**Energimyndigheten**

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| Energimyndighetens titel på projektet – svenska | |
| Förnyelsebart flygbränsle från termokatalytisk omvandling av skogsavfall | |
| Energimyndighetens titel på projektet – engelska | |
| Sustainable aviation fuel from thermocatalytic conversion of forest residues | |
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| Nyckelord: 5-7 st | |
| Sustainable aviation fuel (SAF), catalytic reductive liquefication, sawdust, bark, catalyst development | |

## Preface

This project has been funded by the Swedish Energy Agency and in-kind contribution is provided by SCA. The persons that have been involved in the project are Dr Pouya Sirous Rezaei, Dr Mohammad Abdus Salam, Dr Khanh Tran, Professor Derek Creaser and Professor Louise Olsson from Chemical Engineering, Chalmers and Dr Christian Kugge from SCA R&D centre.

## Table of Contents

## Sammanfattning

Att minska koldioxidavtrycket från fordon genom elektrifiering har visat lovande resultat. Flyget är dock fortfarande beroende av flytande bränsle och det är därför viktigt att producera hållbara flygbränslen (SAF). SAF är mycket paraffinhaltiga och saknar aromatiska innehåll som är avgörande för materialkompatibilitet och smörjegenskaper hos jetbränslen. Detta projekt har fokuserat på utvecklingen av en process för termokatalytisk omvandling av skogsrester för att producera alkylerade aromater och cykloalkaner, som är viktiga komponenter i jetbränslen. Mer specifikt har vi studerat reduktiv katalytisk fraktionering (RCF) av skogsrester, vilket är en teknik som kombinerar depolymerisering och hydrodeoxygenering med hjälp av en katalysator. I detta projekt studeras sågspån och bark genom RCF. Sågspånet karakteriserades först och resultat för flyktiga ämnen, fukt, fixerat kol, aska bestämdes. Även strukturanalys utfördes för att fastställa cellulosa-, hemicellulosa- och ligninhalten. Flera serier av olika katalytiska material framställdes, t ex med användandet av olika metaller, varierande metallinnehåll och olika bärarmaterial. Katalysatorerna karakteriserades i detalj med flera metoder. I detta projekt har vi utvecklat ett katalytiskt material som endast ger 3.9 % fast koks vid användning av sågspån. Tillsats av bark ökar de fasta biprodukterna och vid användning av 20 % bark och 80 % sågspån var den fasta koksbildningen 8.4 %. Resultaten från detta projekt har resulterat i två studier som kommer att publiceras i open access-tidskrifter under 2023. Detta projekt kommer att fortsätta med finansiering av Bo Rydins stiftelse.

## Summary

Reducing carbon footprint from vehicles using electrification has shown promising results. However, aviation remains dependent on liquid fuel and it is therefore critical to produce sustainable aviation fuels (SAF). SAF are highly paraffinic and lack aromatic content that is vital for material compatibility and lubricity characteristics of jet fuels. This project has focused on the development of a process for thermo catalytic conversion of forest residues to produce alkylated aromatics and cycloalkanes, that are important components in jet fuels. More specifically, we have studied reductive catalytic fractionation (RCF) of forest residues, which is a technique that combines depolymerization and hydrodeoxygenation using a catalyst. In this project, sawdust and bark are studied through RCF. The sawdust were first characterized and results for voltile matter, moisture, fixed carbon, ash were retrieved. Also structural analysis were performed determining the cellulose, hemicellulose and lignin content. Several series of different catlytic matererials were prepared, for examle varying the metals, metal content and the support. The catalysts were characterized in detail with multiple methods. In this project we have developed a catalytic material that only gives 3.9% solid char when using sawdust. The addition of bark increases the solid residues and when using 20% bark and 80% sawdust the solid char was 8.4%. The results from this project has resulted in two

studies, that will be published in open access journals during 2023. This project will continue with the funding of Bo Rydin foundation.

