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# Final Report

Energimyndighetens titel på projektet – svenska

Hållbara flygbränslen från termokatalytisk uppgradering av lignin och ligninderivat: utveckling av bioraffinaderikatalysatorer och reaktionssystem

Energimyndighetens titel på projektet – engelska

Sustainable aviation fuel from thermocatalytic refining of lignin and lignin-derivatives: development of biorefinery catalysts and reaction systems

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Slurry Hydroprocessing, Sustainable Aviation Fuel, Lignin, Bio-Oils, Catalyst, Biorefinery



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## Preamble

The project was performed in close collaboration between RISE-Research Institutes of Sweden AB, RenFuel K2B AB, Lund University as well as Hulteberg Chemistry and Engineering AB. Financing was given by the Swedish energy agency as part of the Bio+ program.



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## Sammanfattning

Projektet gav fördjupade insikter i hur lignin och ligninbaserade råvaror kan omvandlas till komponenter för hållbart flygbränsle. Projektet föreslår en vätebehandlingsprocess i två steg med sulfiderade övergångsmetallkatalysatorer, och ger nya insikter i olika katalysatorsystem och deras interaktioner med olika fasta tekniska ligniner och med biooljor (Lignol<sup>®</sup>) som härrör från lignin. Projektet har dessutom demonstrerat hela värdekedjan från lignin till bränslekomponenter i pilotskala, presenterat sina resultat i flera bidrag till vetenskapliga konferenser och arbetar med flera vetenskapliga publikationer.

Vätebehandlingsmetoden i två steg omfattar slurry-vätebehandling av fast lignin eller biooljor med hög ligninhalt (~30 viktprocent), följt av sekundär uppgradering via vätebehandling i trickle-bed-reaktor (TBR). Alternativt testades framgångsrikt direkt vätebehandling i TBR av biooljor med något lägre lignininnehåll (11,5 viktprocent).

Projektet omfattade screening av olika sulfiderade katalytiska system baserade på övergångsmetaller för både slurry- och TBR-vätebehandling av ligninråvaror. För slurry-vätebehandling uppvisade molybdensulfidkatalysatorer utan bärarmaterial bäst effektivitet av alla utvärderade katalytiska system, inklusive olika Mo-, W- och V-baserade katalysatorer med och utan bärarmaterial. Katalysatorer baserade på NiMo och CoMo med bärarmaterial uppvisade bäst effektivitet under TBR-vätebehandling.

Inverkan av ligninråvarans ursprung och egenskaper under slurryvätebehandling testades med olika kraft- och hydrolysbaserade ligniner. Råvarans egenskaper hade en stark inverkan på vätebehandlingens effektivitet och produktens egenskaper, medan effekterna av de använda katalysatorerna verkade vara sekundära jämfört med råvarans egenskaper.

Projektet har visat att hela värdekedjan från lignin till bränsle är genomförbar. De föreslagna tvåstegsprocesserna har demonstrerats i pilotskala, och uppskattningsvis 40 kg lignininnehållande råvara har bearbetats på detta sätt.

## Summary

The project provided new insights into the transformation of lignin and lignin-based feedstocks into aviation fuel components. The project proposes a two-step hydroprocessing route using sulfided transition-metal catalysts and provides new insights into the behaviour of different catalyst systems and their interactions with various solid technical lignins and lignin-derived bio-oils (Lignol®). The project further demonstrated the entire value chain from lignin to fuel at pilot scale, and presented its results in several scientific conference contributions, and is working on several scientific publications.

The two-step hydroprocessing route includes slurry hydroprocessing of solid lignin or high-lignin-content (~30 wt%) bio-oils, followed by secondary upgrading via trickle-bed hydroprocessing. Alternatively, the direct trickle-bed hydroprocessing of intermediate lignin-containing (11.5 wt%) bio-oils was successfully demonstrated.

