



Climate Leading Process Industries: Project 4.2.5 Industrial adaptation of lignin value chains

An open summary report

Authors: RISE/Martin Hedberg; Chalmers Tekniska Högskola/Abdenour Achour, Louise Olsson, Derek Creaser and Anna Anttila; Borealis AB/Lars Pettersson

With financing from Vinnova, Region Västra Götaland and the West Sweden Chemicals and Materials Cluster.

VINNOVA
Sveriges innovationsmyndighet

Med stöd från

 **VÄSTRA
GÖTALANDSREGIONEN**

**VÄSTSVENSKA
Kemi- och
Materialklustret**

TABLE OF CONTENTS

1. SHORT SUMMARY OF THE REPORT 3

2. INTRODUCTION 4

 2.1. PROJECT PARTICIPANTS..... 5

 2.2. PROJECT STRUCTURE AND REPORT OUTLINE 5

3. WP1 – EXPERIMENTAL STUDIES FOR DIRECT UPGRADING OF HL 6

 3.1. EXPERIMENTS PERFORMED 6

 3.2. BRIEF COMMENTS ON THE EXPERIMENTAL RESULTS..... 9

4. WP2 – APPLICABILITY OF THE PRODUCTS OBTAINED, FUTURE RECOMMENDATIONS AND OUTLOOK ... 10

 4.1. APPLICABILITY OF THE PRODUCTS OBTAINED..... 10

 4.1.1. *Comments on the proposed value chain in Figure 4* 12

 4.2. FUTURE RECOMMENDATIONS AND OUTLOOK 13

5. ACKNOWLEDGEMENT 15

1. Short summary of the report

This project is a continuation of the efforts started in the prestudy project within *Climate Leading Process Industries* called *4.2.4 Catalytic hydrodeoxygenation of lignin* to convert hydrolysis lignin (HL) into mixtures of hydrocarbons using so called slurry hydrotreatment.¹ HL is a residue produced from saccharification of lignocellulosic side streams and the starting point for second generation sugar platform chemistry. HL is also structurally different from so-called kraft lignin generated by the kraft pulping/sulfate process, which is today the dominating process for converting wood into wood pulp. Due to the conditions of the project agreement, results from the experimental work cannot be presented in this open report, but experimental activities performed and the results from the work are described and discussed in general together with important conclusions made.

Recommendations regarding further development efforts needed are also discussed. Currently confidential information, disclosed only to the project partners who have signed the project agreement, has been documented separately and constitute together with this open report the total reporting of the efforts in the project. The project has been managed and coordinated by RISE Research institutes of Sweden AB (RISE), the laboratory research and development work has been carried out by Chalmers University of Technology. Borealis AB has provided general petrochemical expertise and advice concerning for instance product quality criteria for starting materials to be used for steam cracking to olefins, as well as generally important input to the reporting of the project. An external industry reference group providing a broad and complementary expertise has also been involved in discussing the progress of the work and general aspects from feedstocks to target products, value chain aspects and production methodologies. The reference group consists of Preem AB, Perstorp AB, VTT Technical Research Centre of Finland Ltd (VTT) and Sekab BioFuels & Chemicals AB (Sekab).

The main conclusions from the project are the following:

- The process research and development work on slurry hydrotreatment conversion of HL (and kraft lignin) with a catalyst are promising for further scale up testing in continuous pilot scale equipment.
- HL is more facile to upgrade than kraft lignin and gives higher liquid yields and lower amounts of solid (char) byproduct. This is discussed further under 3.2 and is very briefly likely due to a much less condensed molecular structure of HL compared with kraft lignin.
- Promising results were obtained in experiments where the same catalyst portion that was used in the initial experimental run was recycled three rounds, recycling also the liquid product as co-feed during repetitive addition of more and more HL using a starting oil concept (see Figures 2 and 3c). Although further characterization of catalyst robustness is needed, the tests performed provide an indication that fully renewable products can be produced also starting from fossil starting oils as co-feeds, like vacuum gas oil (VGO), an at present routinely used fossil raw material in oil refineries.
- Product composition from slurry hydrotreatment upgrading of HL together with VGO show small but distinct differences from VGO upgraded alone, with changed proportions between paraffins, iso-paraffins, olefins, naphthenes and aromatics. Relevant fractions (naphtha/gasoline, diesel/kerosene and heavies for potential use as base oil components) of products can be separated based on their boiling point ranges as determined using thermogravimetric analysis (TGA-Simdist), using fractional vacuum distillation.

- Preliminary assessments made of how an operational value chain could form, has so far very briefly concluded that an entirely new value chain would be needed to reach industrial scale production of lignin-based hydrocarbons in Sweden. The main reasons for this are that no actor in Sweden currently has the required technical equipment to perform slurry hydrotreatment of HL or kraft lignin in full scale and, in the case of HL, that industrial infrastructure for second generation sugar platform chemistry, which produces HL as a byproduct, does only exist on a significant scale outside Sweden (see for instance <https://www.clariant.com/en/Company/Contacts-and-Locations/Key-Sites/Romania> concerning Clariants second generation bioethanol plant in Romania).