## Background

There are various pathways for producing sustainable aviation fuels (SAF). Liquid aviation fuels are expected to be needed long into the future for larger aircraft, the existing fleet of aircraft and those still in the planning stages. Some SAFs have been ASTM certified, including some produced by Fischer-Tropsch synthesis (FT), hyroprocessed fatty esters and acids (HEFA), alcohol to jet fuel (AtJ) however only up to a maximum 50% blend [1]. They are blended with conventional fuels because they lack properties required by jet fuels. Specifically, these FT, HEFA and AtJ fuels are composed of largely n- and iso-alkanes, with very low levels of aromatics or cycloalkanes. Fuel certification (ASTM D7566-14a) requires that SAFs are blended with conventional fuels to achieve a minimum aromatic content of 8 vol% and up to 15 vol% of cycloalkanes [2]. In comparison, today's conventional jet fuels contain on average 19.9 vol% aromatics and 21.2 vol% cycloalkanes [2]. Aromatic compounds in jet fuels are vital for material compatibility and lubricity characteristics of the fuel. SAFs of proper quality and quantities to fully replace today's conventional fuels will likely have to be produced from a blend of renewable sources. In this project we will develop processes for the thermocatalytic conversion of forest residues to jet fuels. In particular, the fuels would have aromatic and cycloalkane contents so that they could be used together with other SAF fuel feedstocks to produce a completely renewable aviation fuel.

Aromatic hydrocarbons and cycloalkanes can add important properties to jet fuel. Aromatic hydrocarbons have higher energy and knock ratings, and better performance for elastomer swelling than alkanes. Whereas cycloalkanes have higher thermal stabilities favoring less coke formation, higher energy densities and shorter ignition times than normal alkanes [2]. It is also known that alkylated aromatics and cycloalkanes are preferred. Aromatics are more prone to soot formation than alkanes, however alkylated aromatics have reduced soot formation and increased reactivity. Also, alkylated cycloalkanes are favored due to improved combustion reactivity. Oil products from thermocatalytic conversion of lignocellulosic materials can be rich in aromatics and cycloalkanes with a suitable choice of catalyst and reaction conditions. This can give them excellent properties as a renewable jet fuel possibly alone, but most likely blended with other SAF fuel feedstocks with high paraffinic contents.

In this project we have focused on the development of a thermocatalytic hydrotreatment process. It offers advantages. Firstly, it could be used with a wet feedstock which is advantageous for treatment of forest residues. It is very beneficial to reduce the need for energy for drying in the process. Secondly, since the process is reductive using hydrogen, catalytic hydrodeoxygenation reactions can potentially produce a product with sufficiently low oxygen content for a fuel in one step. Finally, the use of an active catalyst and hydrogen can suppress the formation of wasteful char byproducts to low levels. There are some studies in the

Energimyndigheten

literature concerning conversion of lignocellulose to bio-oils that will be outlined below.

Forest residues can include branches and tops (GROT, "grenar och toppar"), foliage, and bark that remain from forest harvesting. These materials can be converted to a low value renewable energy by combustion. However, it is of interest to develop processes for their upgrading to higher value and quality fuel products. We see the possibility for their conversion to aromatics and cycloalkanes that could be combined with alkanes produced from FT, HEFA or AtJ fuels to enable 100% renewable jet fuel products. However, there are several challenges for the process using forest residues, since they are very inhomogeneous. For example the lignin content varies from 32% to 42% comparing a 3 year old tree with a 30 year old tree [3]. The next issue is the bark, which is very different in composition, containing as much as 27% extractives (ca 10% in wood) and 4.5% ash (less than 1 % in wood) [3]. Both extractives and ash can cause severe problems in the process, such as increased char formation and catalyst deactivation. It is therefore very important to examine the heterogeneity of different feedstocks in order to develop a robust process for jet fuel production.

The thermocatalytic conversion of raw lignocellulosic biomass, such as forest residues, as proposed in this project is challenging because it involves the single-step simultaneous liquefaction of the cellulose, hemicellulose, lignin and extractives and hydrodeoxygenation of the range of products. Another complication is that the forest residues also contains bark, that has significantly more ash and extractives. One approach is to separate the lignocellulosic biomass into each fraction and convert them separately into different products in a series of stages. Today, for example there is a lot of ongoing research concerning various processes for the valorization of lignin. But in the case of forest residue streams, their direct conversion into a higher value fuel product can be favorable for the overall process economy.

