WELL-TO-TANK DATA FOR ADVANCED TAILOR-MADE BIOFUEL ALTERNATIVES

Stefan Heyne[1], Roman Hackl[2], Karin Pettersson[3], Simon Harvey[4], Sofia Poulikidou[5]
[1] CIT Industriell Energi AB, Chalmers Teknikpark, SE-41288 Göteborg, +46-31-16 10 73, stefan.heyne@cit.chalmers.se
[2] Climate & Sustainable Cities, IVL Swedish Environmental Research Institute
[3] Energy and circular economy, RISE Research Institutes of Sweden
[4] Energy Technology, Department of Space, Earth and Environment, Chalmers University of Technology
[5] Physical Resource Theory, Department of Space, Earth and Environment, Chalmers University of Technology

ABSTRACT: The present work is part of a cross-disciplinary Swedish research project on advanced tailor-made biofuels that aims at identifying drop-in biofuel options for the transport sector that combine excellent combustion properties with sustainable production pathways. The present paper addresses the methodology and primary results of the biofuel production pathway assessment for the diesel fuel alternatives identified within the project. The methodology is illustrated for 2-Ethylhexanol. Three alternative production pathways for 2-Ethylhexanol are analyzed: gasification-based, butanol-based and ethanol-based. The highest biomass to 2-Ethylhexanol conversion (33.9%, lower heating value basis) is achieved for the ethanol-based conversion pathway. The varying spectrum of by-products requires a sophisticated analysis necessary, as addressed in the present work. 2-Ethylhexanol as biofuel cannot outperform conventional biofuels such as e.g. ethanol from a well-to-tank energy performance perspective due to the additional conversion steps necessary. End-use phase benefits such as higher blend-in ratios or reduced pollutant emissions may change the well-to-wheel picture.
Keywords: biofuel, production, integration, transport sector, energy balance, mass balance.

1 INTRODUCTION

The transport sector accounts for almost 25 % of the greenhouse gas (GHG) emissions in Europe and is the main cause of air pollution in cities. As part of the effort to reduce the environmental impact of the transport sector, and to reach the national vision of a vehicle fleet that is independent of fossil fuels by 2030, Sweden has set goals for an increased share of renewables in the transport sector, also following the EU target of at least 10 % by 2020. Within a research collaboration between the Swedish Internal Combustion Engine Consortium (SICEC), Chalmers University of Technology, and a large industrial network, advanced tailor-made biofuel alternatives are being investigated with the aim of identifying fuels with superior performance compared to today's fossil and renewable fuel alternatives. A key aspect of the research collaboration is a close dialogue between the experimental engine research teams, investigating engine performance and biofuel handling and combustion in the engine systems, and the energy systems analysis research groups investigating the biomass potential, production aspects for the respective biofuels, and performance of the entire value chain from well to wheel (WTW). In regular meetings, the results and findings of the research groups are presented and discussed and input from the industrial partners, representing engine manufacturers, fuel suppliers and processing industry is collected and integrated into the further project planning.

Based on a pre-study performed prior to the project [1], a set of initial fuels, so-called A-fuels, was defined for evaluation at the beginning of the project. Based on the results and findings to be obtained from both engine experiments and systems studies, biofuels - or blends of biofuels - with good WTW performance that can be used in improved combustion engine concepts will be suggested. After this first evaluation, it is envisaged to go further with an additional set of fuels, so-called B-fuels, that will been identified during the course of work with the A-fuels. These B-fuels are expected to have improved production pathways from a sustainability perspective and similar or even better combustion performance, or allow for more advanced combustion engine concepts, thereby further improving the WTW performance. The project is inspired by – and planning to establish a collaboration with – a German initiative on tailor-made biofuels at RWTH Aachen University [2]. Comparison will also be made to results on renewable fuel alternatives in the JEC WTW study [3].