2. Introduction

As described in the open report from the previous prestudy project within Climate Leading Process Industries called *4.2.4 Catalytic hydrodeoxygenation of lignin*,¹ enzymatic hydrolysis lignin (HL) is a primary byproduct of the enzymatic hydrolysis step from saccharification of lignocellulose using established technologies for *e.g.* second generation bioethanol production. HL is produced in relatively large quantities but is currently more or less only used as a low-grade fuel.² Due to the relatively mild enzymatic hydrolysis conditions, hydrolysis lignin is, as will be evident also from the work in this project and in reference 1, less recalcitrant and cleaner (lower ash and sulfur contents) than the lignin materials obtained from other chemical processes.³ Research on valorization of HL as a useful carbon source for the chemical industry is so far however for various reasons limited,¹ and much more efforts have so far been spent on kraft lignin. The importance of the conversion of HL to more valuable products than electricity and heat is discussed in some depth in an earlier report from the Climate Leading Process Industries prestudy project *4.2.1 Förstudie möjliga målmolekyler från sockerplattformen*.⁴ In very brief summary, it is clear that in order for the sugar platform⁵ to become an economically feasible alternative to produce chemicals which are today produced from fossil raw materials, efficient processes to convert **both** carbohydrates and HL into high-quality fuels and value added chemicals are required.⁶ From a different perspective, if economically attractive processes can be developed to convert HL to chemicals replacing current fossil ones, this would pave the way for the sugar platform as a major source of chemicals needed in society.

¹ The open summary report for the project *4.2.4 Catalytic hydrodeoxygenation of lignin* is available here: www.klimatledandeprocessindustri.se

² See for instance in a) J. Zakzeski *et al. Chem. Rev.* **2010**, *110*, 3552–3599 (<https://doi.org/10.1021/cr900354u>) and in b) Ponnusamy, V. K. *et al. Bioresour. Technol.* **2019**, *271*, 462–472 (<https://doi.org/https://doi.org/10.1016/j.biortech.2018.09.070>).

³ See for instance in Kim, J.-Y. *et al. Bioresour. Technol.* **2019**, *279*, 373–384 (<https://doi.org/https://doi.org/10.1016/j.biortech.2019.01.055>).

⁴ The summary report in Swedish called "Klimatledande Processindustri, Insatsområde Förnybart: Projekt 4.2.1 Förstudie Möjliga Målmolekyler från Sockerplattformen - En öppen sammanfattningsrapport med föreslagen färdplan" 2020 discusses the topic of HL-valorization as a way to successfully establish also the sugar platform as a source of industrially relevant chemicals. The report is available here: www.klimatledandeprocessindustri.se

⁵ See reference 4 and in Zhou, Z. *et al. Renewable and Sustainable Energy Reviews* **2021**, *146*, 111169 (<https://doi.org/10.1016/j.rser.2021.111169>).

⁶ See for instance in reference 3 and in Tribot, A. *et al. Eur. Polym. J.* **2019**, *112*, 228–240 (<https://doi.org/https://doi.org/10.1016/j.eurpolymj.2019.01.007>).

This report describes efforts to convert HL to mixed hydrocarbons for the petrochemical industry using so called slurry hydrotreatment,⁷ and constitutes the next step after the prestudy in reference 1, eventually targeting pilot plant scale demonstration. As will be discussed more in detail below, the target products of the project are mixed hydrocarbons which can be fractionated by distillation to naphtha, gasoline, diesel and base oil component fractions, partially or fully replacing fossil crude oil as the source of these important starting materials. Naphtha is the starting material for making simple olefins and aromatics on a full industrial scale.⁸ Concerning prior art for the conversion of HL using hydrotreatment techniques and various catalysts, this is discussed in some detail in reference 1 and references therein.

Due to the conditions in the project agreement for this project, this non-confidential summary report does not disclose data from the experimental work, which catalysts were used etc. Instead, the report focuses on a brief high-level open discussion of the results and what they mean in terms of applicability of HL as a carbon source for the chemical and petrochemical industry.

2.1. Project Participants

The following partners worked within this project: RISE/Martin Hedberg; Chalmers/Derek Creaser, Abdenour Achour, Anna Anttila and Louise Olsson; Borealis AB/Lars Pettersson. An industry reference group was formed for the project consisting of Preem AB/Olov Öhrman; Perstorp AB/Oleg Pajalic; VTT/Juha Lehtonen and Sekab/Monica Normark, Tino Lassmann and Mathilda Johansson. Chalmers conducted all of the laboratory work and the project was coordinated by RISE (project manager Martin Hedberg).

2.2. Project structure and report outline

The project was divided into two work packages, each with specific goals. Literature studies were combined with laboratory work and simulations.

WP1 – Experimental studies for direct upgrading of HL

WP2 – Future recommendations, project coordination/administration

Methodology used to convert HL and results from WP1 are reported in chapter 3 with conclusions. Subsequently, chapter 4 provides suggestions for applications for the products obtained, future work and an outlook discussing potential new value chains. Chapter 5 provides acknowledgments.

⁷ For selected references on slurry hydrotreatment of biomass-containing feedstocks (pyrolysis oil, lignin etc) lignin, see for instance in a) Bergvall, N. *et al. Energy and Fuels* **2020**, *34*, 8452–8465 (<https://doi.org/10.1021/acs.energyfuels.0c01322>), b) Meier, D. *et al. Biomass and Bioenergy* **1994**, *7*, 99–105 ([https://doi.org/10.1016/0961-9534\(95\)92632-1](https://doi.org/10.1016/0961-9534(95)92632-1)), c) Information about the RISE slurry hydrotreatment pilot plant facility is available here: https://www.ri.se/sites/default/files/2019-12/Produktblad%20SHC_2019-11-19_150343.pdf and d) Commercial technologies for slurry hydrocracking/hydrotreatment is available for instance from ENI and from Honeywell: https://www.eni.com/assets/documents/eng/company/brochure/2014/eni_EST_esecutivo.pdf and <https://www.honeywell-uop.cn/wp-content/uploads/2011/05/UOP-Uniflex-Heavy-Oil-Upgrading-Paper.pdf>.

