

Energimyndighetens titel på projektet – svenska upGradering av Organosolv Lignin till JET BRÄNSLE (GOLDJET FUEL)	
Energimyndighetens titel på projektet – engelska upGrading of Organosolv Lignin to JET FUEL (GOLDJET FUEL)	
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Förord

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Sammanfattning

To promote the transition to fossil-free flights by 2045 and reduced climate impact the recent submitted inquiry “Biojet för flyget” (SOU 2019:11) propose a greenhouse gas emissions reduction obligation for jet fuels. This translates to a new law proposal where the first reduction obligation for jet fuel comes into force 2021 with a reduction level of approximately 1% (v/v) bio-fuels to increase to the equivalent of approximately 30% by 2030. Current jet turbine fuels originating from fossil feedstock have only to a very limited extent been replaced by biomass-derived fuels due, in part, to the lack of the aromatic and cycloalkane hydrocarbons

in bio-jet fuels. Such molecules play a critical role in traditional jet fuels for combustion characteristics and material compatibility. Efforts to produce jet fuels from renewable resources have been ongoing for several decades. Several alternatives have been developed and implemented with varying degrees of success: 1) Fischer-Tropsch synthetic paraffinic kerosene (FT-SPK), 2) biomass-derived synthetic paraffinic kerosene (Bio-SPK) from Camelina, Jatropha, and algae oils, and 3) hydroprocessed esters and fatty acids (HEFA) from animal fats and plant oils. These renewable jet fuels contain mostly n- and iso-alkanes, and almost no aromatics or cycloalkanes. Renewable jet fuels, therefore, are currently required to be blended with petroleum-based jet fuels for use in commercial aircrafts. Lignin, the only biomass component rich in aromatic benzene ring structures, is currently mainly used for low-value heat or treated as process waste because of its high chemical resistance. Instead of blending renewable jet fuels with petroleum-derived fuels, addition of specific aromatic hydrocarbons and cycloalkanes from lignin-derived bio-oil may enable production of a fully synthesized jet fuel (FSJF). Moreover, due to the lower oxygen content of most lignin derived compounds, they have the possibility to offer a more thermally stable and higher energy density liquid fuel compared to fuels derived from other biomass components. In addition, some technical lignins, like the organosolv lignin, is sulfur-free which is an important factor as there is a maximum limitation for sulfur. (3000 ppm) in order to control sulfur oxide emissions and formation of gums and sediments during storage. Yet there is relatively little research focused on valorization of the so far underutilized lignin relative to cellulose or hemicellulose, especially on the conversion of lignin to the liquid transportation fuels.

To address these issues, the objective of GOLdJET FUEL was to evaluate how the organosolv lignin fractions from a forest biorefinery perspective can be used to generate a liquid aircraft energy carrier in a flexible and integrated concept. In order to achieve our aims, the research and development in GOLdJET FUEL targeted several steps of the process; organosolv sulfur-free lignin production, lignin depolymerization to monomeric phenols by hydrothermal liquefaction (HTL) following by catalytic deoxygenation/alkylation to produce aromatic compounds directly suitable as jet fuel or for blending with existing bio-jet fuels in order to increase the aromatic content. To achieve the best conditions for a successful result, the current project was a collaborative work including the Biochemical Process Engineering (LTU-BPE) and the Chemical Technology (LTU-CT) groups of LTU, the Chemistry group of RISE Processum with research competences that complete each other.

In the project we demonstrated that birch and spruce sawdust are an excellent starting material to be used in a biorefinery for the production of the next generation aviation fuels. Specifically, we developed an organosolv process that was capable to deliver high yields of lignin as a separate stream. Lignin was then treated by HTL and we obtained high yields of bio-oil which was separated into heavy and light bio-oil fractions, whereas biochar and gas were also produced as side products. The heavy oil produced can find application in the marine sector as green fuel, whereas the light oil was treated with zeolites which achieved almost complete

deoxygenation, producing aromatic compounds that are suitable to be used as aviation fuel.

Summary

Valorization of organosolv lignin fraction from forest residues (sawdust) into high value jet fuel, at a high yield and reduced cost will be targeted by depolymerization of the ORGANOSOLV lignin via hydrothermal liquefaction (HTL) followed by catalytic upgrading of biooil using novel ultrathin defect free ZSM-5 crystals as catalyst and production of jet fuel. Collaboration with KIRAM ensured a solid framework for solving challenges in order to commercialize a forest-based biorefinery with complete use of the feedstock.

Inledning/Bakgrund

Petroleum-derived jet fuels are difficult to be completely replaced by biomass-derived fuels because of their compositional differences. Aromatic hydrocarbons and cycloalkanes, essential molecules in traditional jet fuels for properties like elastomeric swelling, material compatibility, and lubricity, are not found in current bio-jet fuels. To develop a fully synthetic jet fuel, a sustainable source of aromatic hydrocarbons and cycloalkanes is needed. Lignin, an abundant and underutilized fraction of biomass, is made of aromatic polymers and could be the source of these compounds. Kraft lignin (alkali lignin) is widely available. However it presents a challenge in processing. During degradation, the sulfur present in the alkali lignin can become incorporated into the degradation products (as sulfides and thiols). The sulfur present will also result in poisoning of many catalysts needed for the upgrading step. There is also a maximum limitation for sulfur (3000 ppm), to control sulfur oxide emissions, and formation of gums and sediments during storage. Moreover, Kraft lignin with more condensed phenolic structures lacks much of its β -O-4 interunit linkages and has higher ash content compared to lignin from organosolv pulping. All these features have a great negative influence on the depolymerisation process when using thermochemical processes. Organosolv and hydrolysis lignin are alternatives to Kraft lignin, though they are not currently available in as large abundance. They are extracted without the use of sulfur compounds and are therefore sulfur-free. As such, the degradation of these lignins produces sulfur-free bio-oil –which is suitable as a feedstock for production of fuels where low sulfur content is demanded. Currently, the maximum sulfur content is 3000 ppm in aviation fuel and 10 ppm in diesel and gasoline. However, it is likely that lower levels will be demanded in aviation fuel in the future. Organosolv pretreatment: Conventional organosolv is able to separately recover hydrophobic lignin, but the cellulose fraction is still rich in lignin since the previously released lignin is re-condensed on cellulose when the process temperature drops. To solve this problem, LTU has developed and installed a semi-continuous 5 kg/h organosolv system which allows the solid/liquid separation to take place at high temperature, preventing the condensation of lignin (SOLVEFUELS project, Swedish Energy Agency-LTU Labfond funded). The Biochemical Process Engineering group has evaluated the efficiency of organosolv lignin isolation from