The project included screening of various sulfided transition-metal-based catalytic systems for both slurry and trickle-bed hydroprocessing of lignin feedstocks. During this screening, unsupported molybdenum sulfide catalysts demonstrated the best overall efficiency in slurry hydroprocessing experiments among all other tested catalytic systems, including various Mo- and W-based supported catalysts. Supported NiMo- and CoMo-based catalysts showed the best overall efficiency during trickle-bed hydroprocessing.

The influence of the origin and properties of the lignin feedstocks during slurry hydrotreatment was tested with different Kraft- and hydrolysis-based lignins. A strong influence of feedstock properties on hydroprocessing performance and product properties was observed, whereas the effects of the catalysts used appeared secondary to those of the feedstock.

The project has demonstrated the feasibility of the entire value chain from lignin to fuel. Its proposed two-step processes has been demonstrated at pilot scale, and an estimated combined 40 kg of lignin-containing feedstock has been processed in this way.

# 1 Introduction and Background

The replacement of fossil-based fuels with more sustainable alternatives is one of the key factors in decarbonising the aviation sector. Current and future mandated blending rates set by, for example, the EU, up to 70% by 2050, create a need to significantly expand production capacity for sustainable aviation fuels (SAF). Currently existing technologies include producing SAF from fatty acids and esters (HEFA), syngas (Fischer-Tropsch), or alcohols (Alcohol-to-Jet, AtJ)<sup>1</sup>. These routes produce feed mainly composed of paraffinic and iso-paraffinic components and require blending to meet the aromatic content requirements (min. 8% according to ASTM D1655) of jet fuel.

One attractive route to produce higher aromatic SAF or SAF blending components is the liquefaction and hydroprocessing of lignin, an aromatic biopolymer currently mostly produced as a byproduct of the pulp and paper industry (Kraft lignin) or from the production of alcohol from lignocellulosic biomass (Hydrolysis Lignin). In addition to the required aromatics content, the otherwise produced naphthenes can enhance the combustion behaviour of the fuels in comparison to paraffinic or iso-paraffinic counterparts.

Previous and current efforts on the hydroprocessing of lignin and lignin derivatives have struggled with either coke formation or a low initial lignin load, or have used less widely available, more cost-intensive lignin sources and/or catalysts. This project has contributed to overcoming these problems and unlocking more lignin types, such as Kraft and Hydrolysis lignin, as feedstocks through a broad experimental approach to understand the behaviour of different lignin feedstocks during hydroprocessing and to develop and scale-up suitable, inexpensive, non-noble catalytic systems and upgrading strategies.

## 2 Implementation

The project was ongoing from 2023-01-01 until 2025-12-31 and was performed by RISE-Research Institutes of Sweden AB (RISE), RenFuel K2B AB (RenFuel), Lund University (Lund) as well as Hulteberg Chemistry and Engineering AB (Hulteberg). The project followed the workflow shown in Figure 1.

