Produktion av fordonsbränslen från lignin genom katalytisk hydrokrackning under nära superkritiska förhållanden

4.4.3   Fresh water phase
4.4.5   Oil phase
4.4.11 DEE extract of fresh water phase at pH 7
4.4.18 DEE extract of fresh water phase at pH 2

Slutrapport för Ångpanneförenings forskningsstiftelse

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Motor fuels from lignin by catalytic hydro-cracking at near supercritical water conditions

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Abstract

Catalytic hydrocracking at near supercritical water conditions has the potential for a very efficient conversion of black liquor or lignin to bio-oil and bio-gas of high value.

Such research activities have been started within a cooperation agreement between Chalmers and Metso and a high pressure reactor plant has been acquired for catalytic hydrocracking at near supercritical water conditions of LignoBoost lignin to motor fuels and/or aromatics chemicals. Further development of the plant has been made possible thanks to a three year research grant from ÅForsk, 2010.

The high pressure reactor plant has during this period been further developed to an operational standard with instant heating up of the lignin feed and stable operation at steady state conditions for many hours for reliable results. The plant has also been developed for easy and safe inline cleaning which has given an increased research capacity.

Through this improvements and increased research capacity the high pressure reactor plant has been made available to one Post Doc and one PhD project, financed by Chalmers Energy Initiative (CEI) and a Licentiate project financed, by the LignoFuel project and Metso. The first results from these joint projects aiming at depolymerization of LignoBoost lignin have been presented at international bio-refinery conferences and journals, Nguyen (2013), Maschietti (2013).

The results of this first test series show an almost quantitative conversion of lignin into 80% aromatic mono-, di- and trimeres with reduced oxygen and low sulfur content together with a 20% char residue. Further developments are aiming at reducing this char residue without addition of external hydrogen or other non-pulp mill chemicals.

Background

Hydrothermal treatment at near supercritical or at supercritical water conditions has fascinated researchers already from the 1920th as a means to convert biomass to more valuable components such as fuel gas, liquid fuels and chemicals. Simple principal technology based on heating up of a water solution or suspension to 300-400 $^{\circ}$C where the reaction will take place followed by simple separation of oil, water and gas after cooling.

In practical tests and pilot plant projects many technical problems have, however been encountered with the high pressures, high corrosion rate, salt crystallization and formation of large amounts of tar and char. Several pilot plant projects have been or are in operation but no commercial plant is in operation today.

The potential of the technology is, however, very high and many research projects have been started up during the last 10 years.

In relation to process efficiency catalytic hydrocracking at near supercritical or supercritical water conditions has several advantages:

- Water is a readily available and environmentally benign solvent with very special behavior at near supercritical and supercritical conditions (Tester, 2004)
- With catalyst, only moderate temperatures are needed for biomass conversion to stable (low oxygen and water) bio-oil with high heating value and/or syngas
- Almost quantitative conversion of biomass heating value to generated products
- Easy process energy integration of primary and secondary heat with pulp mill
- Short residence time (5-10 min) with modern catalyst and near critical conditions
- Low energy losses with compact design
- Pressurization only of liquid media gives a low electricity consumption
- Gas is produced at high pressures for easy cleaning, storage or direct gas turbine operation
- Sulfur will be converted to H_2S and/or Na_2SO_4

With these potential advantages and no commercial plant in operation there are of course several hinders for a quick commercialization. Some of these hinders are:

- Catalyst regeneration and loss will always be an important issue as most processes will require catalyst for acceptable reactions times and control of tar and char formation.
- High pressure operation (220^{+} bar) gives high cost equipment and special design.
- High temperature gives higher corrosion rates.
- Very different operating conditions for water solutions at high pressure and high temperature – new data are needed.
- Salt solutions, e.g. black liquor, will crystallize at high temperatures with risk for fouling of heterogeneous catalyst.
- Generated water soluble organic acids will not separate by simple decanting.