⁸ See for instance in Schaerlaeckens, E. J. M. *et al.* patent EP 3 110 923 B1 to Saudi Basic Industries Corporation and SABIC Global Technologies B.V.

3. WP1 – Experimental studies for direct upgrading of HL

In this project, direct catalytic hydrogenation is used, which is a technique where hydrogen and catalysts are used to convert oxygenated macromolecules like HL (see Figure 1) into in this case mostly mixtures of relatively small hydrocarbons for potential use as fuels and value-added chemicals. This project is, as previously mentioned, a continuation of the prestudy project in reference 1. The main goal of the experiments is to prepare for potential future pilot plant demonstration experiments using continuous slurry hydrotreatment equipment to perform upgrading of lignin-containing mixtures to hydrocarbons for industrial applications.⁷ The latter is discussed in some more detail in 4.2 below.

3.1. Experiments performed

A fossil starting oil in the form of vacuum gas oil (VGO) was selected to be used as liquid co-feed for the solid powder HL during catalytic hydrogenation upgrading. The experiments have been performed by mixing a particular catalyst prepared at Chalmers with HL and VGO, agitating the mixture in a reactor shown in Figure 1 at high temperatures in the presence of a stoichiometric excess of hydrogen at high pressures in a closed batch stainless-steel Parr reactor (Process setup, Figure 1), varying operating conditions.

A fossil starting oil in the form of vacuum gas oil (VGO) was selected to be used as example liquid co-feed for the solid powder HL during catalytic hydrogenation upgrading. Other fossil or renewable co-feeds like light gas oil (LGO), triglyceride fats (animal fats and/or vegetable oils), raw tall diesel (RTD) need to be tested as well, but due to the limited budget in this small project the work focused on VGO as a relevant example co-feed/starting oil.

The hydroconversion experiments were performed in a 450 mL stainless-steel Parr reactor. Typically, the reactor was charged with a catalyst in the range of 0.25-1.0 g and dry HL in the range of 5-10 g in 67g of VGO as a solvent. The reactor was sealed and purged with nitrogen several times to remove oxygen. After leak testing, the reactor was pressurized with hydrogen and then heated to the desired reaction temperature under continuous stirring at 1200 rpm. The time zero was set once the desired reaction temperature and pressure were reached. After 5 h reaction time, the heater was turned off and the reaction was left to cool down. This first process step is denoted 1st reaction cycle (Figure 2). To acquire a recycle-Lignin-VGO process, the 2nd and 3rd reaction cycles were performed on a lab-scale at Chalmers by feeding an addition of 2.5 g dry HL (without adding any new solvent or catalyst) as a feedstock and subsequently the reactions were carried out at same operating conditions, as shown in Figure 2.

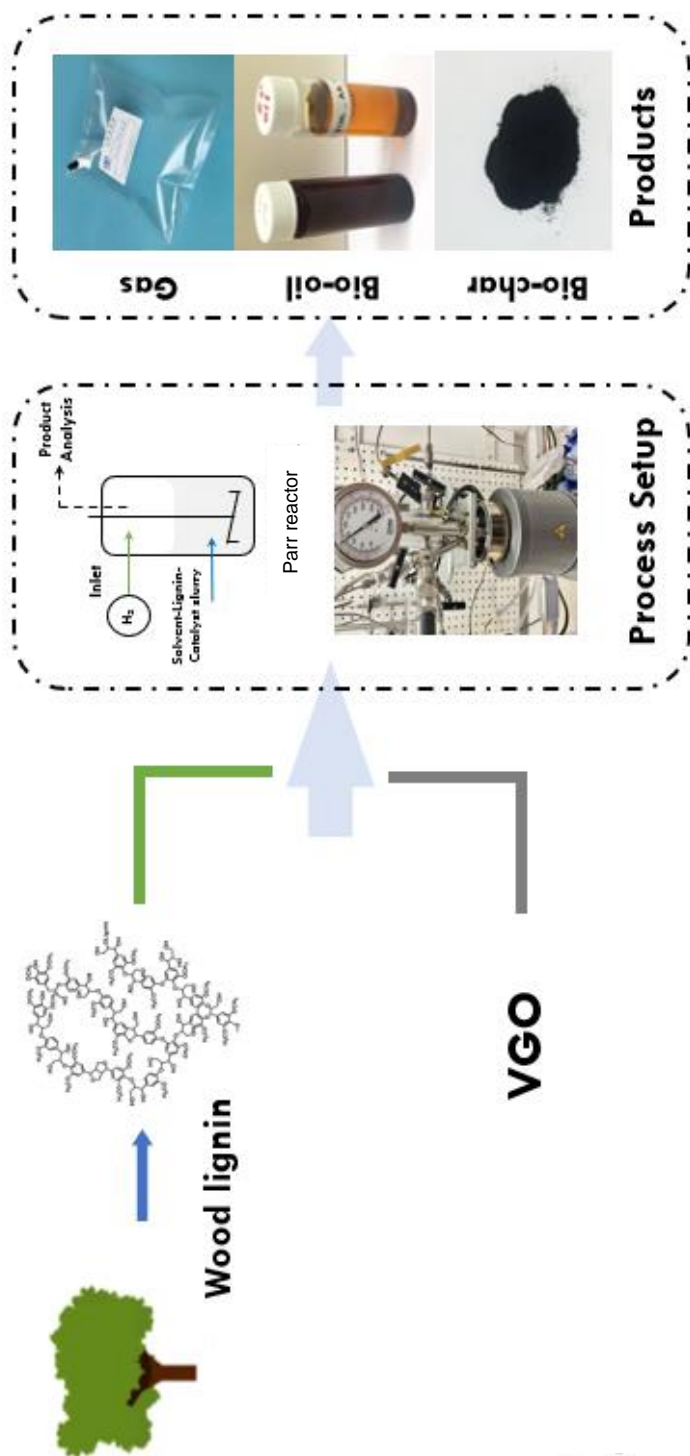


Figure 1. Schematic illustration of the HL-upgrading experiments performed in this project.