hardwood (birch) and softwood (spruce) as well as the purity and structural characteristics of the isolated lignin fractions (1,2). It's worth mentioning that the obtained lignin was sulfur-free with a low molecular mass and narrow distribution ranging from < 1000 to 3000 g mol^{-1} make it an ideal feedstock for depolymerization and catalytic upgrading. Moreover, preliminary work compared a range of mesoporous and microporous ZSM-5 zeolite catalysts for their reductive depolymerization efficacy for organosolv lignin derived from spruce and birch using catalytic fast pyrolysis (CFP) at $600 \text{ }^\circ\text{C}$.

HTL of isolated organosolv lignin: Hydrothermal liquefaction (HTL) is a thermochemical conversion method by which biomass feedstock is converted at temperatures from 280 to 450°C , pressures up to 35 MPa and residence times from 5 to 30 min , to a bio-crude with very high carbon conversion ratios. Water is a prerequisite for the process, making it especially suitable for wet biomasses, such as sewage sludge, manure, wet agricultural residues, etc. As residual streams often contain significant amounts of water, this renders a drying step redundant. Thus, HTL offers a unique way of reclaiming water from energy processes. The wet lignin fraction from the organosolv fraction is particularly suitable for the HTL process. In the LTU process, after the solvent has been removed from the black liqueur, the lignin cake has a moisture content of $20\text{-}35\%$ and can go directly to a high temperature process attractive for wet feedstocks, such as HTL or catalytic depolymerization. In other thermochemical conversion processes (i.e., pyrolysis and gasification), the actual conversion process is typically preceded by an energy-intensive drying step. Moreover, with the current moisture contents, pumpability is permitted reflected in the use of continuous flow reactor systems, in which the biomass slurry needs to be introduced into a high-pressure reactor on a continuous basis. By the HTL process, almost $50\text{-}75\%$ of the carbon and hydrogen in the biomass feed is converted to oil, corresponding to ER (energy recovery ratio) in the range $50\text{-}80\%$, with heating values for the bio-crudes of approximately 35 MJ/kg and oxygen contents of $2\text{-}15\%$. RISE-Processum is running a continuous flow HTL at the pulp- and paper and chemical industrial site in Domsjö which will be used for test in the current project. Very recently, full upgrading of lignocellulosic HTL bio-crude has been achieved through coupling of fractional distillation and mild hydrotreatment to obtain yields above $55 \text{ wt}\%$ in the gasoline and middle-distillate (diesel, jet fuel) ranges, as well as distillation residues as low as $10\% \text{ wt}$. Recently it was reported that bio-oils rich in monoaromatic phenolic compounds were produced by a hydrothermal treatment in a batch reactor from organosolv lignin derived from beech wood (3).

HTL bio-crude catalytic upgrading to aviation fuels using ultrathin defect free ZSM-5 crystals: Lignin-derived bio-oil cannot be utilized directly as transportation fuels due to its high oxygen content, acidity, instability, high viscosity, and complexity of constituent compounds. Lignin-derived bio-oils are composed predominately of monomeric or dimeric alkoxyphenols; petroleum-based jet fuels contain 20% n-alkanes, 40% isoalkanes, 20% cyclic alkanes, and 20% aromatic hydrocarbons. The O/C and H/C ratios of fossil oil range from 0 to 0.03 and from 1.6 to 2.1 , respectively. In contrast, the O/C and H/C ratios of crude bio-oil range from 0.6 to 0.71 and from 1.0 to 1.35 , respectively. Catalytic upgrading of bio-oil

should, therefore, target oxygen removal, carbon preservation, and hydrogenation of unsaturated carbon bonds. Traditional ZSM-5 catalysts can be used to convert the bio-oil to an aromatic fraction with low oxygen content. However, the catalyst performance is not sufficient for practical application for production of biofuels from biomass. The main problem with the traditional ZSM-5 catalyst is rapid deactivation due to coke formation in defects. Ultra-thin (35 nm), defect free ZSM-5 catalysts have recently been developed by the Chemical Technology group. These catalysts are by far the thinnest ever reported and the catalytic deoxygenation performance of methanol to aromatic hydrocarbons was shown to be superior to traditional ZSM-5 catalysts (4-5). Of particular importance for the proposed project is the very high catalytic activity, high yield of aromatic hydrocarbons and very low deactivation rate. The high catalytic activity is a result of the very short diffusion path of the ultra-thin catalyst. The short diffusion path also results in very high yield of aromatic compounds. The low deactivation rate is a result from the combination of short diffusion path and the absence of defects, which results in very low coke formation. In these defect free crystals, the pore size is exactly 5.5 Å and no coke can form in the pores, and the catalysts only deactivate due to slow formation of external coke. In traditional catalysts, defects in the lattice results in a few larger pores with a size of one or a few nanometers, where coke can form. This catalyst will be further developed in the proposed project and optimized for the deoxygenation of bio-oil produced by HTL processing of organosolv lignin. The high catalytic activity and very slow deactivation rate will be explored to effectively convert bio-oil to aromatics. In addition, the short diffusion path will be beneficial to allow the relatively heavy molecules in the bio-oil to effectively enter the catalyst pores.