Xia et al. investigated the hydroconversion of birch sawdust to bio-oils with a Pt/NbOPO$_4$ catalyst and cyclohexane solvent [8]. The products included various alkanes and alkylcyclohexanes. No aromatic products were detected probably due to the high hydrogenation activity of the noble metal-based catalysts and long residence times used (20 h). However, an effective catalyst was considered to combine a metal with good hydrogen activation properties and support combining different acid sites. Santini and coworkers reported the thermocatalytic transformation of pine wood into biofuel with a catalyst based on Ru and Cu on heteropolyacids and without solvents [9, 10]. Product yields of up to 30 wt.% were achieved and they consisted of largely cycloalkanes, and aromatics with some phenolics. Other products included light gaseous hydrocarbons, higher molecular weight fragments (tar) and char. Grilc et al. [11, 12] studied the influence of reaction conditions and catalysts on the yields of tar, char, gases and oil for the hydrodoxygenation of wood sawdusts in tetralin solvent. A kinetic model was developed that predicted the yield of the different product fractions. The presence of hydrogen was found to be crucial for suppressing char formation.

From literature it can be seen the yields and nature of products can vary significantly depending on the catalyst and reaction conditions used. The yield of liquid fuel products with low oxygen content required for fuels is promising, however yields of solid char products of 15 to 35 wt.% can be problematic. There are no reported studies using forest residue feedstocks, which poses additional challenges. For example, bark contain as much as 27% extractives and 4.5% ash [3], which likely would increase the char formation as well as catalyst deactivation. Another issue is that the wood itself contains different amounts of cellulose, lignin and extractives depending on the age of the tree [3], but also depending on which type of tree [13]. In order to make large scale conversion of forest residues it is critical to understand how the changes in feedstock over time will influence the process, the process conditions and the produced products.

## Implementation

The persons that have been involved in the project are Dr Pouya Sirous Rezaei, Dr Mohammad Abdus Salam, Dr Khanh Tran, Professor Derek Creaser, Professor Louise Olsson from Chemical Engineering, Chalmers and Dr Christian Kugge from SCA R&D centre.

Sawdust and bark were provided to the project by SCA. The sawdust and bark were thoroughly characterized using TGA and elemental analysis.

Several catalysts were synthesized, with all details shown in Appendix 2 and 3. The catalysts were characterized using different techniques as shown in Table 1:

Table 1. Catalyst characterization techniques.

| Technique | Characterization |
|---|---|
| XRD | Crystallinity |
| BET | Surface area |
| SEM | Morphology |
| ICP | Metal content |
| XPS | Oxidation state |
| $NH_3$ TPD | Acidity of the catalyst |
| Raman spectroscopy | Phases of the metal species in the catalysts |

Nitrogen physisorption properties were measured at -196 °C using a TriStar 3000 gas adsorption-desorption analyzer. Before the measurement, the catalysts were dried under an $N_2$ atmosphere. The Brunauer–Emmett–Teller (BET) method

was employed to determine the specific surface areas, while the t-plot and the Barrett–Joyner–Halenda (BJH) methods were used to calculate the micropore volume and the average diameter of the mesopores, respectively. The metal contents were measured by Inductively Coupled Plasma-Sector Field Mass Spectroscopy (ICP-SFMS, ALS Scandinavia AB, Luleå, Sweden). $NH_3$-temperature-programmed desorption (TPD) was used to measure the total acidity of the catalyst. The oxidation states of the catalysts were characterized by X-ray Photoelectron Spectroscopy (XPS) using a Perkin Elmer PHI 5000 VersaProbe III Scanning XPS Microprobe. In an ultra-high vacuum chamber, the sample was exposed to a monochromatic Al-Kα source of high binding energy (1486.6 eV) and the photoelectrons thus emitted were detected by the energy analyzer. Casa XPS was used to analyze the data with C1s binding energy of 284.6 eV as the reference. The deconvolution of the spectra was performed using a Shirley background.