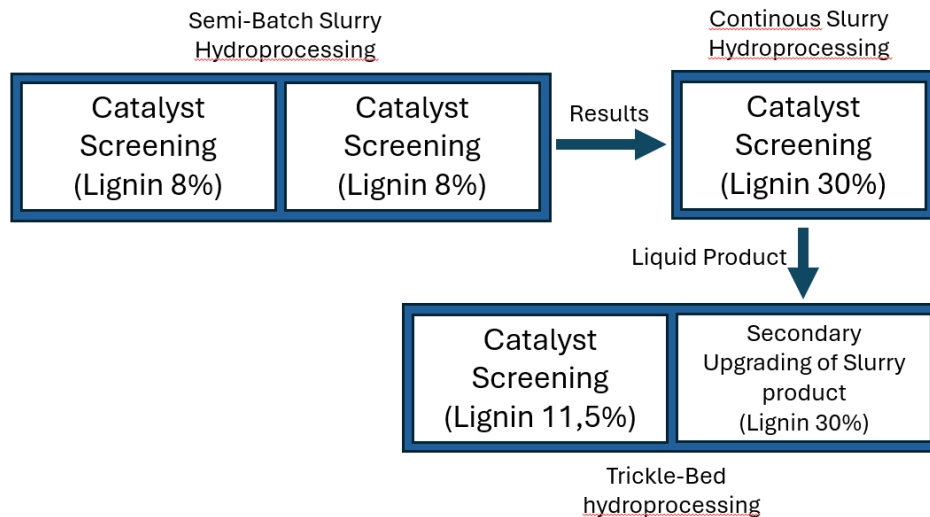


Figure1: Experimental Workflow of the project.

The work at RISE was conducted in Piteå and Södertälje. The project was coordinated by RISE Piteå. Experimental work in RISE Piteå involved slurry hydroprocessing experiments in both semi-batch and continuous modes using the available slurry hydrocracking pilot plant. Typical hydroprocessing experiments in both semi-batch and continuous operation involved the reaction of a lignin-containing feedstock and, potentially, a fossil carrier with hydrogen at elevated pressure (100 bar) and temperature (425 °C), using a dispersed heterogeneous catalyst that was activated during the experiments. In addition, analytical work related to the characterisation of feedstocks, products, and catalysts was conducted.

The experimental work in Södertälje was focused on trickle-bed hydroprocessing of lignin feedstock or products from continuous slurry hydroprocessing in Piteå. The work was carried out in the Minirefine pilot plant environment, involving the reaction of liquid lignin-derived feedstock or a slurry hydroprocessing product with hydrogen at elevated temperatures (340-360 °C) and pressure (70-100 bar) over a fixed bed of a supported heterogeneous catalyst, which was activated prior to the reaction. Other work included characterisation of feedstocks and products, as well as fractionation of the final product mixtures into final fuel fractions.

RenFuel has contributed to the project via their competence in lignin processing and industrial outlook. They have played an active role in the conceptualisation, planning, and reporting of the project and research. In addition, they were actively involved in feedstock acquisition and processing through their Lignol®-Process. This active participation has helped enable the successful scale-up of lignin hydroprocessing.

The work at Lund was carried out in the facilities of the Department of Process and Life Science Engineering and NanoLund. Their work was mainly concerned with the characterisation of the catalysts used in the activities performed at RISE. This, along with their active participation in the conceptualisation and reporting of the project and research, has helped gain a better understanding of the behaviour of the used catalysts and the possible mechanisms related to deactivation.

Hulteberg participated in the work, drawing on their expertise in catalysis, and helped select and produce suitable candidates of catalysts for the hydroprocessing of lignin feedstocks at the necessary scale. Furthermore, their knowledge of hydroprocessing aided the successful implementation of activities at RISE and the publicization of the project's results.

The broad range of expertise combined in this project has been a key factor in its successful implementation. The project has contributed to a deeper understanding of the underlying processes of lignin hydroprocessing and will serve as a stepping stone for further efforts to scale up and commercialise lignin-to-fuel technology tracks.

### 3 Results

Results of this project have been presented at several scientific conferences and will be further publicised in two research articles in greater detail. A summary of the obtained results can be found below.

A screening study of sulfided transition-metal catalysts for the slurry hydroprocessing of a Kraft-lignin-derived Lignol® (KL Lignol®), a lignin-derived bio-oil produced through the derivatisation of lignin with fatty acids, was conducted in semi-batch experiments with a lignin loading of 8 wt%. The screening included four alumina-supported catalysts based on molybdenum (Mo) or tungsten (W) as the primary metal and nickel (Ni) or cobalt (Co) as the secondary metal, and an unsupported Mo-based catalyst produced from an oil-soluble catalyst precursor. All catalysts showed good hydroprocessing performance with high hydrodeoxygenation (HDO) performance reaching a minimum of 80% oxygen removal after 2h of reaction. Furthermore, only minimal coke formation (<1%) was observed while achieving a lignin conversion of >94% into liquid products. The unsupported Mo-catalyst showed the highest oxygen removal (~90%) and lignin conversion (>99%), while the best supported candidate, the CoMo-catalyst, showed oxygen removal of about 84% and lignin conversion at a comparable level (>98%). Differences in the product distribution were observed between Mo- and W-based catalysts. The W-catalysts produced a

liquid product with a lower boiling-point distribution and reduced levels of carbon monoxide (CO) in the evolved process gases.