Genomförande

WP1: Isolation of pumpable wet organosolv lignin from forest residues (sawdust) treated with the semi-continuous 5 kg/h Organosolv LTU system (LTU-BPE) M1-14.

In WP1 we worked with birch and spruce sawdust as feedstock and the optimization of the organosolv process parameters for enhanced delignification yields. The aim was to deliver a lignin stream to WP2 to be used as feedstock for hydrothermal conversion to bio-oil. Specifically we tested the effect of process parameters such as temperature, time, ethanol content and addition of acidic catalyst in the efficiency of organosolv fractionation for both spruce and birch sawdust. The cellulose enriched pretreated solids, lignin and solubilized hemicellulosic sugars were recovered and chemically analyzed. Selected lignin samples were delivered to WP2.

WP2: Bio-oil production via HTL of organosolv lignin fractions (RISE-PROCESSUM) M4-14.

In WP2 lignin from WP1 was hydrothermally converted into bio-oils. The conversion was determined for four different lignins, then the bio-oils were fractionated into a light and a heavy bio-oil. The light bio-oil -with its high content of monomeric aromatics that were small enough to diffuse into the zeolite structure-

was later tested in WP3. Several grams could be produced in semi-continuous and continuous reactions.

WP3: Bio-crude upgrading to jet fuel (LTU-CT) M1-16.

In WP3, we have first prepared ultra-thin, defect free ZSM-5 crystals with a thickness of 35 nm and a Si/Al ratio of 34. In the next step, these crystals have been mixed with several types of supports in order to optimize the catalyst formulation. Four types of supports and several particle sizes and concentrations of catalysts in the support were evaluated. The performance of the catalysts has first been evaluated by feeding methanol to the catalysts in order to optimize the catalyst formulation. Finally, the optimized catalyst formulation has been explored for deoxygenation of HTL oil produced in WP2.

WP4: Develop site-specific business case, implementation of the process (KIRAM) M12-18.

A business plan detailing how to proceed after the project lifetime and take the project expected results to market was developed.

Resultat

During the current project we initially optimized the organosolv fractionation process parameters for birch sawdust (BSD) and spruce sawdust (SSD). Upon arrival, BSD and SSD were air-dried and then the remaining humidity was measured in an oven at 105 °C. The dried samples were stored at room temperature (Figure 1). The study of the effect of organosolv pretreatment process parameters was performed by examining the effect of different temperatures (180 °C and 200 °C), pretreatment duration (15 and 30 minutes), organic solvent content (50% and 60% v/v ethanol) and presence or absence of catalyst (1% w/w_{Biomass} H₂SO₄). An overview of the experimental design that includes the treatment combinations can be found in Table 1.



Figure 1: Birch sawdust and solvent solutions before organosolv pretreatment

Table 1: Experimental conditions for the sawdust organosolv pretreatment. B- Birch sawdust S- Spruce sawdust.

CODE	Temperature (°C)	Time (min)	OS (% v/v)	Catalyst (% w/w _{biomass})
B0A5a	200 °C	15	50	-
B0A6a	200 °C	15	60	-
B0A6c	200 °C	15	60	1% H ₂ SO ₄
B0B5a	200 °C	30	50	-
B0B6a	200 °C	30	60	-
B1A5a	180°C	15	50	-
B1A6a	180°C	15	60	-
B1B5a	180°C	30	50	-
B1B6a	180°C	30	60	-
S0A5a	200 °C	15	50	-
S0A6a	200 °C	15	60	-
S0B5a	200 °C	30	50	-
S0B5c	200 °C	30	50	1% H ₂ SO ₄
S0B6a	200 °C	30	60	-
S1A5a	180°C	15	50	-
S1A6a	180°C	15	60	-
S1B5a	180°C	30	50	-
S1B6a	180°C	30	60	-

After the pretreatment, the treatment solutions were left to cool down at room temperature and the slurries were vacuum filtered aiming to isolate the cellulose enriched pretreated biomass from the liquor. The pretreated biomass was then washed on the same conditions and volume of the pretreatment, air-dried, and stored in plastic bottles at room temperature until further use (Figure 2). Selected samples of lignin were delivered to RISE Processum for the HTL trials. Specifically, initially 2 BSD and 2 SSD lignins were delivered at 30 g each (B0A6a, B0A6c, S0B5a, S0B5c). After the first trials 100g of B0A6c and S0B5c were delivered and at the last stage of the study 500g of B0A6c.

