

Value Chain for Production of Bio-oil from Kraft Lignin for use as Bio-jet Fuel

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Abstract

In the LignoJet project, a technical concept for production of lignin-oil with low oxygen content through hydrogenolytic depolymerisation was researched. The feedstock investigated was kraft lignin from softwood and eucalyptus black liquor separated through membrane ultrafiltration followed by precipitation of the permeate and reduction of inorganic metals according to the LignoBoost technology. LignoBoost lignin without fractionation was also produced and used for comparative purposes.

The results indicate that lignin-oils with similar oxygen content were produced, regardless of origin and fractionation technique. Stable pumpable oils with melting point <25-50°C and with a 20-30% lower oxygen content and aromatic content suitable as jet fuel precursors were obtained.

Introduction

Today, the aviation sector is responsible for about 2% of the total global CO₂ emissions or about 775 Mtonne of CO₂ in 2015 (IATA, 2016). Greenhouse gas emissions from the aviation sector grow faster than most other sectors, with a growth rate of about 5%/year. At present, the sector has managed to improve its fuel efficiency resulting in a CO₂ emissions growth of 2-3%/year. This is far from sufficient to reach the internationally agreed goals of carbon neutral growth by 2020, and 50% reduced CO₂ emissions by 2050 (from 2005 levels), (ATAG, 2013). Consequently, the aviation sector is increasingly focusing on developing the technical standards, the legal framework and production infrastructure for sustainable jet fuel from biomass raw materials.

Overview

In the LignoJet project, a technical concept for production of lignin-oil with low oxygen content through combined catalysed depolymerization and hydrodeoxygenation, so called hydrogenolytic depolymerisation, of kraft lignin has been researched. The work included experimental investigations, concept development and techno-economic evaluation. The goal of the project was to reach an intermediate lignin-oil product that is miscible with fossil feedstock and has a significantly reduced oxygen content. The main process steps are outlined in Figure 5, with lignin separation followed by depolymerisation and refinery upgrading. Separation of lignin from the black liquor is one way of exploiting the energy surplus of a modern kraft pulp mill. This gives the pulp mill an opportunity for additional revenues when the by-product, lignin, is used in valuable products instead of generating electricity and process steam in the pulp mill. Lignin separation has the additional advantage of providing an incremental capacity increase, by off-loading the recovery boiler when pulp production is increased. The recovery boiler is the most expensive unit in a pulp mill and retrofit measures to increase its capacity are expensive and not always possible.

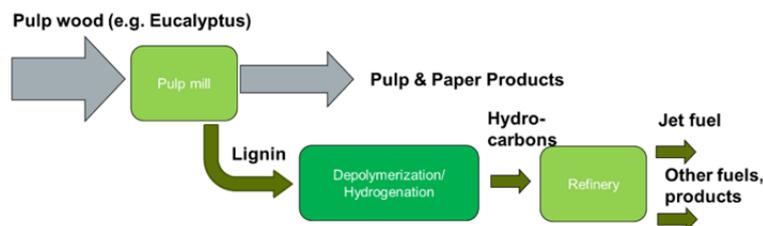


Figure 5 The overall LignoJet process concept.

Experimental

Lignin fractionation, separation and purification

The feedstock used was kraft lignin separated through membrane ultrafiltration from softwood and eucalyptus black liquor, followed by precipitation through LignoBoost technology. A reference LignoBoost lignin without fractionation was produced for comparison.

The motivation for selecting ultrafiltration is to achieve a clean lignin with low levels of carbohydrates and ash. In addition, the molecular weight distribution could impact lignin-oil yield, coke and gas formation as well as other lignin-oil properties. The permeate stream was the main focus of the study. Low levels of inorganic impurities in the lignin-oil is of great importance to avoid downstream catalyst deactivation, so it was decided to precipitate and wash the separated lignin using the LignoBoost process before conversion in the depolymerisation reactor.

The ultrafiltration of the Eucalyptus black liquor was performed using Innventia's laboratory scale equipment filtrating about 50 L black liquor. The membrane filtration equipment consists of a feed liquor tank with a heating coil, a circulation pump, and ceramic membranes (Orélis, France). Membranes having a molecular weight cut-off of 150 and 15 kDa were used. The feed to the membrane process was added at room temperature and circulated through the membranes without taking out any permeate. The temperature was then increased 2°C/min from room temperature to 120°C where it was held constant. Permeate was collected and weighed via a water-cooled outlet. A pilot scale ceramic membrane filtration unit from Orelis, N 120, was used to ultrafiltrate 1-2 m³ softwood black liquor. The membrane unit was equipped with 38 membranes (150 and 15 kDa cut-off was used). The membranes were installed in two modules connected in series (19 membranes per module). The total filtration area was 9.3 m².