A more detailed description of the experiments follows here:

Studies on the repetitive addition of more and more lignin, without adding more VGO or catalyst, were performed to increase the green (biogenic) carbon content of the product mixture, simulating a process concept which in a continuous mode of operation would provide completely green upgraded

product (see Figure 2 for a schematic illustration). After each experiment, different fractions of lignin products were recovered and analyzed. The typical products are (see Products, Figure 1):

- A mixture of gases (excess hydrogen and gases formed in the reaction like for instance methane).
- A liquid product dominated by different hydrocarbons as a result of, among other reactions occurring, hydrodeoxygenation⁹ of HL.
- Small (if any) amounts of partially or fully unconverted lignin.
- Char/biochar, which is a carbon-rich insoluble material in many cases mostly consisting of carbon.

The products were analyzed using various analytical techniques, like elemental analysis to determine the C, H, O, N and S content, gas chromatography (GC-TCD) to characterize gases formed during HL- and VGO-hydroconversion, and two-dimensional gas chromatography with mass spectrometry (GC×GC-MS/FID) to identify and quantify monomers formed in the liquid product oils, in turn monitoring effects of the catalyst used. Thermogravimetric analysis (TGA-Simdist) was used to characterize the boiling point ranges of the liquid product from HL-upgrading experiments. The amount of water formed from the hydrodeoxygenation of lignin was determined by performing Karl Fischer (KF) titration of the liquid products.

The structural and surface characterization of the prepared catalysts were also performed using other techniques:

- The crystallinity of the catalysts was characterized by powder X-ray diffraction (XRD).
- Textural properties such as specific surface area, pore size and pore volume were evaluated by using a nitrogen physisorption analyzer.
- Scanning electron microscopy (SEM) was used to observe the surface structure and morphologies of the catalyst particles.
- The quantity and acidity of acid sites present on the catalyst were characterized using a temperature-programmed desorption of ammonia (NH₃-TPD) technique.

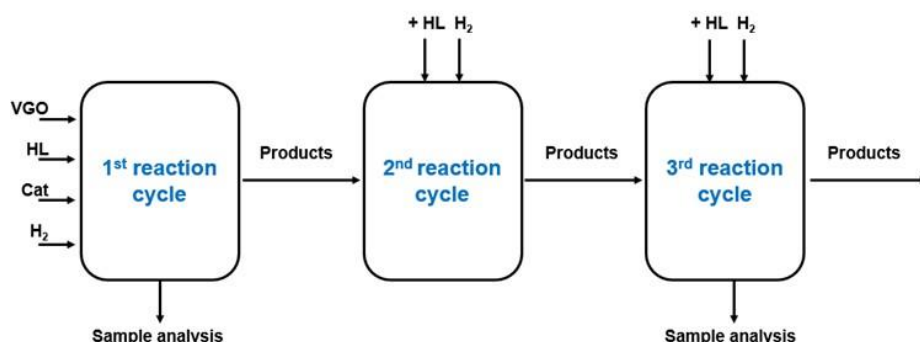


Figure 2. Simplified recycling catalytic hydrogenation process used at Chalmers to study the repetitive recycling of the product as co-feed during HL-upgrading.

⁹ For references on hydrodeoxygenation of different lignins, see reference 1 and references therein. For a recent review article on this topic, see in Jing, Y. *et al. ChemSusChem* **2020**, *13*, 4181 – 4198 (<https://doi.org/10.1002/cssc.201903174>).

3.2. Brief comments on the experimental results

The experiments performed in this project have provided the basis for assessing the impact of HL feeds on operating conditions and their incorporation into the liquid product. In addition, key information has been collected which is needed in order to design pilot plant demonstration experiments, scaling reactions up towards significantly increased process understanding and a generally higher technology readiness (TRL) level. As mentioned above, repetitive manual recycling was performed to simulate continuous product and catalyst recycling, the liquid product being used as co-feed for HL-upgrading in a batch reactor (Figure 2). A reference blank experiment was also performed excluding the catalyst but having a maintained high pressure hydrogen atmosphere in the reactor, something which gave a solid char type product resulting from poor or no liquefaction of the added HL in the absence of the catalyst. Important results are briefly the following:

- High yields of liquid products dominated by aromatic and aliphatic hydrocarbons were obtained where parts of the products clearly originate from HL. In the absence of catalyst (reference experiment), very high amounts of char were obtained.
- Small but significant effects of HL-addition on the hydrotreatment co-upgrading product was observed, causing slightly different proportions between paraffins, iso-paraffins, olefins, naphthenes and aromatics compared with upgrading pure fossil feedstocks.
- Promising results were obtained for the product/catalyst batch mode recycling experiments, with complete conversion of HL also after the third recycling step with, in total, about 10 % w/w of char/biochar being produced.
- As previously observed in the prestudy 4.2.4 *Catalytic hydrodeoxygenation of lignin*,¹⁰ HL is more readily upgraded by catalytic hydrogenation than kraft lignin, likely explained by a less condensed and thereby less recalcitrant molecular structure of HL.¹⁰ Compared with the reactions starting from kraft lignin, less char/biochar is produced and liquid product yields are higher.
- Liquid products are dominated by mixtures of hydrocarbons which can be separated into different fractions by fractional distillation: a lighter gasoline/naphtha fraction, an intermediate diesel/kerosene boiling point range product, and a heavier fraction. Assessment of the applicability of these fractions for the chemical industry is discussed below in chapter 4.
- Kraft lignin and to a lesser extent also HL deviates structurally from native lignin in the plant or tree and have longer carbon chains and condensed ring structures,¹⁰ which form during the Kraft process and during the saccharification of lignocellulose respectively. This likely explains the slightly increased content of heavier molecules observed in the liquid products when adding lignins to for instance vacuum gas oil (VGO) before hydrotreatment.
- Chalmers has in their work developed a catalyst.

¹⁰ For examples of references which use structural characterization data for different lignin types to assess recalcitrance of lignins towards upgrading, see in a) Constant, S. *et al. Green Chem.*, **2016**, *18*, 2651-2665 (<https://doi.org/10.1039/C5GC03043A>), in b) Lancefield, C. S. *et al. Chem. Sci.*, **2018**, *9*, 6348-6360 (<https://doi.org/10.1039/C8SC02000K>) and in c) Li, T. and Takkellapati, S. *Biofuels, Bioprod. Bioref.* **2018**, *12*, 756-787 (<https://doi.org/10.1002/bbb.1913>).

4. WP2 – Applicability of the products obtained, future recommendations and outlook

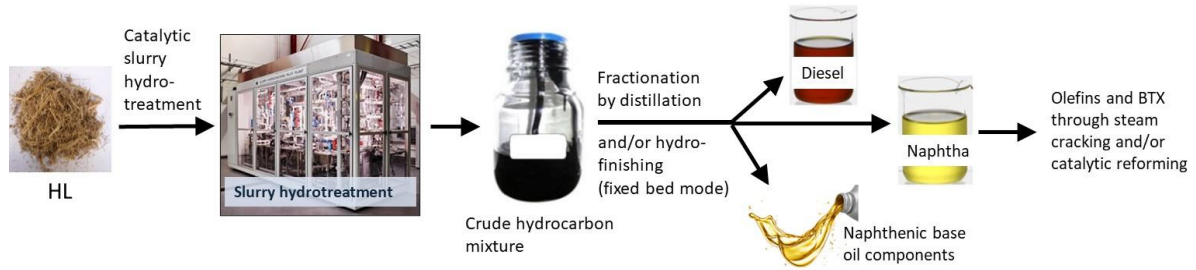
As mentioned above, the creation of attractive value chains for HL is key also to successfully establishing the sugar platform as a complementary source of industrial chemicals replacing fossil crude oil as a starting material, something which has been discussed in some more detail in previous reports from other projects within the Climate Leading Process Industries initiative.⁴ HL has the potential to be an abundantly available source of carbon for the chemical industry at similar or even larger volumes than kraft lignin. RISE, Chalmers, Borealis and the Reference group have in this project focused on the partly new valorization process concept, with some technical aspects schematically illustrated in Figure 3 and a tentative new value chain illustrated in Figure 4, to introduce HL as a relevant renewable carbon source for the manufacture of transport fuels, bulk and specialty chemicals going forward.

4.1. Applicability of the products obtained

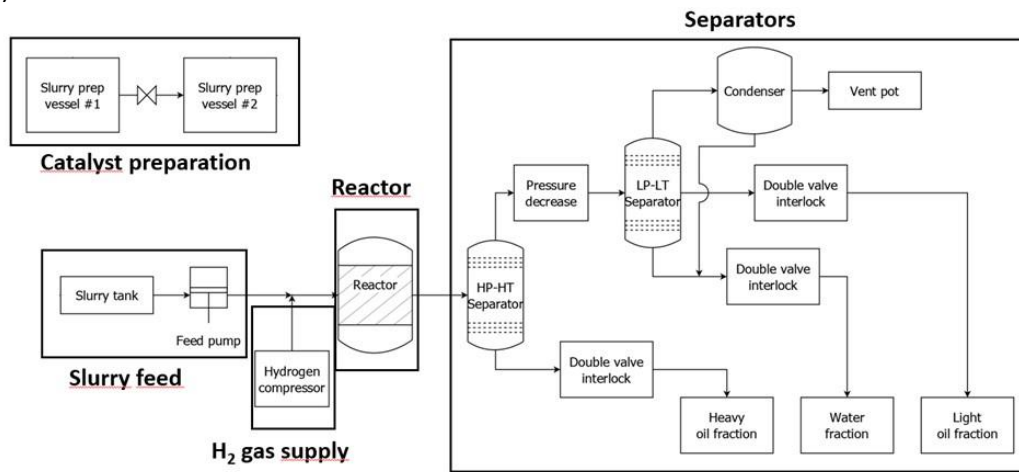
The continued efforts in this project largely confirm the conclusions made regarding the usefulness of the product mixtures obtained from catalytic hydrogenation of HL-containing starting materials discussed in chapter 5 of reference 1.¹ Analytical characterization of the liquid form product mixtures confirm that they consist of mixtures of lower boiling range molecules (<180-220°C, naphtha and gasoline-like fraction) with mid boiling range products (~180-360°C diesel/kerosene-like fraction) and heavier hydrocarbons (~375-600°C) which may be useful as base oil components (components in *e.g.* lubricants, extender oils, transformer oils and other industrially used heavier oil components). The product mixtures also contain low amounts of oxygenates like phenols and ethers which will likely need to be hydrodeoxygenated to achieve target quality oxygen-free products, requiring at least a catalytic hydrofinishing step in standard oil refinery infrastructure as illustrated schematically in Figure 3a). The above fractions can be separated from each other using fractional vacuum distillation where fractions are cut according to the schematic illustration in Figure 5, which is based on a boiling point curve measured for a non-project related hydrocarbon mixture using thermogravimetric analysis with simulated distillation (TGA-Simdist). Catalytic cracking/hydrocracking would further increase the share of lighter hydrocarbons in the product before fractionation and can be added as a separate step before or after hydrofinishing and/or fractional distillation in Figure 3a). Increasing the yield of naphtha, which on a molecular level is a mixture of mainly saturated substituted acyclic and monocyclic hydrocarbons having between four to eleven carbon atoms, may be important for the production of renewable olefins like ethylene, propene or renewable BTEX (benzene, toluene, ethylbenzene and xylenes). As mentioned also in reference 1, sustainable air fuel (SAF) could be another very interesting product from HL upgrading also since SAF should contain significant amounts of aromatic hydrocarbons,¹¹ which should of course also originate from renewable raw materials where contributions from lignin could be one way of providing these.