The present paper presents preliminary results for the production pathways for the A-fuels chosen for the compression-ignition (CI) engine combustion experiments. These eight biofuels are:

- PolyDME (or POMDME)
- n-Octanol
- 2-Methyltetrahydrofuran (2-MTHF)
- 2-Ethylhexanol (2-EH)
- n-Decanol
- 2-Propylheptanol
- Di-n-butyl-ether (DNBE)
- Caromax 28

An overview of potential production pathways for the eight biofuel alternatives is given and a more detailed analysis is presented for one of the biofuels, 2-ethylhexanol (2-EH), focusing on WTT energy performance.

2 RELATED RESEARCH AND NOVELTY OF PRESENT WORK

There are a number of research projects simultaneously investigating production pathways and combustion performance of biofuels. The U.S. Department of Energy has launched the initiative "Co-Optimization of Fuels & Engines" [4] exploring synergies among new bio-based fuels, engines, powertrains, and fueling infrastructure. The project aims both at designing engines that run more efficiently on biofuels, as well as at designing fuels to decrease engine emissions and improve efficiency. Strategies for successful marketing of new fuels and vehicle technology among industry and

consumers are included in the project.

In Germany, the Cluster of Excellence "Tailor-Made Fuels from Biomass" [2] started in 2007 with the goal to establish innovative processes for biomass conversion to tailor-made fuels adapted to novel combustion engine concepts with high efficiency and low emissions. A holistic and interdisciplinary research approach is adopted with the objective of identifying "a well-defined blend of distinct molecular components with optimized physicochemical properties for future combustion systems, which can be produced by sustainable and economical production processes" [2].

Another research initiative that relates to the present work is the CatchBio Program in the Netherlands [5] focusing on efficiently processing the various components present in biomass (cellulose, hemi-cellulose, lignin, proteins and oils) into useful fuels, chemicals and pharmaceuticals. The focus is on catalyst development but even socio-economical and ethical aspects are considered. 2- Ethylhexanol –a bulk chemical mainly used for production of ester plasticizers [6], and the biofuel investigated more in detail within the present paper – was investigated as part of the CatchBio project within an early-stage sustainability assessment of new bio-based processes [7], indicating potentially favorable production pathways and highlighting the need for further research.

The present research project entitled "Future alternative transportation fuels" focuses on transportation fuels for both road and marine transport, and combines combustion engine research and evaluation of fuel properties with investigation of the sustainability performance of the fuel alternatives from a resource and production process perspective. Industrially relevant production pathways for sustainable biofuels are identified and evaluated, highlighting process integration opportunities fostering easier implementation of the identified biofuel alternatives as well as improving their overall performance with respect to energy efficiency and GHG emissions.

2 METHODOLOGY

In order to identify the industrially relevant and sustainable production pathways for the most interesting biofuels from a combustion engine performance perspective, the following approach is adopted:

- Screening of promising fuels based on literature review
- Production pathway analysis to identify the different options for producing the fuels identified as interesting
- Process synthesis establishing mass- and energy balances
- Process integration study for identifying potential for co-generation of heat and electricity as well as integration opportunities with existing (or newly built) industry infrastructure allowing for efficient use of co-generated by-products and services
- Evaluation of process concepts with respect to energy, environmental and economic performance

Biofuel production processes often have a number of co-generated by-products and/or services. The co-generation of by-products has been accounted for and, where relevant, co-generation of heat and power from the processes' excess heat has been evaluated using a systematic approach based on process integration methodology [11].