Both black liquor samples and the fractionated permeate qualities described above were concentrated through precipitation and washed using the LignoBoost concept to recover the lignin in the sample. In this process the precipitation and washing of lignin consumes carbon dioxide (CO₂) and sulfuric acid (H₂SO₄).

Hydrogenolytic depolymerisation

The hydrogenolytic depolymerisation process is outlined in Figure 6. Permeate or reference lignin is mixed with a solvent (ethanol) and a catalyst and subjected to a temperature of 290°C and 80 bars for 4 hrs, conditions during which ethanol becomes supercritical, increasing its diffusivity and ability to dissolve the kraft lignin, facilitating catalytic hydrogenolysis. The mixture is cooled and the oil is separated from the catalyst and both are recycled. The lignin-oil is washed if necessary and mixed with other feeds and sent to downstream refinery treatment.

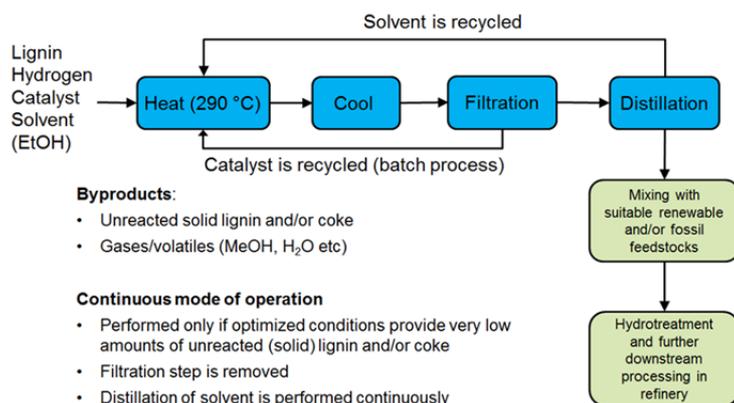


Figure 6 LignoJet approach for combined depolymerisation and hydrodeoxygenation (HDO), i.e. hydrogenolytic depolymerisation.

Several different catalysts and reaction conditions were screened in the experimental work on combined depolymerisation and hydrodeoxygenation. The first screening test focusing on the metal activity identified Ni-catalysts as a suitable material displaying a high but balanced reactivity in relation to other catalysts tested (Pd/C, Pt/C, Ru/C, Ni/C, Raney Ni, Raney Co and homogeneous ethanol-soluble catalyst iron(III) acetylacetonate, Fe(acac)₃). A set of different nickel-catalyst forms and supports were evaluated next. Nickel impregnated on combined carrier alumina/silica (Ni/Al₂O₃/SiO₂) was found to give a good yield (85%) and an acceptable melting point together with a relatively low hydroxyl number of the lignin-oil.

Results and Discussion

Lignin fractionation, separation and purification

The separated solid lignins samples have been characterized and compared with the reference LignoBoost samples:

- The fractionated samples have lower carbohydrate content compared with the reference. The lignin from the membrane with lowest cut off has the lowest content.
- The ash content in the studied samples is comparable. The samples have a low ash content, around 0.5% and lower.
- Sulphur content in the lignin is in the range 2-3 % w/w. The fractionated eucalyptus lignin samples have higher content than the reference sample.
- Ca content is higher in the reference eucalyptus lignin sample probably due to interaction between Ca and carboxylic groups in the eucalyptus xylan.
- An increase of coniferyl alcohol (G) is observed in the fractionated softwood samples in comparison with the reference sample. The content of aliphatic OH group is lower in the fractionated samples both for eucalyptus and softwood.
- A large difference in molecular mass distribution was seen in the case of softwood, both 150 and 15 kDa permeate. When looking at the lignin isolated from the eucalyptus black liquor, no large differences are seen, Table 3.

Table 3 Molecular weight distribution by Innventia in-house method (MW – weight average, MN- number average).

	SW ref	SW 15kDa	SW 150 kDa	HW ref	HW 15 kDa	HW150 kDa
MW (g/mole)	5700	3100	2300	2700	2400	2800
MN (g/mole)	1800	1400	1200	1200	1200	1200

Hydrogenolytic depolymerisation

The analytical results of the depolymerisation experiments with the kraft lignins show similar residual oxygen levels of the different fractionated and non-fractionated kraft lignins, despite the differences in initial oxygen levels between eucalyptus and softwood kraft lignins. Accordingly, hydrogen consumption is higher for eucalyptus than for softwood lignin because of the higher starting oxygen content. Molecular weight distributions are similar regardless of which kraft lignin sample is used. Molecular weight distributions of obtained biooil are significantly lower than in the kraft lignin starting materials but do not reach weight average molecular weight-values below 500-600 g/mole, ranges which can be found for instance in whole biomass pyrolysis oils.