¹¹ See for instance in ASTM D7566-21 concerning requirements for content of aromatic hydrocarbons in jet fuel containing also synthetic components, available for instance at <https://www.astm.org/d7566-21.html>. In Jet A1 specifications 8-25% w/w of the hydrocarbon content should be monocyclic aromatic hydrocarbons, see for instance at <https://www.exxonmobil.com/en/aviation/products-and-services/products/exxonmobil-jet-a-1>.

a)



b)



c)

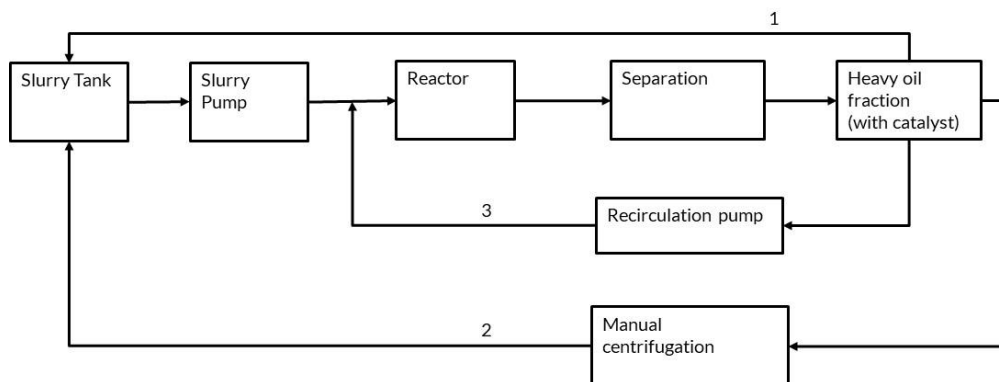


Figure 3. a) Schematic illustration of what RISE and Chalmers believe is a viable process concept for conversion of HL into key hydrocarbon-based products. b) Schematic illustration of the slurry hydrotreatment pilot plant equipment at RISE in Piteå, mimicking full scale. c) Schematic illustration of different options for product and catalyst recirculation for the slurry hydrotreatment pilot plant equipment at RISE in Piteå, something which was tested in lab scale in this project.

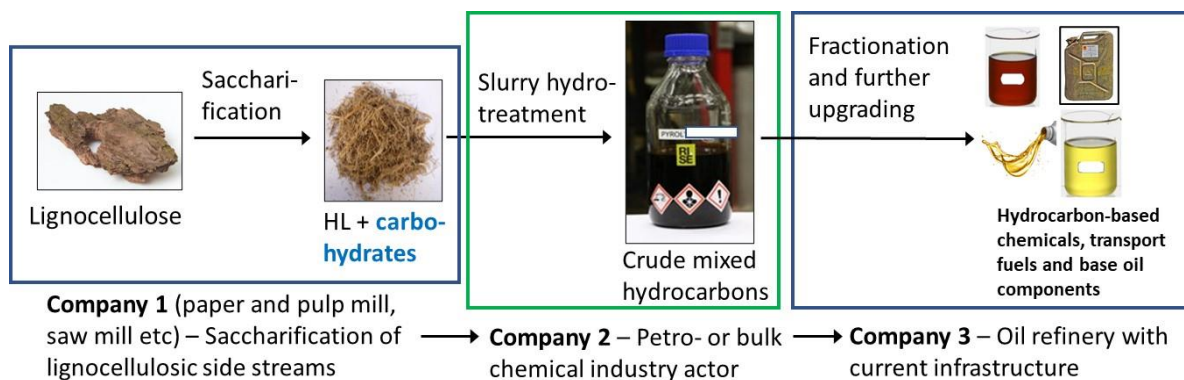


Figure 4. Schematic illustration of the value chain which is necessary to establish HL as a routine raw material for the both environmentally and economically sustainable manufacture of hydrocarbon-based products, thereby also facilitating a more commercially viable production via sugar platform chemistry of selected target molecules from carbohydrates which are important to society (carbohydrates in blue are starting materials for the sugar platform).⁴