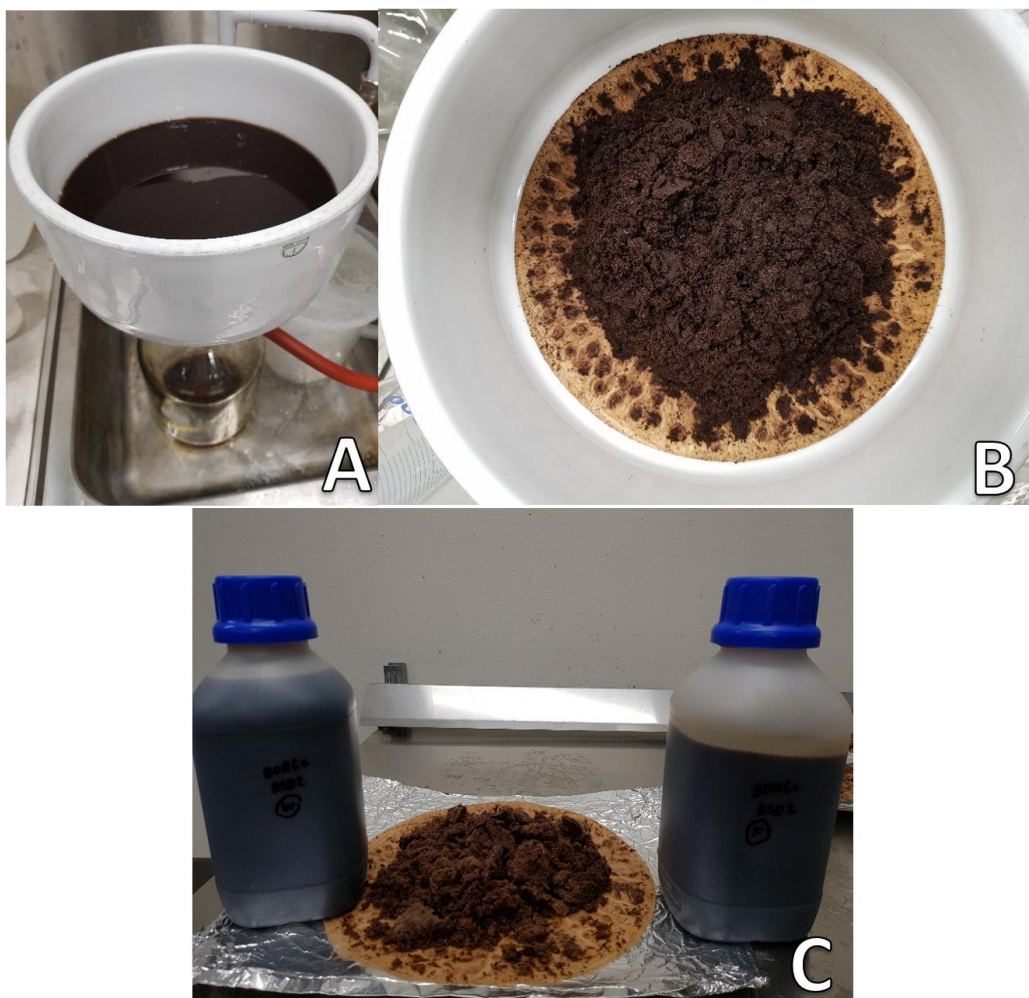


Figure 2: Processing of sawdust sample after pretreatment. A- Vacuum filtration
 B- Isolated biomass C- Liquor, filtrate, and air-dried biomass

By processing the liquor with a rota-evaporator, the ethanol was evaporated and recycled with the potentials to be re-used in the subsequent organosolv fractionation process. Reduction of ethanol concentration in the liquor effectively reduced lignin solubility which was recovered by centrifugation at 12,000 g for 10 minutes at 4 °C. The recovered lignin was freeze-dried and then stored at room temperature until further use (Figure 3) while the remaining hemicellulose-rich liquid was stored at 4

°C and analyzed for hemicellulosic sugars. The pretreated biomasses, lignins and hemicellulose-rich liquids were analysed following the NREL protocol for determination of structural carbohydrates and lignin in biomass (6), the ashes content was analysed on a furnace for 550 °C for 3 hours. The lignins were also analysed through gel permeation chromatography aiming the determination of their molecular weight. For birch sawdust, the cellulose content in the pretreated biomass ranged from 44.16% to 69.20% reaching up to 87.91% of delignification while for spruce sawdust, the cellulose content in the biomass ranged from 34.31% to 74% with delignification as high as 58.37%. The lignin samples recovered were of very high purity, with the carbohydrate impurities to be less than 4.5% w/w and ash impurities to be less than 0.7% w/w in most of the cases.

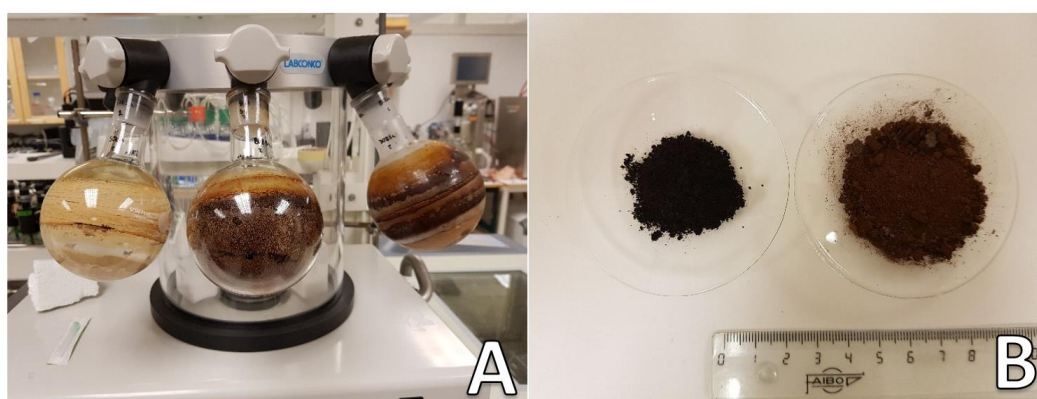


Figure 3: Processing of lignin. A- freeze-drying B- final processed sawdust lignin

The pretreated biomass was used for assessing its enzymatic saccharification potential with the commercial enzyme Cellic® CTEc2 at 50 °C for 48h. For the BSD samples, up to complete cellulose saccharification to glucose was observed, whereas for SSD samples reached an enzymatic saccharification yield of up to 75% of cellulose.

