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Analysis of sustainability metrics and application to the catalytic production of higher alcohols from ethanol

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ABSTRACT

Use of sustainability metrics can help channel chemical research toward important long-term societal goals. For effective outcomes, it is important to understand the strengths and weaknesses of the sustainability assessment methods that can be applied in the chemical process development chain. In this paper we report the results from application of sustainability metrics in parallel with findings from laboratory research for production of higher alcohols from ethanol by application of the Guerbet reaction. 2-Ethyl-1-hexanol is used as an exemplary compound for the targeted higher alcohols. The accuracy of early-stage sustainability metrics using laboratory data is evaluated by comparing the results with metrics based on detailed process simulation models, techno-economic analysis and life cycle assessment. The analysis has provided insights on pitfalls to avoid and effective application of early-stage metrics considering the dynamic nature of information available from laboratory research. Anticipation of the process configuration was found to be particularly important for effective application of early-stage metrics. The results from catalysis research for 2-ethyl-1-hexanol highlight the potential opportunities for higher chain Guerbet alcohols from biobased ethanol. The comparison of this biobased route with conventional fossil based process shows the challenges for such a process from an economic and environmental perspective.

1. Introduction

Chemical research has been an important contributor to our societal progress. The future of this progress depends on harnessing the potential of chemical research to address crucial sustainability issues like resource depletion, global warming and affordable access to renewable resources. Hence it is imperative to supplement laboratory research with metrics which enable incorporation of sustainability aspects in chemical process development, i.e. at early stage. Anastas' Twelve Principles of Green Chemistry [1] were a milestone in this respect and since then, there have been some developments toward quantitative operationalization of these principles [2,3]. The renewability of feedstocks is one of the core characteristics of a sustainable chemical process. Hence there has been increased research interest in the development of new routes to produce chemicals and fuels from biobased resources [4]. Continuing research and development efforts in this direction have resulted in the commercialization of renewables based chemical processes for production of ethanol, ethene, propylene glycol, butanol [5] among others. The production of these chemicals and fuels from biobased resources has been shown to offer environmental benefits like lower greenhouse gas emissions and non-renewable energy use [6–9]. However, continued progress on this path hinges on the development of novel inherently sustainable chemical processes which are optimized across economic, environmental and social parameters.

In the past decade, there has been a significant increase in the production of bioethanol [10] from first generation biobased feedstocks like corn and sugarcane. For the medium to long term, the production from lignocellulosic resources offers a potentially

Abbreviations: 2-EH, 2-ethyl-1-hexanol; TE, techno-economic; LCA, life cycle assessment; ESA, early stage assessment; EU, European Union; EUR, euros (currency); kg, kilogram; μm, micrometer; mL, milliliter; K, temperature in Kelvin; CNF, carbon nano-fibers; MgO, magnesium oxide; CaO, calcium oxide; BaO, barium oxide; MgAl, magnesium–aluminum; H_2, hydrogen gas; N_2, nitrogen gas; i.d., internal diameter; GC, gas chromatography; PM, physical mixture; EF, electricity factor; CHP, combined heat and power; GHG, greenhouse gases; CED, cumulative energy demand; NREU, non-renewable energy use; REU, renewable energy use; SIR, sustainability index ratio.

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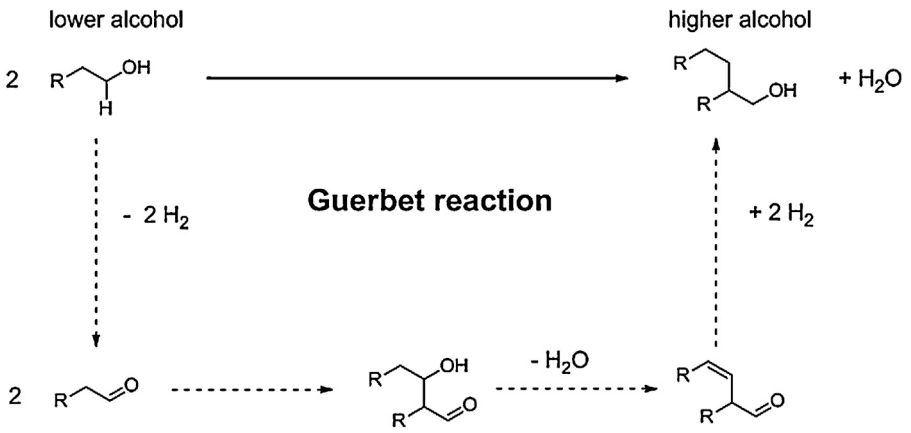

Fig. 1. Guerbet reaction represented as a sequence of four different reaction steps: dehydrogenation, aldol condensation, dehydration and hydrogenation.