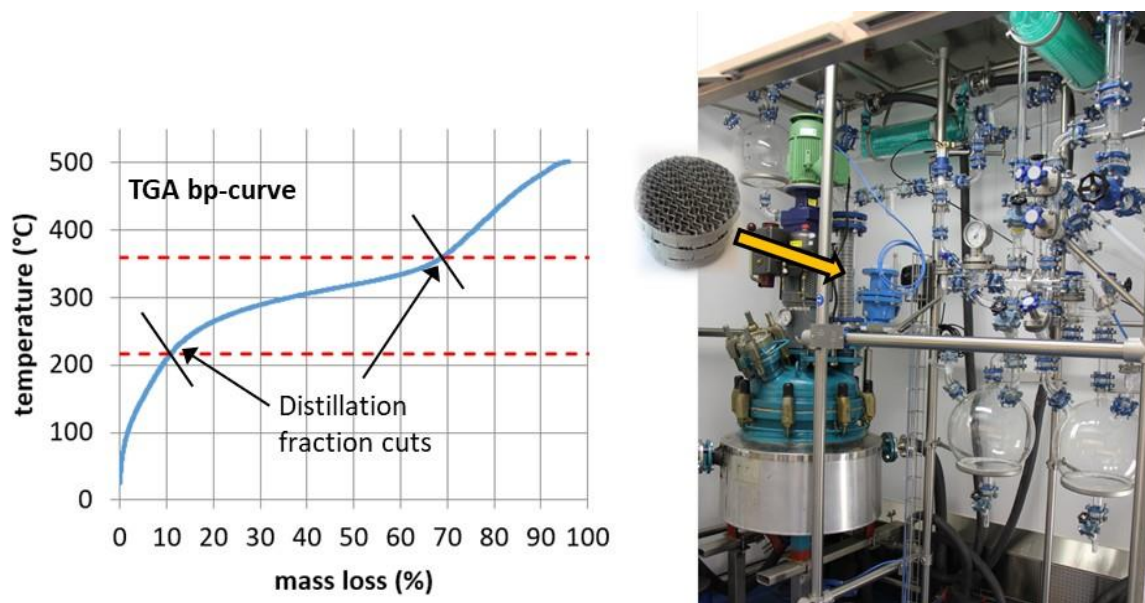


Figure 5. *Left picture:* Boiling point curve measured for a non-project related hydrocarbon mixture using TGA-Simdist with red dotted lines indicating the approximate diesel boiling point range, below which gasoline/naphtha is boiling and above which heavier oils like base oil components are boiling. Suitable cut points for fractional distillation are highlighted with arrows. *Right picture:* Example of distillation equipment at RISE with yellow arrow showing the position of the distillation column with structured column packing shown in the small expansion picture.

4.1.1. Comments on the proposed value chain in Figure 4

As discussed for instance in reference 1 and 7, the properties of lignocellulosic feedstocks like HL, kraft lignin and in fact also thermochemical biooils, call for new conversion technologies to efficiently upgrade abundantly available and renewable lignocellulosic raw materials (which in addition do not compete with food or feed production) into renewable hydrocarbons for the chemical and petrochemical industry. Slurry hydrotreatment is a promising technology for converting these raw materials to crude hydrocarbons for refinery integration but currently there is no actor in Sweden

which has the technical equipment and infrastructure available to operate such processes on an industrial scale. This means that to establish the sugar platform as a source of chemicals manufactured from carbohydrate monomers and in that process also produce HL as a side stream, significant investments are needed both in industrial infrastructure for the saccharification of lignocellulosic side products from forestry, paper and pulp industries and agriculture, but also in full scale slurry hydrotreatment equipment with associated infrastructure to upgrade the HL. Further efforts will be needed to characterize different scenarios for how shared investments, legislation and other driving forces can provide an operational value chain, something which was not possible to perform in this relatively small project. Some selected activities to address these aspects are listed below under 4.2.

4.2. Future recommendations and outlook

This project has provided further process understanding of the slurry hydrotreatment process for upgrading HL to mixtures of hydrocarbons which are interesting to integrate and use as starting material in current oil refineries. Further efforts will naturally focus on detailed optimization and demonstration of the process concept in pilot plant scale, aiming at reaching TRL 5-6. This will in addition produce relevant amounts of product mixtures for fractional distillation and/or cracking/isomerization/hydrofinishing upgrading targeting product fractions which are fulfilling important specification criteria for use in the production of chemicals, transport fuels and base oil products. The following development activities are judged as very important going forward and can be performed either in few large collaboration projects or more stepwise in several targeted smaller projects:

- Further process optimization of the process steps illustrated in Figure 3a), at first in lab scale, is required. Preferably optimization is performed in iteration with further techno-economic analyses and pilot plant runs, optimizing catalyst type, amount and loading, further repetitive catalyst/product recycling studies to understand catalyst robustness, HL-loading and co-feed type and amount in relation to feed pumpability and product composition, and to optimize the liquid hourly space velocity (LHSV), thereby maximizing the capacity of the process. In other words, the development work should identify an optimal residence time in the hydrotreatment reactor in relation to product quality and yield criteria with the natural overall goal of optimizing production costs.
- Semi-batch and continuous mode slurry hydrotreatment pilot plant runs should be performed, performing also tests with recycling the catalyst and parts of the heavier product for repetitive slurry hydrotreatment upgrading using part of the heavier product as co-feed for freshly added HL in a repetitive fashion. Up to 72 h continuous tests can be performed at RISE in Piteå (for information about the slurry hydrotreatment pilot plant, see for instance https://www.ri.se/sites/default/files/2019-12/Produktblad%20SHC_2019-11-19_150343.pdf). This will give both crucially important information for in depth techno-economic assessment as well as a lot of material for downstream process steps (fractionation and/or further upgrading as discussed above) to reach selected quality criteria for the product fractions.
- Crude hydrocarbon mixtures from slurry hydrotreatment should be analyzed and assessed against selected specification criteria for refinery integration as raw materials in an oil refinery. If trace element/inorganics content is too high, routine desalting and demineralization processes like aqueous counter-current extraction and fractional distillation should be performed to reach qualities of fractions which are in line with routine refinery operation requirements.