For evaluation of the different process alternatives in the present paper, two energy efficiency indicators (both based on the lower heating value (LHV)) are defined:

$$\eta_{bio-to-fuel} = \frac{\dot{m}_{fuel} \cdot LHV_{fuel}}{\dot{m}_{biomass} \cdot LHV_{biomass}} \quad (1)$$

$$\eta_{tot} = \frac{\sum_i \dot{m}_i^- \cdot LHV_i + \dot{W}^- + \dot{Q}^-}{\sum_j \dot{m}_j^+ \cdot LHV_j + \dot{W}^+ + \dot{Q}^+} \quad (2)$$

$\eta_{\text{bio-to-fuel}}$ represents the biomass to fuel energy conversion efficiency only accounting for the main fuel produced from the process and the biomass feedstock energy used. The overall efficiency η_{tot} accounts for all energy streams generated and consumed by the process only accounting for net streams. The electricity ($\dot{W}$) and heat ($\dot{Q}$) only is accounted for either as import (index "+") or export (index "-").

In order to enable a more differentiated evaluation of the performance of the different process pathways, a number of additional assumptions regarding e.g. the assumed energy market scenarios and the primary energy use for different services – in particular electricity generation – are necessary. A first step is made in this paper comparing the primary energy demand for the fuel production processes to data on conventional biofuels presented in the JEC WTW study [3].

A case-study based approach is adopted, applying the methodology for selected fuels and pathways, in order to identify generally valid bottlenecks within the WTW performance that apply to a larger number of fuels identified during fuel screening. The acquired knowledge will help in focusing on the most promising fuel alternatives and pathways in the long run. 2-EH has been chosen as biofuel for illustrating the methodology.

3 PRODUCTION PATHWAY ANALYSIS

A literature survey on production pathways has been performed for the eight CI engine fuels chosen within the project for engine tests (A-fuels mentioned previously) [8]. An overview of the feedstock to fuel conversion pathways is illustrated in Fig. 1.

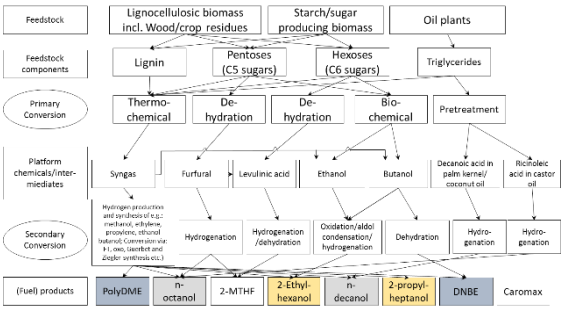

Figure 1: Production pathways for the eight CI engine fuels [8].

The analysis shows that there is both a large spectrum of possible pathways, as well as a large variation in the

state of the development for the different production processes and intermediate stages. None of the bio-based processes routes identified is currently used on an industrial scale, even though several process steps are commercially available. There are well-developed processes for the production of bio-based intermediates which several of the eight fuels can be produced from, e.g. the Biofine process for the production of levulinic acid and furfural [9,10], in turn intermediates for the production of 2-MTHF and n-octanol. For other fuels the development of production routes based on renewable feedstock is less developed, even though there are fossil-based routes that can be mimicked by e.g. production processes based on biomass gasification.

Based on the production pathway analysis, a single fuel – 2-Ethylhexanol – that also has been tested within the overall research project in engine combustion experiments has been evaluated for different production pathways and their energy performance. The results form the basis for a more sophisticated evaluation in the form of life cycle assessment, aiming at identifying critical bottlenecks with the different pathways. This will guide the future choice of fuel alternatives and production pathways that are to be evaluated in detail.

4 PRODUCTION OF 2-ETHYLHEXANOL

Three production pathways for 2-EH have been synthesized and evaluated. All processes are based on a thermal input of biomass corresponding to 100 MW_{LHV}. The pathways are described more in detail in the following paragraphs

4.1 Gasification-based 2-EH

The large scale fossil based production of 2-EH is based on conversion of propylene and syngas (H_2 and CO) to n-butyraldehyde and a condensation and hydrogenation reaction to yield 2-EH via 2-Ethylhexenal. Propylene is most often provided by steam cracking of fossil oil, whereas the syngas generally is produced through steam reforming of natural gas [6]. This production route can be mimicked based on biogenic feedstock by thermal gasification.