The catalytic depolymerisation of sawdust and bark was ran in an autoclave (300 mL, Parr Inc). The biomass feedstock was mixed with catalyst and hexadecane then added subsequently to the reactor. The gas products were collected and analysed with GC. The reactor after the reaction was washed to remove the mixture of solid residue and liquid. The mixture was filtered to remove the solid residue from the mixture. Then solid product was dried. The organic phase rich in acetone and hexadecane were evaporated using a rotary evaporatar. The following equations were used to calculate the mass balance, yields, selectivity for products, respectively.

$$Gas = \frac{m_{gas\ bag\ after\ reaction} - m_{gas\ bag\ initial}}{m_{biomass}} \times 100\ (wt\%)$$

$$Solid = \frac{m_{solid\ residue} - m_{catalyst}}{m_{biomass}} \times 100\ (wt\%)$$

$$Liquid = 100 - wt\%\ Gas - wt\%\ Solid\ (wt\%)$$

The selectivity and yield of liquid component were determined using following equations:

$$Selectivity = \frac{amount\ of\ product\ (g)}{total\ detected\ products\ (g)} \times 100\ (wt\%)$$

$$Yield = \frac{amount\ of\ product\ (g)}{biomass\ feedstock\ (g)} \times 100\ (wt\%)$$

and then analyzed by GC-MS (Agilent 7890B–5977A, Agilent). The GC is equipped with a DB-5 column (30 m x 250 μm x 0.25 μm), and BPX-50 column (2.5 m x 100 μm x 0.1 μm)  was used for the separation of the reaction mixture.

## Results and discussion

Sawdust and bark were provided to the project by SCA, see Figure 1.



**Sawdust**



**Bark**

Figure 1. Sawdust and bark used in the project. It was provided by SCA.

First the sawdust were characterized and results for voltile matter, moisture, fixed carbon, ash were retrieved. Also structural analysis were performed determining the cellulose, hemicellulose and lignin content.

Several series of different catlytic matererials were prepared, for examle varying the metals, metal content and the support. The catalysts were characterized in detail using BET, XRD, SEM, XPS and $NH_3$ TPD. The catalyst, sawdust and or bark was added to the reactor (see Figure 2) together with hexadecane as a solvent. Several reductive catalytic depolymersiation expeiments were peformed, varying temperature, pressure, catalyst amount and catalyst compositon. The amount of solid phase, bio-liquid and gas was quantified. The composiion o the bio-oils were determined with GCxGC/MS and NMR. The water content was measured using Karl Fisher.
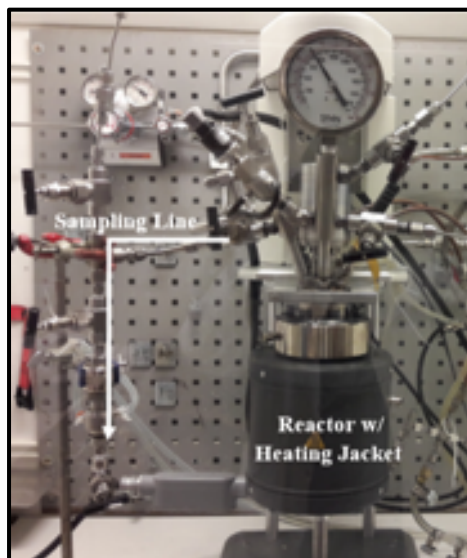
Figure 2. The reactor used in the experiments.

The results from this project has resulted in two studies, that will be published in open access journals during 2023. Since the papers are not published yet, they are appended to this final report as closed appendixes. And the results will be avaible to all shortly, when the papers are published.

## Publication list

- Reductive liquefaction of sawdust: insight into structure-activity relationships, Muhammad Abdus Salam, Quoc Khanh Tran, Phuoc Hoang Ho, You Wayne Cheah, Joanna Wojtasz-Mucha, Christian Kugge, Louise Olsson , and Derek Creaser, In manuscript. (Appendix 2).

- Reductive catalytic fractionation of forest waste residues to potential aviation fuel over hybrid catalyst, Quoc Khanh Tran, Muhammad Abdus Salam, Phuoc Hoang Ho, Christian Kugge, Derek Creaser and Louise Olsson, In preparation. (Appendix 3).

## Appendix

Appendix 1: Administrative appendix

Appendix 2: Reductive liquefaction of sawdust: insight into structure-activity relationships, by Muhammad Abdus Salam, Quoc Khanh Tran, Phuoc Hoang Ho, You Wayne Cheah, Joanna Wojtasz-Mucha, Christian Kugge, Louise Olsson , and Derek Creaser, In manuscript.

Appendix 3: Reductive catalytic fractionation of forest waste residues to potential aviation fuel over hybrid catalyst, Quoc Khanh Tran, Muhammad Abdus Salam, Phuoc Hoang Ho, Christian Kugge, Derek Creaser and Louise Olsson, In preparation.

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