Phenolic OH-groups are essentially the only remaining OH-groups after the hydrodeoxygenation reactions whereas almost all other types (aliphatic and carboxylic OH-groups) are removed. A significant reduction of aromatic ring structures to saturated analogues is observed in proton-NMR. However, a relevant share of the original content of aromatic structures remains in the lignin-oils obtained. This may support high blend-in levels, which is often a limitation in using renewable components in jet fuels, for instance HVO.

Regarding downstream processing aspects, it is noted that many of the product mixtures obtained are oils which are possible to pump at temperatures below 50°C, a crucial property for practical large scale application. However, some oils are still not miscible with for instance fatty acid mixtures and oxygen-free fossil hydrocarbon mixtures. A liquid/liquid two-phase mixture is created, which perhaps would be possible to directly treat further in refinery hydrotreatment/catalytic cracking-equipment if proper mixing is constantly maintained. Noticeably, the same lignin-oil separates very well from water, making it possible to lower trace elements and salt levels using counter-current aqueous extraction, a method which is used to desalt crude petrochemical feedstocks.

The relatively high oxygen content of around 20% remaining in the produced lignin-oils in combination with other analytical data and information all indicate a clear possibility for further optimization of hydrogenolytic catalyst and process conditions. It is expected that potential further hydrotreatment in the refinery will generate mixtures dominated by molecules having boiling points around 300°C or less, suitable for jet-fuels. The lignin-oils may also contain longer carbon chains and/or heavily condensed ring-structure molecules, which after refinery hydrotreatment will not display boiling points <300°C (or other properties in line with jet fuel specs). These more high-boiling molecules can be separated from the desired low-boiling fractions by distillation, and used for other economically attractive products (lubricants, transformer oils etc.). There may, focusing on renewable jet fuel production, be a yield penalty associated with their presence in the lignin-oils. Hydrocracking might be required.

It may be necessary to modify refinery catalysts to handle the significantly higher oxygen contents of the lignin-oils in the subsequent hydrotreatment/catalytic cracking steps to make jet fuel mixtures. In addition, it may be necessary to dilute the lignin-oils with oxygen-free fossil feedstock to lower the concentration of water building up in the process deteriorating the catalyst over time and to avoid coke-formation.

Techno- economic assessment

A first assessment was made of the techno-economic feasibility of integrating the LignoJet concept in a 1.5 MADt/y theoretical Brazilian pulp mill using eucalyptus pulp wood. The experimental data and a WinGEMS software model of a BAT 2010 Brazilian Eucalyptus pulp mill developed by Innventia in other projects were used.

By integration of the LignoJet concept into the Kraft pulp reference mill, changes in some areas will clearly occur, e.g. NaOH make-up and steam consumption. These changes were calculated with the model. The costs were estimated and thereafter allocated to the lignin-oils. Figure 7 gives an overview of the mass-balance.

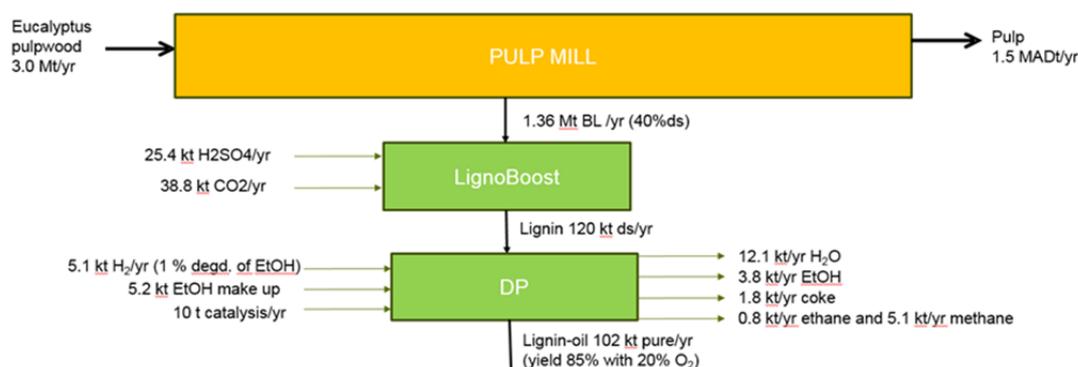


Figure 7 Mass balance of the LignoJet concept integrated in a BAT Brazilian pulp mill.