Propylene can be produced as a fraction of light olefins via methanol or dimethyl ether (DME) from biomass-gasification [12]–[14]. A comparative assessment of the two alternative processes indicates that – from a thermodynamic viewpoint – both process alternatives have similar process performance [13]. As the syngas for the DME process route is shifted to a H_2:CO ratio of 1, that can be directly used in downstream n-butyraldehyde synthesis, this process route is chosen within the present study.

The additional hydrogen necessary for hydrogenation of 2-Ethylhexenal to 2-EH could also be provided from the syngas, making a separation process – e.g. membrane separation necessary. In the present study the hydrogen supply for the final hydrogenation step is considered as an external feedstock stream however, provided by electrolysis with a conversion efficiency of 65% on an LHV basis [3]. The oxygen that is generated during electrolysis can be used in the gasification process, decreasing the demand for production of oxygen via air-separation. An overview of the process steps is illustrated in Fig. 2.

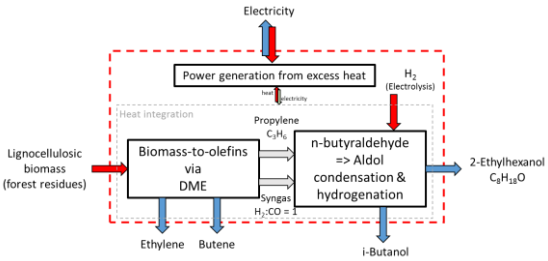

Figure 2: Process overview for gasification-based 2-EH production.

The synthesis of propylene and syngas yields both n- and i-butyraldehyde as well as some other by-products. The i-butyraldehyde is assumed to be further converted to i-butanol as final by-product, increasing the hydrogen demand of the process. The conversions and yields for the different reaction steps are taken from references on fossil-based 2-EH production from propylene, based on the Rhodium-based catalyst [15]. The major assumptions are summarized in Table I.

Table I: Major assumptions for gasification-based 2-EH production process.

Process step	**Assumptions**
Biomass-to-olefins via DME	Based on Arvidsson *et al.* [13]
OXO-synthesis	*Propylene conversion:* - 98% *Product composition:* - i-butyraldehyde: 5 wt-% - n-butyraldehyde: 94 wt-% - heavy ends: 1 wt-%
Aldolisation & hydrogenation	- 98% of n-butyraldehyde converted to 2-EH - 3% excess H_2 - 99% of i-butyraldehyde converted to i-butanol
Electricity demand	- based on Arvidsson *et al.* [13] for DME to olefins process - 0,85 kWh/kg 2-EH for propylene to 2-EH conversion
Heat balance	- based on Arvidsson *et al.* [13] for DME to olefins process - propylene to 2-EH process assumed thermally neutral (combustion of waste-streams)

As the gasification process generates a considerable amount of excess heat, co-generation of electricity with a steam cycle has been considered. Figure 3 illustrates the heat streams available from the 2-EH process as well as the steam cycle integration. 17.5 MW of electricity can be generated from the overall process excess heat, not completely covering the overall process electricity demand of 18.4 MW. The major process electricity

demand stems from the pressurized gasification section (4.6 MW including pretreatment), oxygen-production for gasification (3.5 MW), hydrogen-production (4.6 MW) and various compressors within the process.

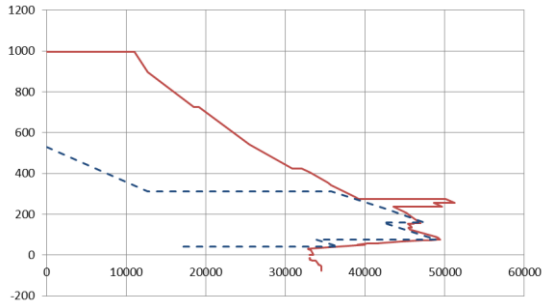

Figure 3: Steam cycle heat integration for gasification-based 2-EH production.

