_3	Song et al. (2010)	Steam cracking of naphtha	51.7	Raw material	1120–1370
1,3-Butadiene	0.51 (0.44)	350	γ_7, γ_{13}, γ_{14}	Ohnishi et al. (1985)	Steam cracking of naphtha	12.2	Raw material	1845–2255
IsoButylene	0.34 (0.28)	450	γ_1, γ_5, γ_7	Sun et al. (2011)	Steam cracking of naphtha	24.4	Raw material	520–640
Hydrogen	0.21 (4.79)	450	γ_6, γ_{17}, γ_{18}	Liu et al. (2010)	Methane steam reforming	54.1	Chemical agent	1745–2135
Acetaldehyde	0.75 (0.78)	230	γ_7, γ_{18}	Chen et al. (2007)	Oxidation of ethylene	3.5	Raw matrial	745–910
Ethylene oxide	0.92 (0.96)	325	γ_1, γ_4,	Lippits and Nieuwenhuys (2010)	Oxidation of ethylene	20.4	Raw material	1235–1510
n-Butanol	0.21 (0.13)	400	γ_1, γ_5, γ_7, γ_9,	Tsuchida et al. (2006))	Propylene hydroformilation	3.1	Raw material and solvent	920–1125
Acetic acid	1.25 (0.96)	150	γ_{10}, γ_{18}	Jørgensen et al. (2007)	Methanol carbonylation	11.3	Raw material and solvent	765–935
Ethyl acetate	0.63 (0.33)	260	γ_7, γ_{11},	Santacesaria et al. (2012)	Esterif. of acetic acid with ethanol	1.7	Solvent and coating agent	1010–1230
Acetone	0.57 (0.46)	400	γ_1, γ_{12}	Nakajima et al. (1989)	Cumene oxidation (Hock process)	6.2	Raw material and solvent	920–1125
Diethyl ether	0.59 (0.37)	350	γ_1, γ_{15},	Ali et al. (2010)	Direct hydration of ethylene	14.4	Solvent	1730–2115

[a] See Fig. 1.
[b] For 2008–2011.

Cherubini and Strømman (2011)) due to the technological complexity related to each processing step (e.g., collection and pretreatment of biomass, production and separation of precursors, conversion of precursors to chemical building blocks and production of secondary chemicals/products (Cherubini and Strømman, 2011)). Since both biorefinery concepts and bioethanol conversion alternatives are still under development, it is a challenge to perform a preliminarily sustainability assessment of these conversion systems with the limited information available.[1] Against this background, one of the objectives of this paper is to identify those bioethanol derivatives that offer largest benefits in sustainability terms. The other main goal is to explore whether the applied methodology is more suitable to pinpoint the conversion steps that are particularly attractive for future biorefinery systems. To this end, various bioethanol conversion alternatives were compared from a sustainability point of view (i.e., covering economic, environmental, and health and safety aspects) with respect to their petrochemical counterparts and the plausibility of the results was checked by conducting sensitivity, scenarios and uncertainty analyses. This study focuses exclusively on the chemical conversion of bioethanol, thereby excluding other strategies for improved sustainability such as choice of crop, cultivation method or location.



* Reactions γ_{16}, γ_{17} and γ_{18} refer to the production of: ethane, methane and carbon dioxide, respectively.

Fig. 1. Derivatives of bioethanol by catalytic conversion.

2. Methodology

After a comprehensive literature survey on bioethanol conversion (more than 200 papers), 12 final derivatives were identified as candidates to be analyzed as shown in Fig. 1. The highest reported yields and other important information related to the reactive systems and markets are shown in Table 1.

Screening of either synthesis pathways (i.e., from different raw materials to one specific product) or conversion alternatives (i.e., from one specific raw material to different products) is one of the first steps related to the design of new chemical conversion routes. The task was successfully addressed by Sugiyama et al. (2008) who developed a multi-objective decision framework which allows to screen processes based on information that is available at early design stages. The inputs required for the decision framework were: reaction mass balances, prices of raw materials and products, life-cycle environmental impacts represented by cumulative energy demand (CED) and greenhouse gas (GHG) emissions of the feedstocks, physical–chemical properties of reactants and products, and hazards. This framework was later modified by Patel et al. (2012) in order to better account for circumstances related to the production of bio-based chemicals. This goal was achieved by including features such as the need for biomass pretreatment, distribution of environmental burdens by product allocation, number of co-products, risk aspects and

[1] Most of the sustainability assessment approaches and indicators have been developed for bio-energy systems. However, these methods could in principle be extended to bio-based products. For instance, this is case of the 24 GBEP (Global Bioenergy Partnership) sustainability indicators for bioenergy. But this type of approaches require in general detailed information which is not available at early design phases.

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