A total of 12 reactions (see Table 2) were run in the HTL process using four different lignins from WP1. In reaction #1-3, the bio-oil was collected in one phase, later a light oil (LO) and heavy oil (HO) phase were isolated. Other product streams of the process were gas, char and a fraction called condensates (light organic molecules with bp < 200 °C). In reactions #1 to #3 it could be shown that high oil yields can be achieved using organosolv lignin. The values are in the range of 60 % mass yield, 65 % carbon yield and 67 % energy yield. Then isolation of a monomeric fraction of the bio-oil was tested. This could be achieved by extracting the crude water phase with ethyl acetate. The extracted LO yielded in average with 8.9 (±1)% mass with an average of 85 % content of identified monomers (one aromatic ring), see Table 3. It is a light brown well flowing oil with similar elemental composition as the starting material (C = 60-65 %, O=28-35 %) and HHV of 23-28 kJ·kg⁻¹. A blank value for LO (i.e., no reaction, just extraction of lignin with water) gave a yield of 1.0 %. Later in #12, it could be shown, that the LO

fraction does not necessarily have to be extracted, the water could simply be evaporated (Sample #12 or JF138 LO Ev) since the following upgrading step benefits from some water content. The other part of the oil was isolated as a dark powder with an average yield of 50 %. Monomeric content in that fraction is small (0.1 – 2.1 %) a large portion of the deoxygenated material can be isolated in that fraction. The carbon content is higher (70 %) and the oxygen content is lower (20 %). That leads to a higher energy yield, HO has typically a HHV of 30 kJ·kg⁻¹.

Table 2: All run HTL experiments.

Nr.	Code	t / h	T / °C	Reactor	Lignin	m(Lignin) / g
1	57_1	30	320	semi-cont.	S0B5a	15
2	57_2	30	320	semi-cont.	S0B5c	15
3	75	30	320	semi-cont.	B0A6c	15
4	88	30	320	semi-cont.	B0A6a	15
5	90	30	320	semi-cont.	S0B5a	6
6	92	30	320	semi-cont.	S0B5c	6
7	93	30	320	semi-cont.	B0A6c	6
8	127	30	320	semi-cont.	B0A6c	100
9	128	30	320	semi-cont.	S0B5c	20
10	129	20	320	cont.	S0B5c	80
11	127_2	30	320	semi-cont.	HO (Nr.8)	20
12	138	30	320	cont.	B0A6c	470

The production of char was much lower than commonly seen in literature, which is a very positive characteristic when aiming to produce bio-oil as higher yields are achieved. The char values for #4 to #12 were < 1 %. The low amount of char lead to the decision to omit tests using an alkali catalyst that otherwise usually aids in reducing char which has a positive impact in the process. The focus was set on the production of more material instead. In #8 5 semi-cont. reactions were run with 100 g total lignin to produce 8 g LO for testing the zeolite catalyst in WP3. In #11 the HO was used as starting material instead of the lignin to see if more LO could be produced from the heavy fraction. The result was that 5 % LO was obtained, consisting of 38 % of monomers and 0.3 % char. If this yield is added to the original LO yield, a combined 10.5 % yield with a total of 9.4 % monomers is reached. This shows that the HO phase could be recycled but the efficiency dropped by 38 % (8 % yield with fresh feed, 5 % yield LO with heavy fraction as feed).

The reduced amount of char in the continuous process can most likely be explained by the fast heating rates to reach the process temperature; in this case the process conditions are only briefly in the hydrothermal carbonification (HTC) range of 180-250 °C where mainly char is produced. To further increase the temperature profile, the continuous reactor was used in #10. Due to limited amounts of lignin, the

starting feed concentration was reduced to 5 % lignin in water. It could be shown that the LO yield is higher in this reaction (33 %), but the monomer yield stayed at the 8.9 %, comparable to the results from semi-continuous experiments. The mass balance in this reaction was only 40 % due to technical issues, so the yields should be considered with this in mind. A new batch of organosolv lignin produced (500 g) and the reaction was repeated at 10 % lignin content in #12. The gas production was measured with a flow meter calibrated on carbon dioxide. It was assumed that 95 % of the gas composition would be carbon dioxide; the fate of removed oxygen is usually carbon dioxide and water. To further close the mass balance, the evaporated water phase was analyzed on organic content. 5 % mass yield was found in the evaporated water phase. Unfortunately, the reactor plugged after one hour of reaction time and only a fraction of the feed could be converted. This also made it more difficult to close the mass balance, especially because some of the material was stuck in the reactor which had to be discarded afterwards. #12 yielded in lower LO yields than in all reactions before (4 %) and HO was stuck in the reactor. The reaction has shown that running at 10 % lignin concentration creates technical problems.

Table 3: Overview of yields. Mean values are taken from semi-cont. reactions. The colors represent the different lignins (S0B5a, S0B5c, B0A6a, B0A6c).

Reaction	5	9	10	6	4	8	7	12	12*	Mean [§]
Light Oil	9%	9%	33%	9%	10%	8%	8%	4%	4%	8,9%
Heavy Oil	46%	43%	7,1%	57%	49%	50%	56%	0%	0%	50%
Char	0%	1,3%	1,0%	0%	1%	1,5%	0%	0%	0%	0,6%
Monomers	8,0%	7,3%	8,9%	6,4%	8,0%	8,0%	8,0%	2,8%	2,8%	7,6%
Mass balance	55%	52%	40%	66%	59%	58%	64%	4%	4%	59,1%

*When water phase was concentrated directly, not extracted with EtOAc.

[§]Only semi-cont. reactions (5 ,9 ,6, 4, 8, 7).