more sustainable [11] and reliable supply of bioethanol. With these feedstock and chemical process developments, bioethanol is emerging as one of the key building blocks for production of renewable chemicals. This has led to identification of several conventionally produced chemicals for which production from bioethanol is an attractive alternative [12]. One such potentially interesting family of products is Guerbet alcohols which are widely used in the chemical industry for applications like cosmetics, chemical intermediates, lubricants and solvents [13,14]. The process of producing higher alcohols from ethanol via Guerbet reaction has already been known for over a century [15]. It is generally accepted that the Guerbet reaction is a sequence of different reactions starting from dehydrogenation of alcohol, followed by aldol condensation, dehydration and finally hydrogenation of the unsaturated aldehyde (Fig. 1). However, there have also been studies that claim a direct condensation of starting alcohol without intermediate aldol condensation step [16].

Depending on the starting alcohols the Guerbet alcohols are either linear or branched primary alcohols. One of the most widely known Guerbet alcohols is 2-ethyl-1-hexanol (2-EH) which is used primarily for the production of plasticizers (dioctylphthalate) and has a global market volume of 2.5 million metric tonne per year [17]. Industrially, homogeneous catalysts are applied to convert starting alcohols containing usually more than 6 carbon atoms toward Guerbet alcohols. Usually corrosive bases such as potassium hydroxide with or without the presence of a soluble metal complex are used. The water produced is continuously removed by the addition of a desiccant like CaO [18–22]. Apart from reliance on conventional fossil feedstocks, one other disadvantage of this approach is the corrosive nature of soluble bases used. This leads to high initial capital costs and high amounts of spent catalyst per tonne of product leading to increased requirements for wastewater treatment. Consequently 30% of the selling price is product purification and waste treatment [23]. Hence a potential solution, which is the target of current research, is to perform this reaction in gas phase utilizing a heterogeneous catalyst and bioethanol as starting alcohol. There are several examples in the literature that utilize heterogeneous catalysts, mainly for the Guerbet conversion of ethanol to 1-butanol. Catalysts used are mainly MgO, MgAl mixed oxides and hydroxyapatites. A good review of applied heterogeneous catalysts for ethanol condensation toward 1-butanol is given by Kozlowski [24]. In our research we used alkaline earth metal oxide nanoparticles of different base strength supported on carbon nano-fibers (CNF) as catalysts. CNF have a relatively high surface area ($\sim$150 $m^2\,g^{-1}$) and are inert and therefore suitable as catalyst support under demanding conditions. Simple base oxides are capable of, next to performing the aldol reaction, conducting dehydrogenation/hydrogenation reactions (first and last step of Guerbet reaction, see Fig. 1). For the latter steps often high temperatures are required with these catalysts rendering the catalytic system less sustainable in terms of energy consumption [25]. A possible solution to decrease the amount of energy required, i.e. by lowering the reaction temperature is to add a metal function to the basic oxide as metals are far more efficient dehydrogenation/hydrogenation catalysts [26]. More elaborate information on the current state of the art on heterogeneously catalyzed Guerbet reaction has been included in Appendix D1 [23,24,27–42].

In this article we use 2-ethyl-1-hexanol (2-EH) as a representative compound for higher Guerbet alcohols and report the application of different sustainability metrics in parallel with catalyst developments. We highlight the laboratory developments alongside stepwise sustainability analysis at different stages. Thus, we present the advances in catalytic research and also analyze the accuracy of the early-stage sustainability assessment method and explore how it could be improved. Accordingly the following facets are covered in this study:

(1) Laboratory developments for Guerbet alcohols.
(2) Primary early-stage sustainability assessment (primary ESA) at the onset of laboratory research.
(3) Detailed analysis based on process design, techno-economic (TE) analysis and life cycle assessment (LCA) for 2-EH as an example for Guerbet alcohols.
(4) Updated early-stage sustainability assessment (updated ESA) based on new insights gained in process design.

An important aim of this research is to bring together quantitative sustainability assessment methods and laboratory research to enable effective development of sustainable chemical processes. Using very early stage information and results at the onset of this chemical research, sustainability assessments for nine processes were performed [43] based on the methodology reported in Patel et al. [2]. One of these early-stage analyses was based on a one reactor approach for the production of 2-EH from ethanol and helped to highlight the potential benefits and drawbacks of this process. The assessment indicated that a biobased process would be potentially favorable. Following this first assessment, we present in this paper a more detailed analysis that was performed with techno-economic (TE) analysis and life cycle assessment (LCA), based on a conceptual process simulation model. In the course of process model development it was found that instead of one reactor, a scheme involving four reactors is more feasible for this process which was therefore the basis for the simulation model (including economic assessment and LCA). Considering the change in lay-out,