4.2 Butanol-based 2-EH

Direct synthesis of alcohols in general and 2-EH production from butanol in particular via the classic Guerbet condensation reaction has received renewed interest from both researchers and industry [16]–[19]. A review by Gabriëls et al. [17] presents an overview of homogeneous, heterogeneous and combined catalytic systems.

The butanol production in the present work is assumed to be based on corn stover acetone-butanol-ethnaol (ABE) fermentation. Besides n-butanol, acetone and ethanol are produced as by-products. Published data from Tao *et al.* [20] is used. The process scheme is illustrated in Figure 4.

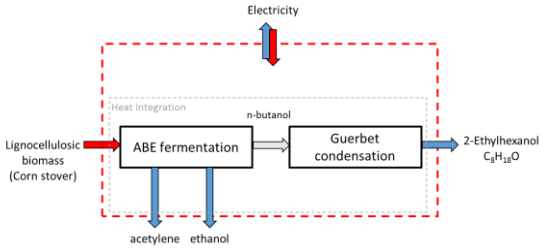

Figure 4: Process overview for butanol-based 2-EH production.

The lignin fraction and biogas produced from the fermentation broth are used for steam and power generation. Tao *et al.* state that excess electricity can be produced from the process. This excess electricity is reduced by the electricity demand of the downstream Guerbet condensation reaction accordingly. The conversion of n-butanol to 2-EH is assumed to be nearly complete and the recovery of 2-EH in the downstream purification as high as 99%. Heat demand for the butanol to 2-EH conversion is assumed to reduce the electricity generation from excess heat from the ABE fermentation with an assumed heat-to-electricity conversion efficiency of 40%. The major assumption for the butanol-based 2-EH production are given in Table II.

Table II: Major assumptions for butanol-based 2-EH production process ([19]–[21]).

Process step	Assumptions
ABE fermentation	- based on Tao *et al.* [20]
n-butanol to 2-EH	- 99.5% conversion - 99% recovery of 2-EH from product mixture
Electricity demand	- based on Tao *et al.* [20] for ABE fermentation process - butanol to 2-EH: based on n-butanol compression to 50 bar for Guerbet condensation reaction plus additional 50% for remaining demand
Heat demand (reducing corresponding electricity)	- 10 kJ/l 2-EH produced plus additional 50% for heating reactants

4.3 Ethanol-based 2-EH

The ethanol-based 2-EH production route is based on a cellulosic ethanol process, follow by acetaldehyde production and conversion to crotonaldehyde, n-butyraldehyde and finally aldolisation and hydrogenation to 2-EH. The project scheme is illustrated in Fig. 5.

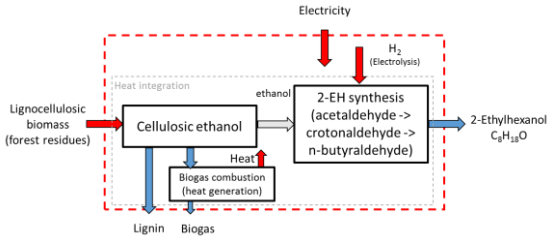

Figure 5: Process overview for ethanol-based 2-EH production.

In addition to the assumptions made in the used reference work [22], [23], the following assumptions were made:

- Biogas produced in the ethanol production process is used for heat generation (steam production), excess biogas being exported
- The lignin generated is considered a product with a market value
- The hydrogen necessary for the process is produced by electrolysis

Ethanol is produced from woody biomass, with lignin, biogas and CO_2 as by-products. The steam and electricity balance for the ethanol process is altered by the extension with 2-EH production due to steam generation in the ethanol to acetaldehyde conversion that decreases the ethanol process steam demand. The conversion of acetaldehyde to 2-EH is based on data for acetaldehyde conversion to n-butanol [23] with the first step – the conversion to n-butyraldehyde – being identical. The n-

butanol process is stated to be a potential steam generator but has not been accounted for decreasing the steam demand in the referred source. This is done similarly in the present study. The hydrogen demand is estimated based on the stoichiometric amounts with an assumed hydrogen loss of 3% as in the reference butanol production process. The specific electricity demand is increased by 50% for the conversion from acetaldehyde to 2-EH in comparison to the reference butanol process to account for the increased number of processing steps. The major assumptions for the ethanol-based production route are given in Table III.