The best catalyst formulation was a mixture of 7% ultra-thin and defect free ZSM-5 crystals with a thickness of 35 nm supported on spherical SiO₂ particles with a diameter of 500 nm. This mixture was compacted, calcined, crushed and sieved to a particle size of 250-500 μm. This particle size is ideal for the small reactor we used in the experimental work, and larger particles could certainly be prepared for a larger reactor. This catalyst gave high conversion of methanol for long time, the product was rich in aromatic compounds, and the pressure drop over the reactor was very low.

The optimized catalyst formulation was then used for conversion of the light HTL oil from WP 2. The received oil was nearly water free as it had been recovered by extraction or dried by evaporation. This step was performed in the project to generate a pure oil free from water, but this may be counterproductive in a real

process. On the contrary, the first experiments showed that the feed line to the reactor was blocked after a few hours of feeding. To solve this issue, the HTL oil was diluted with varying concentrations of water. However, it was not possible to obtain a homogeneous mixture by only adding water, and methanol was added as a homogenizing compound. The best results were obtained with a mixture of 10 w% HTL oil, 30% methanol and 50% water and three different HTL oils were successfully deoxygenated by the optimized catalyst. It is possible that less methanol would have been sufficient, but as only very small amounts of HTL oil were available at a very late stage in the project, there was not enough quantity or time to optimize this mixture further. In any case, this mixture is not too different compared to the composition of the HTL oil produced by the HTL reactor before extraction or evaporation. This oil would contain about 90% water and in addition HTL oil and other water soluble compounds such as methanol and acetic acid.

Quite similar results were obtained for all three oils (B0A6c-L0, JFB8-L0ex, JFB8-L0ev). The diluted oils were fed at a weigh hourly space velocity of 0.3 g diluted oil/g ZSM-5/h to the reactor kept at 350°C. A small flow of nitrogen was also fed as carrier gas. Under these conditions, the feed of 10% HTL oil and 30% methanol (and 60% water) could be almost completely deoxygenated during about 20 h on the optimized catalyst. During this time, the conversion was 90-100 % and no partially deoxygenated products (such as dimethyl ether or phenol) could be detected. The yield of light deoxygenated compounds with five carbon atoms or less (mainly ethylene) was about 65%. The yield of heavier deoxygenated compounds with six carbon atoms or more (mainly aromatic compounds such as trimethyl benzene) was about 35%.

After about 20 h, the catalyst deactivated rapidly, likely due to formation of a small amount of coke on the catalyst. However, no coke could be detected by weighing the catalyst before and after each experiment, which shows that the coke formation must be quite small. We also showed that the activity of the catalyst could be re-established after calcination of the catalyst.

Before deactivation of the catalyst, one gram ZSM-5 converted 0.29 g C in HTL oil and 0.64 g C in methanol to oxygen free products. In a real process, no methanol should be added and additional C in HTL oil may certainly be converted before the oil deactivates in this case. It may be assumed that this additional amount corresponds to 50% of the 0.64 g C in the methanol that was converted. Under this assumption, one gram of ZSM-5 would be able to convert $0.29 + 0.64 * 50\% = 0.61$ g C (or 0.71 g CH₂) in HTL oil before the catalyst deactivates. As HTL oil contains only about 50% C and the average conversion was about 95%, one gram of ZSM-5 catalyst should be able process about 1.28 g pure HTL oil before it deactivates.

In a real process for synthesis of jet fuel or aromatics, a distillation column would be used after the reactor to separate the light deoxygenated compound from the heavy deoxygenated compounds and the water. As the light compounds contains a large fraction of reactive compounds such as ethylene, these compounds should be fed to a second reactor or alternatively re-cycled to the reactor for further conversion to heavier compounds. It may be further assumed that the yield of heavy compounds from the process may increase by an amount corresponding to 50% of the light components in this way. Under these two assumptions, the catalyst should be able to process about 1.28 g HTL oil/g ZM5, which would yield 0.23 g light

deoxygenated compounds (5 carbon atoms or less) and 0.48 g heavier deoxygenated compounds. The mass of the deoxygenated products is less than the mass of the HTL oil, due to the removal as oxygen in the form of water from the HTL oil in the deoxygenation process.

The techno-economic performance of standalone biorefinery concepts that utilize organosolv pretreatment technique was investigated. The assessments were made based on a mathematical process model developed in UniSim Design software using LTU inhouse experimental data.

The biorefinery concepts simulated are based on woody-biomass feedstock derived from the processing of soft- and hardwood. To derive mass and energy balance, a flowsheet of the biorefinery concept was simulated in UniSim Design R460.1 developed by Honeywell. The plant was assumed to be in Sweden, with annual operational time of 7881 h, corresponding to 355 days with an availability of 92.5%. The thermodynamic model non-random two liquids (NRTL) was applied. The target production capacity was set to 50 ktons of dry lignin per year, which is possible to be converted to 25 ktons heavy bio-oil and 4.5 ktons light bio-oil which can be further converted to 1.65 ktons of oxygen-free aromatics and 0.8 kton alkanes using the technology developed in the GOLDJETFUEL project. Figure 4 presents systemic overview of the simulated process.