Table 4 Prices used in economic assessment.

Parameter	Price	
Electricity	55	EUR/MWh
H ₂ SO ₄	75	EUR/ton
CO ₂	290	EUR/ton
Ethanol (make-up)	700	EUR/ton
Natural gas (for H ₂ production)	0.4	EUR/m ³
Catalysis	100 000	EUR/yr
NaOH make-up	460	EUR/t
Labour	15 000	EUR/man-year
Maintenance	2%	of investment

Table 5 Calculation of production cost of lignin-oil (20 wt% oxygen).

	Consumption per ton lignin-oil	Cost EUR/ton lignin-oil	Cost MEUR/yr
Lignin cost (as loss in sold power)	3.1 MWh	174	17.8
Electricity (used in the process)	0.13 MWh	7.2	0.7
Steam cost (as loss in sold power)	0.26 MWh	14.3	1.5
H ₂ SO ₄	249 kg	18.7	1.9
CO ₂	381 kg	111	11.3
EtOH (make-up)	51.3 kg	35.9	3.7
Natural gas (H ₂ production)	203 m ³	81.3	8.3
Catalysis	-	1	0.1
NaOH make-up	124 kg	57.0	5.8
Labour	-	18	0.6
Maintenance	-	32.2	3.3
OPEX		550	54.9
CAPEX		161	16.4
Production cost		711	71.3

There is also an impact on the overall energy balance. Electricity production is reduced with 37 MW due to removal of lignin from the recovery boiler. In addition, around 1.6 MW electricity is used in the LignoJet process and steam used in the LignoJet process causes an additional reduction in electricity production of 3.1 MW. In case the turbine is also a bottleneck, the benefits of investing in boiler and turbine capacity should be weighed against investment in the LignoJet concept.

The lignin-oil production cost is calculated based on an installed equipment cost estimate, including the LignoBoost equipment, of 164 MEUR. Using an annuity factor of 0.1 and Brazilian costs for consumables and energy, Table 4, results in a production cost, Table 5. Adding 40% on the installed equipment cost to allow for balance of plant, utilities, site preparation and contingency will bring the total installed cost to around 230 MEUR and the production cost to about 770 EUR/tonne lignin-oil (20wt% oxygen). The CAPEX makes up ca. 30% of the production cost. As this is a very early estimation, not all equipment has been identified and the uncertainty range is large, most likely $> \pm 50\%$. On an energy basis, the production cost of lignin oils is equivalent to 26 EUR/GJ with a heating value of 30 MJ/kg based on the measured elemental composition. The cost of fossil crude oil is currently about 8 EUR/GJ (based on a crude oil price of US\$ 50/barrel), i.e. the lignin-oil has a production cost that is more than three times higher than today's crude oil price.

The operating cost is the most important part of the production cost. CAPEX is about 30% of the total production cost. A sensitivity analysis reveals that the main individual influence on the cost is related to the capital cost. The alternative use of the lignin is important, here power production is assumed and the electricity price therefore has a large influence on production cost, On-site production of CO₂ from flue gases or to purchase from ethanol plants is a large opportunity to reduce costs.

Conclusions

- A difference in lignin properties was noted between ultrafiltration of softwood and eucalyptus black liquor through 15 and 150 kDa ceramic membranes.
- The depolymerisation results indicate that all produced lignin-oils had similar oxygen content of about 20%. Since also other properties were similar regardless of lignin and fractionation technique, it is suggested to simplify the LignoJet concept by omitting the ultrafiltration and separate the lignin using the LignoBoost concept.
- A lignin-oil with favorable properties as precursor for refinery integration for jet fuel production was produced in small-scale batch experiments using the selected Ni-based catalyst at 290°C and 80 bars and a reaction time of 4 hrs.
- Further optimization of catalyst and process conditions is necessary to reach lower oxygen content of the lignin-oil before refinery integration.
- The estimated production cost is competitive with the production cost of other liquid biofuels. Additional revenues could potentially be achieved by also producing chemical and materials from suitable fractions of the lignin-oil
- CO₂ prices are relatively high in Brazil and therefore in this study. Further reduction of cost may be possible by integration of CO₂ and H₂ production in the pulp mill.
- Downstream processing and refinery integration need to be developed and qualified.
- The technology needs to be scaled up and qualified to reduce technology risks. The current TRL of 2-3 of the depolymerisation needs to be focused on first.

Acknowledgements

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