Concurrently with the catalyst screening, a feedstock screening study was conducted by performing slurry hydroprocessing experiments at a lignin loading of 8 wt%. For this, several solid lignins, including one Kraft lignin (KL) and two Hydrolysis lignins (HL) of different origins were included. Besides the tested solid lignins, two different Lignols® were included in the study, including the KL Lignol® mentioned in the previous paragraph and a HL-derived Lignol® (HL Lignol®). As the catalyst, a supported sulfided NiMo-catalyst was chosen. Application of lignin in the form of Lignol® improved overall oxygen removal after 2 h reaction time (KL: 59% to 81%; HL: 29% to 86%). Furthermore, the use of solid lignin resulted in the formation of a gel-like meltable product fraction, which was absent when Lignol® was used. Origin and properties of the used lignin had a major influence on the hydroprocessing performance. The degree of oxygen removal varied strongly from 29% for one solid HL with low residual sugar content (~2 wt%) from the hydrolysis process to 59% for KL and 63% for the other HL with high residual sugar content (~41 wt%).

The catalysts used in both screening studies were characterised by powder X-ray diffraction (XRD) and N<sub>2</sub>-physisorption. All catalysts used in the catalyst screening study processing KL Lignol® were characterised by a high dispersion of the active phase (for the supported catalysts) or by low crystallinity (for the unsupported Mo-catalyst), both before and after reaction. This indicates high accessibility of the active phase to the lignin molecules. After the reaction, no major signs of graphitic coke species were detected for any of the catalysts, and no major decrease in surface area was observed. Variation in the feedstock, however, had a major influence on the structural changes of the sulfided NiMo catalyst. After the reaction, a low stacking number was maintained only for KL Lignol® and the high-sugar HL,. For the low-sugar HL, KL, and HL Lignol®, a significant increase in the stacking number was observed, indicating aggregation of the active phase. For all feedstocks except KL Lignol®, graphitic coke formation was detected by XRD, concurrent with a simultaneous decrease in surface area.

Based on the results of both catalyst and feedstock screening studies, the unsupported Mo-based catalyst, the supported CoMo catalyst, and KL Lignol® were selected as the catalysts and feedstock for scaling up the semi-batch process to continuous slurry hydroprocessing. The lignin content of the reaction mixture was thereby increased to 30 wt% with a residence time of 2.5 h. The process resulted in high HDO (Unsupp. Mo: 87%; CoMo: 70%) and high lignin conversion (Unsupp. Mo: 97%; CoMo: 96%), producing a low-viscosity, low-oxygen (O-

content: 2-5 wt%) product. Characterisation of the spent catalyst revealed an increased stacking number compared to that observed in semi-batch experiments. In addition, for the unsupported Mo-based catalyst, a significantly lower surface area was observed compared to the semi-batch results, whereas the CoMo catalyst maintained most of its surface area. A combined total of 40 kg of KL-Lignol® was processed in this way.