Table III: Major assumptions for ethanol-based 2-EH production process [22], [23].

Process step	**Assumptions**
Cellulosic ethanol	- based on [22]
Ethanol to acetaledhyde	- based on [23]
Acetaldehyde to 2-EH	- 3% excess H_2 - electricity demand: 0.034 kWh/kg Acetaldehyde - heat demand: covered by combustion of by-products

5 RESULTS & DISCUSSION

Table IV provides a summary of the process thermal input and output as well as the efficiencies according to eq. (1) and (2). The ethanol-based process shows the highest biomass to 2-EH conversion efficiency of 33.9%, followed by the butanol-pathway (32.7%) and the gasification-based process (27.5%). All processes show a varying spectrum of byproducts, but considering the overall efficiency η_{tot} the ethanol pathway still performs best.

This however, is partially attributed to the high electricity input for the ethanol-process that – in the present study – is not co-generating electricity from by-products but only covering the heat demand and exporting lignin (and some biogas). The butanol-based case however uses biogas and lignin generated in the ABE fermentation for co-generation of electricity, explaining to some extent the lower efficiency.

Table IV: Energy balance and efficiency for the three 2-EH production pathways

		Gasification -based	**Butanol-based**	**Ethanol-based**
Input				
Biomass	MW	**100**	**100**	**100**
Electricity	MW	**0.9**	**-**	**22.9**
Output				
2-EH	MW	**27.5**	**32.7**	**33.9**
Electricity	MW	**-**	**3.0**	**-**
Ethanol	MW	**-**	**5.0**	**-**
Acetone	MW	**-**	**1.5**	**-**
Biogas	MW	**-**	**-**	**1.4**
Lignin	MW	**-**	**-**	**40.0**
i-Butanol	MW	**1.5**	**-**	**-**
C_2	MW	**18.9**	**-**	**-**
C_4	MW	**8.8**	**-**	**-**
Efficiencies				
$\eta_{bio\text{-}to\text{-}fuel}$		**0.275**	**0.327**	**0.339**
η_{tot}		**0.561**	**0.422**	**0.612**

To perform a more thorough comparison of the energy performance, all energy streams should be converted to primary energy demand, accounting for the respective conversion efficiencies for the in- and output streams. In a first step, this has been done comparing all energy input to the biofuel energy output. Electricity being the only additional input, a conversion efficiency of 32% (as used for biomass-based electricity in the JEC WTW study [3]) has been used. This efficiency definition results in 26.7%, 32.7% and 19.7% for the gasification, butanol and ethanol processes then become, respectively. The butanol pathway – that is considered using rather optimistic estimates from reference [20] with comparable studies being more conservative in the butanol yield and by-product generation [24] – appears to be the most efficient when taking primary energy for electricity input into account. As no electricity input is necessary for the butanol process as presented here, the efficiency is the same as the biomass-to-biofuel efficiency η_{tot}. This conversion to primary energy also allows an approximate comparison of the well-to-tank (WTT) data of 2-EH production to data published for conventional biofuels. Table V presents the WTT energy demand for the 2-EH production in comparison to ethanol from forest residue presented in [3].