- More comprehensive analytical characterization of the crude hydrocarbon mixtures from slurry hydrotreatment is needed to understand the composition with regard to compound classes like phenols, carboxylic acids, alcohols, ethers, aromatics and aliphatic hydrocarbons, cyclic aliphatic hydrocarbons etc, using a combination of analytical techniques, some of which have been used in this project like for instance nuclear magnetic resonance spectroscopy (NMR including ^{31}P -NMR for hydroxyl number determination), gas chromatography with different detectors (GC-MS, GC-FID, GC-SIMDIST, PONA/PIONA for lighter fractions etc), liquid chromatography with different detectors (LC-MS, LC-UV, LC-RI etc), elemental analysis and as mentioned above trace element analysis.
- If crude hydrocarbon mixtures from slurry hydrotreatment contain too much of oxygenated molecules (ethers, phenols etc) and if the product mixture profile is not optimal in relation to which end products are targeted (naphtha and gasoline or diesel/kerosene or base oil components), fractional distillation and/or further hydrotreatment and/or cracking/isomerization of the crude hydrocarbon mixtures from slurry hydrotreatment is needed, using standard fixed bed continuous flow reactor equipment in pilot scale which mimics routine equipment in full scale at oil refineries. Such equipment is available for instance at RISE Chemical Process and Pharmaceutical Development in Södertälje, Sweden (the “MiniRefine” test bed, <https://www.bioinnovation.se/en/projekt/minirefine-demonstration-of-new-biotransport-fuel-manufacturing-processes/> with presentation from Henrik Rådberg at Preem on Youtube: [MiniRefine – Henrik Rådberg, Preem - YouTube](#)).
- Further upgraded products from fractionation and fixed bed continuous flow hydrotreatment and/or cracking should be subjected to analytical characterization, largely as described above for the characterization of the crude hydrocarbon mixtures. Products should be assessed against key specification criteria for various applications: Isolated naphtha fractions should be analyzed against quality criteria for naphtha, diesel/kerosene-fractions should be assessed against criteria for this product category etc.
 - There may potentially be an interest for performing steam cracking tests in lab and pilot scale, both for distilled crude hydrocarbon mixtures from slurry hydrotreatment and/or further upgraded product fractions. For information about the steam cracking pilot plant facility with associated services available at Ghent University, see [The Pilot Steam Cracker | Laboratory for Chemical Technology \(ugent.be\)](#). Samples of selected materials for tests can potentially be produced at RISE and then sent to Ghent University for pilot tests.
- Based on all the data from the work including analytical characterization data, different process simulations are proposed to be performed, followed by iterative techno-economic modelling of the processes for different value chain and process integration scenarios:
 - Naphtha fractions analytical data are used to simulate performance of isolated partly or fully biobased naphtha fractions as starting materials for steam cracking to ethylene, propene etc. There are different published methods and software available for performing these simulations, for instance the so called Symmetry Process Software Platform (for information, see [Page 14 \(15\)](https://www.google.se/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&cad=rja&uact=8&ved=2ahUKEwj8gOPyg5P3AhUYQ_EDHQonB48QFnoECAUQAQ&url=https%3A%2F%2Fwww.software.slb.com%2F-%2Fmedia%2Fsoftware-media-items%2Fsoftware%2Fdocuments%2Fexternal%2Fproduct-sheets%2F19_is_000003_bro_symmetry_cracking_furnace_feb_2020.pdf&usg=AOvVaw0AgUieOh5zADXi5E_yDrJP).</div><div data-bbox=)

-
- The slurry hydrotreatment process as well as subsequent downstream upgrading steps listed above (fractionation by distillation and further hydrotreatment and/or cracking/isomerization in standard fixed bed continuous flow reactor equipment) should be modeled using AspenTech software (Aspen Plus, <https://www.aspentech.com/en/products/engineering/aspens-plus>), providing the basis for detailed techno-economic assessment of process variants using programmed Excel-sheets to calculate capital expenditures (CAPEX), operational expenditures (OPEX), net present value (NPV) etc for full scale production designs. This is performed in iteration with lab and pilot scale optimization of the process steps.
 - A value-chain analysis should be performed with different integration scenarios involving partner organizations involved.
 - Environmental impact of process variants should be assessed using standard life cycle assessment (LCA)-tools estimating also net greenhouse gas (GHG-) emission levels depending on which production scenario is used. Impact of any waste streams like water formed in the hydrodeoxygenation steps needs to be purified, how many times the catalyst can be recycled and what the impact is of producing fresh catalyst etc.
 - A natural goal for the above coordinated development activities would, of course depending on the results from the work, be to generate a plan for commercialization of the technology including needed next steps towards achieving a complete technical demonstration of an operational process for selected target products.

5. Acknowledgement

The project partners thank Johanneberg Science Park and the Climate Leading Process Industries initiative, which is financed by Vinnova, Region Västra Götaland and the members of West Sweden Chemicals and Materials Cluster, for the opportunity to conduct the work. The project also acknowledges the partners which have invested their own time in the project (Borealis AB, Perstorp AB and VTT), something which has been essential for the implementation of the project. The project partners also thank the members of the industry reference group, which consist of the companies listed above but also Preem AB and Sekab, for constructive and useful dialogue and input.