Four alumina-supported catalysts (NiMo, CoMo, NiW, CoW) were screened for direct trickle-bed hydroprocessing of Kraft-based Lignol® with a lignin content of 11.5 wt%. All catalysts showed high HDO, with Mo-based catalysts (NiMo: 92%; CoMo: 88%) demonstrating superior HDO than W-based alternatives (NiW: 87%; CoW: 81%). Hydroprocessing of the Lignol® with all catalysts led to a near-complete removal of acid or aldehyde functionalities and olefinic components from the feedstock (>99%). After the use of W-based catalysts, small amounts of aliphatic alcohols (0.15-0,5 mmol/g) remained in the product fraction, whereas with Mo-based catalysts, the product was free of aliphatic alcohols. No significant change in aromatic alcohol content was detected after hydroprocessing at the chosen conditions. No indication of deactivation was observed for the Mo-based catalyst during 96 h of runtime. In contrast, a gradual increase in the concentration of aliphatic alcohol in the product from hydroprocessing with W-catalyst indicates slow deactivation behaviour after 30 h on stream.

Based on trickle-bed hydroprocessing screening experiments, CoMo was selected for secondary trickle-bed hydroprocessing of both products from the continuous slurry hydroprocessing experiments<sup>1</sup>. Secondary hydroprocessing of both fractions led to a further decrease in oxygen content (~0.5 wt%). Similar to the direct hydroprocessing of Lignol®, a significant reduction in olefin content (0.5 mmol/g to 0.01 mmol/g) and aliphatic alcohol concentration (0.11 mmol/g to 0.04 mmol/g) was observed, while the phenolic content reduced only slightly.

The final oil product obtained from the two-step upgrading route, including continuous slurry hydroprocessing (unsupported Mo-catalyst) and trickle-bed hydroprocessing (CoMo-catalyst), was further separated into boiling-point fractions via vacuum distillation. The fractionation included a light naphtha fraction (<150 °C; 8%), a jet fuel fraction (150-300 °C; 16%), and a heavy residue fraction (>300 °C; 76%). Oxygen content progressively increased with increasing boiling point (0.3 – 0.6 wt%). The obtained jet fraction was characterised by a high aromatic content of 20 – 23 wt%.

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<sup>1</sup> 30 wt% lignin feed in the form of KL Lignol®, hydroprocessed using the unsupported Mo-catalyst and the supported CoMo catalyst, respectively

## 4 Discussion

This project has demonstrated the technical feasibility of the transformation of lignin, from Kraft paper mills and from the hydrolysis of lignocellulosic biomass for ethanol production, into SAF or SAF blending components. Different hydrotreatment catalysts have been explored for effective liquefaction and the removal of oxygen and sulfur. The project expands on the results from laboratory studies at intermediate TRLs and identifies potential challenges for the technology's scale-up. It further highlights the necessity to complement results from laboratory research, often focusing on batch operation on low lignin contents, with more industrially relevant research to reach more accurate conclusion for potential scale-up.

The results of this project suggest that sulfided hydroprocessing catalysts, similar to those used in the hydroprocessing of fossil feedstocks, are suitable for lignin hydroprocessing. All tested catalysts for either trickle-bed or slurry hydroprocessing show high HDO at standard conditions, which are not yet fully optimised. Mo-based catalysts, in the limited sample size of this study, were superior to W-based catalysts. Though, depending on the targeted product and needed product properties, also W-based catalysts can be a consideration. Furthermore, the results of this study suggest a focus on unsupported catalysts for lignin upgrading in slurry reactors.

The project further suggests that feedstock properties strongly influence hydrotreatment performance. No clear dependence on the origin of the feedstock (hydrolysis vs. the Kraft process) was found, while properties such as purity were found to be of high importance. Additionally, due to the small sample size, no definite conclusions could be drawn about which exact properties of the lignin feedstock had the greatest influence on hydrotreatment performance. However, the impact of differences between the tested lignin-containing feedstocks was found to be greater than that of the tested catalysts. This suggests the necessity to assign a higher priority to identifying problematic properties of the lignin to help assess the scope of possible lignin feedstocks. It can further be concluded that pretreatment and homogenisation of the lignin feedstock, including derivatisation, transformation into a bio-oil prior to hydrotreatment and or washing procedures like in the Lignol®-process, can significantly improve the processability of the feedstock and reduce variations between different lignin feedstocks.