Table V: Approximate comparison of production process energy performance of 2-EH and ethanol for WTT data

	WTT [MJ/MJ$_{fuel}$] (production process only)
Gasification-based 2-EH	2.74
Butanol-based 2-EH	2.06
Ethanol-based 2-EH	4.07
Forest-based ethanol (WW/WFET1) [3]	1.81

This comparison indicates that 2-EH has a worse WTT performance than forest-based ethanol considering the rest of the WTT process chain to be similar. However, a credit for substituting other products/services with the exported energy streams has to be accounted for in order to obtain a clear answer.

6 CONCLUSIONS

A systematic overview of the production pathways for a selection of promising CI engine fuels that are evaluated within a cross-disciplinary research project evaluating potential future tailor made biofuels for the transportation sector has been presented. The detailed energy and mass balances for three production pathways for one of the fuels – 2-EH – have been established and the energy efficiency evaluated. The highest biomass to 2-EH conversion (33.9%) on a lower heating value basis is achieved for the ethanol-based conversion pathway, that even show the highest overall conversion efficiency (61.2%).

The varying spectrum of by-products however, makes a more sophisticated analysis necessary. 2-EH as biofuel cannot outperform conventional biofuels such as e.g. ethanol form a WTT energy performance perspective due to the additional conversion steps necessary. End-use phase benefits such as higher blend-in ratios or reduced pollutant emissions may change the WTW picture. A life cycle assessment accounting for byproducts by system expansion will be part of further work to allow a better comparison to published WTT data and to identify the critical steps in the production of advanced tailor-made biofuels to guide the future choice of biofuel pathways to be analyzed in more detail within the overall research project.

7 REFERENCES

[1] M. Grahn and F. Sprei, "Future alternative transportation fuels - A synthesis report from literature reviews on fuel properties, combustion engine performance and environmental effects," Göteborg, Sweden, 2015.

[2] TMFB, "Cluster of Excellence Tailor-Made Fuels from Biomass," 2016. [Online]. Available: http://www.fuelcenter.rwth-aachen.de/. [Accessed: 01-Dec-2016].

[3] R. Edwards, J.-F. Larivé, D. Rickeard, W. Weindorf, E. Commission, J. R. Centre, and I. for E. and Sustainability, *JEC well-to-wheels analysis*. Luxembourg, 2013.

[4] Office of Energy Efficiency & Renewable Energy, "Co-Optimization of Fuels & Engines," 2016. [Online]. Available: https://www.energy.gov/eere/bioenergy/co-optimization-fuels-engines. [Accessed: 01-Jun-2017].

[5] Netherlands Organisation for Scientific Research, "CatchBio," 2016. [Online]. Available: www.catchbio.com. [Accessed: 01-Jun-2017].

[6] H. Bahrmann, H.-D. Hahn, D. Mayer, and G. D. Frey, "2-Ethylhexanol," *Ullmann's Encycl. Ind. Chem.*, pp. 1–6, 2013.

[7] A. D. Patel, K. Meesters, H. den Uil, E. de Jong, E. Worrell, and M. K. Patel, "Early-Stage Comparative Sustainability Assessment of New Bio-based Processes," *ChemSusChem*, vol. 6, no. 9, pp. 1724–1736, Sep. 2013.

[8] R. Hackl, "Literature review: Future Fuels," Stockholm, 2016.

[9] D. J. Hayes, S. Fitzpatrick, M. H. B. Hayes, and J. R. H. Ross, "The Biofine process-Production of levulinic acid, furfural, and formic acid from lignocellulosic feedstocks," *Biorefineries–Industrial Process. Prod.*, vol. 1, pp. 139–164, 2006.

[10] J. Lynch, "Biofine Technology." 2015.

[11] I. C. Kemp, *Pinch Analysis and Process Integration - a user guide on process integration for the efficient use of energy*, 2nd ed. Butterworth-Heinemann, 2007.

[12] P. Haro, P. Ollero, Á. L. Villanueva Perales, and F. Vidal-Barrero, "Potential routes for thermochemical biorefineries," *Biofuels, Bioprod. Biorefining*, vol. 7, no. 5, pp. 551–572, Sep. 2013.