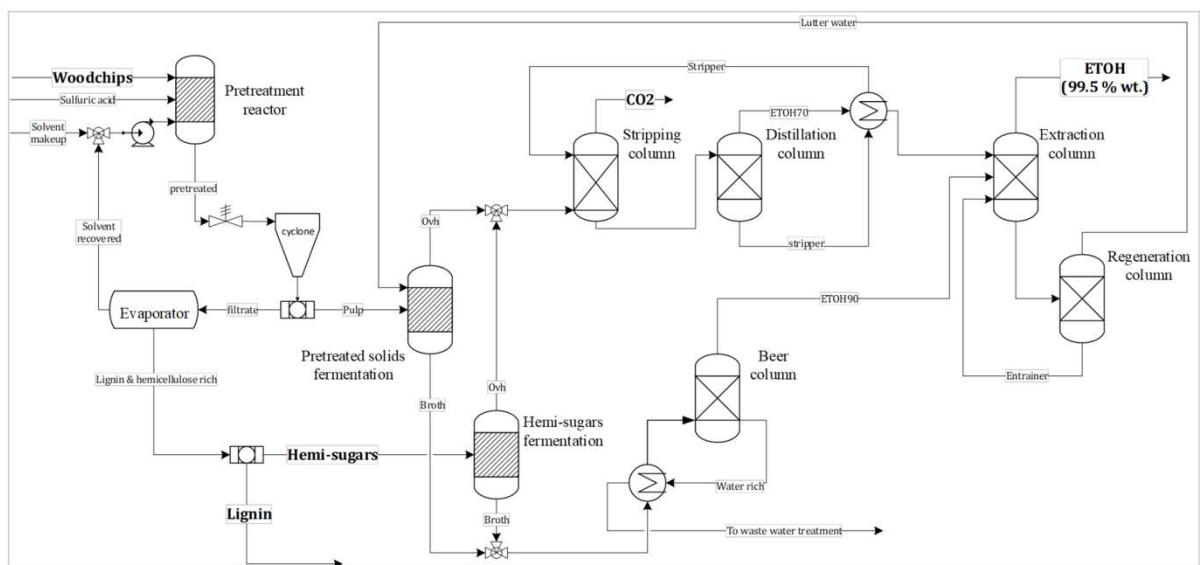


Figure 4. Process flow diagram and system boundary of the biorefinery concept. IPS: intermediate pressure steam; LPS: low-pressure steam; SSF: simultaneous saccharification and fermentation.

Sawdust or chipped wood was mixed with ethanol in a solvent to dry biomass ratio of 6:1 for hardwood and 5:1 for softwood. The reactor was heated to 200 °C by addition of saturated steam at 3 MPa to achieve ethanol concentration of 60% v/v and 52% v/v for hardwood and softwood, respectively. The solvent recovery and the evaporator for concentrating hemicellulose sugars were simulated as mechanical vapor recompression (MVR) evaporators. The incoming streams were

flashed to 0.06 MPa and the vapor generated was recompressed to 0.1 MPa and used as a heat source for the evaporation units. The process and economic performance of the biorefinery concepts were evaluated based on the mass and energy balance derived from the simulation flowsheet developed.

For the biorefinery concepts studied, the targeted final products were ethanol, organosolv lignin and hemicellulose syrup. Minimum ethanol selling price (MESP) and Internal rate of return (IRR) were evaluated as economic indicators of the investigated biorefinery concepts. Depending on the configuration, and allocating all costs to ethanol, MESP in the range 0.53–0.95 €/L were required for the biorefinery concepts to break even. Compared to the reference price of ethanol, 0.55 €/L (700 €/t), a premium of 171% would be required for the worst performing configuration to breakeven. This was calculated with a price of produced lignin and hemicellulose of 600 and 1000 €/dry ton, respectively. Using the GoldjetFuel technology the price of products from lignin (heavy bio-oil and free-oxygen aromatics and alkanes is approx. 1000 €/dry ton and 2000 €/dry ton, respectively). It should be noted that all the biorefinery configurations were tuned to produce 6.34 tons/h dry organosolv lignin to establish a common ground for comparison. The mass balances for the HW and the SW cases required nearly 53 and 45 tons/h of dry feedstock, respectively.

Ethanol was targeted as final product given the investigative nature of the study. **Nonetheless, the combined earnings from lignin and hemicellulose syrup contributed more than the ethanol sales.** This indicates targeting high value products would improve process economics. Lignin, being the second major product of the biorefinery, generated significant part of the income. The lignin market, currently under development phase, is expected to grow fast depending on the intended application area and this why lignin was the target stream in the GOLDJETFUEL project.

In conclusion, hardwood and softwood sawdust based biorefinery concepts based on 1 ton of sawdust are producing cellulose (0,291 t), lignin (0,217 t) and sugars (0,241 t), and extractives (0.1 t) and degradation compounds (such as organic acids and furans) which were not part of the current study. From the produced lignin, we produced with the GOLDJETFUEL technology, heavy bio-oil (0,109 t), oxygen-free aromatics (0.007 t), oxygen-free alkanes (0.004 t), and bio-char (1.3 kg). Use of a continuous HTL reactor resulted in the production of 30-35% of light-oil (preliminary results obtained in the frame of the current project that have to be further confirmed) allowing the maximization of the production of oxygen-free aromatics (0.12 t) and oxygen-free alkanes (0.06 t) through the GOLDJETFUEL technology.

The biorefinery concepts were derived from a full-scale simulation model that was developed based on lab scale experimental data from LTU. Under the assumed economic condition, the biorefinery concepts resulted in net present value ranging from -198 to 15 M€ and the corresponding IRR in the range -1.75–10.7%. However, the sensitivity analysis with projected values of key technical and economic parameters showed potential for profitability, resulting in IRR as high as 17% which can also increase using the GOLDJETFUEL technology for lignin valorisation into bio-oil and oxygen free aromatics and alkanes.