Two possible strategies for lignin hydroprocessing have been demonstrated in this project (Figure 2). The first approach includes derivatisation of lignin with fatty acids and transformation into a bio-oil, followed by blending with other hydroprocessing feeds and direct trickle-bed hydroprocessing. This approach is thereby limited in lignin content (here 11.5 wt%) due to issues of stability, heat

management during hydroprocessing, and flow properties<sup>2-4</sup>. As an alternative for similar lignin oils with higher lignin content (here 30 wt%), or slurries of solid lignin, a two-step hydroprocessing track, consisting of slurry hydroprocessing followed by trickle-bed hydroprocessing, to produce fuel-like hydrocarbon mixtures, has been demonstrated during this project.

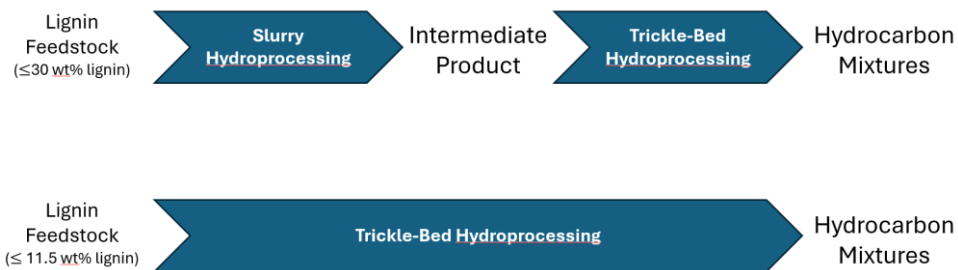


Figure 2: Strategies for the upgrading of lignin into SAF components

Combining all these results, these key conclusions can be drawn:

1. The transformation of lignin into fuel and fuel blending components via hydroprocessing routes is possible and technically feasible.
2. Existing hydroprocessing technology, including traditional sulfided catalysts are capable of transforming lignin. However, catalyst systems and processes need to be optimised and adapted to the new feedstocks to improve yields and stability, aiming to achieve feedstock agnosticism.
3. The heterogeneity of available feedstocks and their properties, along with the resulting processing problems, needs to be addressed before further scale-up. The development of technologies for pretreatment and homogenisation of feedstocks is therefore key to achieving the large production capacities required for the future.

## 5 List of Publications

### Conference Contributions:

#### ISCRE 28- Turku/Åbo Finland- 2024

##### Poster Presentation

“Hot-injection slurry hydrotreating of lignin – Steering feedstock reactivity by advanced reaction control.”

#### NWBC 11- Örnsköldsvik Sweden- 2024

##### Oral Presentation

“Hydrotreating of lignin and lignin derived bio-oils with non-noble metal catalysts”

#### EuropaCat 16- Trondheim Norway- 2025

##### Poster Presentation

“Unlocking solid technical lignins and lignin bio-oils for the production of sustainable aviation fuels (SAF) through slurry hydrotreatment: scale-up and choice of catalyst”

### Manuscripts under preparation:

Manuscript related to result of slurry hydroprocessing:

“Slurry Hydroprocessing of solid technical lignins and lignin-derived bio-oils with transition metal sulfide catalysts: From batch to continuous processing.”

Submitted to Chemical Engineering Journal-Status Under Review.

Manuscript related to result of trickle-bed hydroprocessing of Lignol (title preliminary)

“Hydrotreatment of lignin-derived feedstocks in a pilot-scale trickle-bed reactor for the production of sustainable aviation fuels.”

Manuscript related to result of trickle-bed hydroprocessing of slurry product (title preliminary)

Hydrotreatment of slurry upgraded lignin-derived feedstocks in a pilot-scale trickle-bed reactor to produce sustainable aviation fuels.

## 6 References

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## 7 Bilagor

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