[13] M. Arvidsson, P. Haro, M. Morandin, and S. Harvey, "Comparative thermodynamic analysis of biomass gasification-based light olefin production using methanol or DME as the platform chemical," *Chem. Eng. Res. Des.*, vol. 115, pp. 182–194, Nov. 2016.

[14] P. Haro, F. Trippe, R. Stahl, and E. Henrich, "Bio-syngas to gasoline and olefins via DME – A comprehensive techno-economic assessment," *Appl. Energy*, vol. 108, pp. 54–65, Aug. 2013.

[15] G. D. C. D. Kessen, B. D. C. D. Cornils, J. D. I. Hibbel, H. D. C. D. Bach, W. D. C. D. Gick, E. Wiebus, and W. Zgorzelski, "Verfahren zur herstellung von 2-ethylhexanol," DE 3530839 A1, 1987.

[16] D. Liu, X. Chen, G. Xu, J. Guan, Q. Cao, B. Dong, Y. Qi, C. Li, and X. Mu, "Iridium nanoparticles supported on hierarchical porous N-doped carbon: an efficient water-tolerant catalyst for bio-alcohol condensation in water," *Sci. Rep.*, vol. 6, no. October 2015, p. 21365, Feb. 2016.

[17] D. Gabriëls, W. Y. Hernández, B. Sels, P. Van Der Voort, and A. Verberckmoes, "Review of catalytic systems and thermodynamics for the Guerbet condensation reaction and challenges for biomass valorization," *Catal. Sci. Technol.*, vol. 5, no. 8, pp. 3876–3902, 2015.

[18] M. Biermann, H. Gruß, W. Hummel, and H. Gröger, "Guerbet Alcohols: From Processes under Harsh Conditions to Synthesis at Room Temperature under Ambient Pressure," *ChemCatChem*, vol. 8, no. 5, pp. 895–899, Mar. 2016.

[19] K. Breitkreuz, A. Menne, and A. Kraft, "New process for sustainable fuels and chemicals from bio-based alcohols and acetone," *Biofuels, Bioprod. Biorefining*, vol. 8, no. 4, pp. 504–515, 2014.

[20] L. Tao, E. C. D. Tan, R. McCormick, M. Zhang, A. Aden, X. He, and B. T. Zigler, "Techno-economic analysis and life-cycle assessment of cellulosic

isobutanol and comparison with cellulosic ethanol and n-butanol," *Biofuels, Bioprod. Biorefining*, vol. 8, no. 1, pp. 30–48, Jan. 2014.

[21] C. Carlini, A. Macinai, A. M. Raspolli Galletti, and G. Sbrana, "Selective synthesis of 2-ethyl-1-hexanol from n-butanol through the Guerbet reaction by using bifunctional catalysts based on copper or palladium precursors and sodium butoxide," *J. Mol. Catal. A Chem.*, vol. 212, no. 1–2, pp. 65–70, Apr. 2004.

[22] J. M. Joelsson, C. Engström, and L. Heuts, "From green forest to green commodity chemicals," Stockholm, Sweden, 2015.

[23] J. Eliasson, "Design of an Plant for Manufacturing of Acetaldehyde," Lund University, 2010.

[24] N. R. Baral and A. Shah, "Techno-Economic Analysis of Cellulosic Butanol Production from Corn Stover through Acetone–Butanol–Ethanol Fermentation," *Energy & Fuels*, vol. 30, no. 7, pp. 5779–5790, Jul. 2016.

8 ACKNOWLEDGEMENTS

This work is conducted within the project "Future alternative transportation fuels" funded by the Swedish Energy Agency (project nr. 41139-1). The industrial partners supporting the project are Chevron, Lantmännen, Perstorp, Preem, Scania, st1, Saybolt Sweden, Stena Line, Volvo AB and Volvo Cars.