Challenges that must be solved for a market introduction to be realistic:

1. The organosolv pretreatment is an energy intensive process requiring significant amounts of pressure steam that adversely affected the process economy. Hence, possibilities for an integration of the biorefinery with an existing Combined Heat and Power system or a sawmill with a boiler should be investigated to further improve the economic performance.
2. Suggestions of other market opportunities than aviation fuel: Aromatics with much higher value than jet fuel and use of heavy bio-oil as sulfur-free marine fuel. It is worth to notice that marine shipping is the largest global source of anthropogenic SO_x emissions which has forced constitution of new rules from 2020, where ships outside designated emission control areas are banned to use fuel with sulfur content higher than 0.5 wt.%, while the current sulfur limitation is 3.5 wt.%. For ships operating in SECA areas, the limit of sulfur for all bunker oil on board ships is set at 0.10 wt.%. This restriction will be very crucial for the marine sector and consequently it is facing an urgent demand (higher than the aviation sector) for fuel alternatives with both lowered sulfur content and CO₂ emissions.
3. Use of a continuous HTL reactor is necessary to allow maximization of the production of oxygen-free aromatics and oxygen-free alkanes through the GOLDJETFUEL technology.
4. Organosolv lignin has proven to be a feed with high likelihood for reactor plugging. Longer studies in pilot and demo scale are needed to test different pumping speeds, temperatures and potentially co-solvents to find a setting that is less sensitive for plugs. Currently we achieve an incomplete mass balance; when the system can be operated trustfully, the mass balance will be less challenging. The parameter screening could be used to optimize the yield for light oils. Wastewater treatment needs to be implemented for a commercial plant. In addition, recyclability of the water phase will be crucial to reduce the load on the wastewater treatment. The results will most probably show that an increase of the dry matter content in the feed is required (reducing load on wastewater treatment and enhance process intensification). To test feed concentrations of above 10 %, a different pumping system must be used than what was used in this project so far. The feed can be prepared with a screw press to form a paste with a dry matter content of 20 to 30 %. The best option is organosolv lignin to be provided in an ethanol-soluble form just after the organosolv pretreatment than as a dry powder.
5. It was demonstrated that HTL oil can be completely converted to oxygen free products in the form of valuable aromatics and alkanes, roughly in a 2/1 weight ratio, without using any hydrogen at 350 °C. It should be possible to convert about 1.3 ton oil/ton with ZSM-5 before the catalyst must be regenerated. The ZSM-5 catalyst deactivated rapidly, but can be regenerated

by feeding air to the reactor at 500 °C. This frequent re-generation would of course be costly and would certainly lead to a relatively short catalyst lifetime. This problem must likely be solved for a successful commercialization and there are several possible alternatives that could be researched in the future.

Diskussion

In WP1 we demonstrated that birch and spruce sawdust are an excellent raw material for organosolv fractionation aiming to establish a biomass biorefinery concept. Specifically we tested how a range of organosolv process parameters and how they affected the fractionation efficiency of both biomass sources. Our results demonstrated that high fractionation yields can be obtained with very high recovery of cellulose, hemicellulose and lignin fractions in separate streams. The pretreated solids were also tested for the enzymatic saccharification potentials, yielding very high conversion yields of cellulose and thus making them very promising materials for bioconversions. The obtained lignin was of very high purity with low levels of sugar and ash impurities, making such lignins ideal for the subsequent hydrothermal liquefaction.

WP2 shows that high yields in crude bio-oils can be achieved with organosolv lignins. The reactions in the semi-continuous system showed a constant yield but relatively low mass balances. The continuous system suffered from technical problems and could not close the mass balance either. A challenge for the process is to keep the lignin in the feed suspended; it sediments very rapidly when not operated quickly enough (happened in #10), leading to plugging the pumps. After the pumps were adjusted accordingly, a plug was formed in the reactor directly after the heating phase ($T > 300$ °C, $t = 2$ min). To solve this problem, the pumping speed could be increased, or the feed could be diluted (#10 at 5 % Lignin, #12 at 10 % Lignin). Unfortunately, these parameters could not be tested within the borders of this project. Nevertheless, #10 has shown high yields of LO with a similar monomer content as in the semi-cont. reactions leading to the interpretation, that the depolymerization grade was higher in the cont. system. It is believed that large quantities of HO were trapped in the reactor. It was not quantified when the reactor was cleaned, but there was clearly HO left in the reactor outside the mass balance. The yield in LO could potentially be increased by longer reaction times according to #11 where parts of the HO were recycled.

In WP3, we showed that the optimized catalyst is promising for conversion of HTL-oil to aromatic compounds that has the potential as an additive to other bio-jet fuels with too low aromatic content. The route is promising since the conversion is nearly complete, the yield is high and no hydrogen is needed. However, despite the excellent performance of the catalyst, it deactivated rapidly. Further activities should be focused of reduction of the deactivation rate.

In WP4 we showed that GOLDJETFUEL is promising but some challenges must be solved for a market introduction to be realistic such as a) the integration of the biorefinery with an existing Combined Heat and Power system or a sawmill b) suggestions of other market opportunities than aviation fuel like aromatics and

sulfur-free marine fuel c) use of a continuous HTL reactor to allow maximization of the production of oxygen-free aromatics and oxygen-free alkanes d) organosolv lignin to be provided in a ethanol-soluble form just after the organosolv pretreatment than as a dry powder in order to avoid HTL reactor plugging d) regeneration of the ZSM-catalyst using economical efficient methods.

Publikationslista

Monção MM, Hrůzová K, Rova U, Matsakas L, Christakopoulos P: Development of organosolv fractionation of birch sawdust towards establishing a biomass biorefinery. *Under preparation*

Monção MM, Hrůzová K, Rova U, Matsakas L, Christakopoulos P: High fractionation efficiency of spruce sawdust by an advanced organosolv fractionation approach. *Under preparation*

Zhou M, Bodenmuller N, Hedlund J: An excellent ZSM-5 catalyst for deoxygenation of bio oil. Manuscript to be submitted to Catalysis Science & Technology

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