Lignin and black liquor valorization potential

In the pulp and paper industry wood biomass is converted to chemical pulp at a yield slightly below 50% leaving the remaining flow as a residual stream of black liquor, lignin or solid residues of wood and/or bark. The value of the produced pulp is higher than the cost of the utilized wood sources but the capital cost for the pulp mill is very

high and the residual biomass streams are normally only utilized as an energy source for operation of the pulp mill.

The main driving force for conversion of LignoBoost lignin or black liquor (BL) to hydrocracking oil and gas is the higher potential values of generated products. As an example, the valorization potential for the case of full capacity black liquor hydrocracking is illustrated in the column chart below. On energy per ton of pulp basis, the valorization potential from pulp wood to pulp and from black liquor to hydrocracking oil and gas, shows in a simplified way the inherent value of the technology. Please note that the area of the columns in the figure represents the total value as €/ADt.
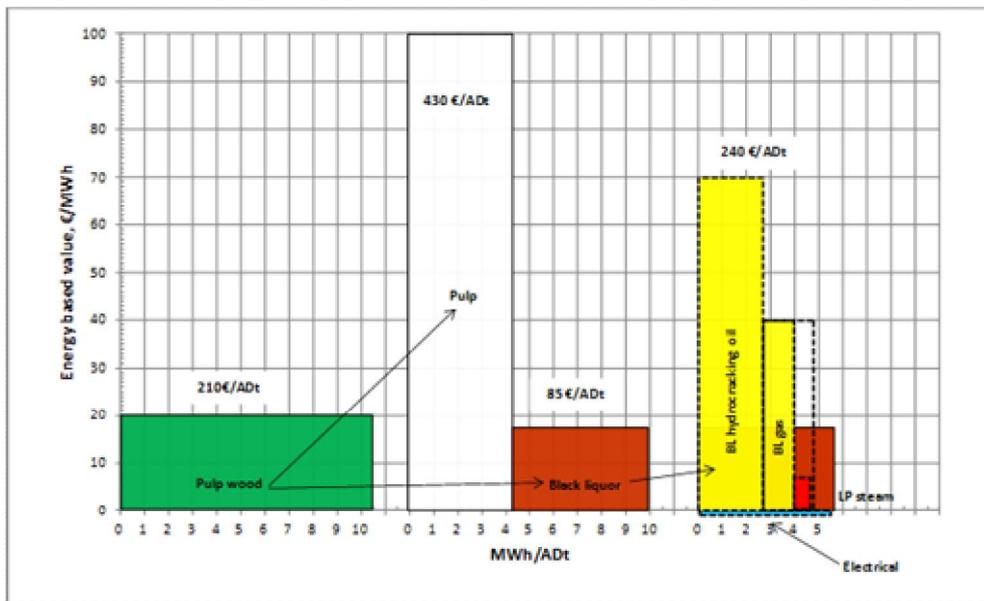
Valorization potential with full flow black liquor hydrocracking

On an energy basis the value of pulp is 100 €/MWh (at 430 €/ADt) but the value of the residual biomass is only about 20 €/MWh. The potential value of this biomass could, however, be up to the level of the pulp itself if it could be converted to liquid fuels, motor fuels or aromatic chemicals. Considerable mill export of such converted biomass is possible without additional fuel import by implementation of known technology for energy saving measures.

The proposed route for such a conversion of pulp industry biomass residues utilizes the capacity of the pulp mill to handle these residues as mixtures or suspensions in water, subject the mixtures to hydrocracking under mild conditions not to destroy their basic aromatic chemical structures, and totally recover utilized heat in the cracking process as energy for the pulping processes.

The potential for liquid phase hydrothermal conversion is related to black liquor, which already is handled as a liquid, wood or bark residues which has been studied subjected to hydrothermal conversion as suspensions and lignin which is easily handled in suspension.

The main focus of this first step is hydrothermal conversion of LignoBoost lignin which in comparison with black liquor is a very homogenous product with practically no salt

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content. Lowest project risk is therefore expected with the present research focus on lignin hydrocracking.
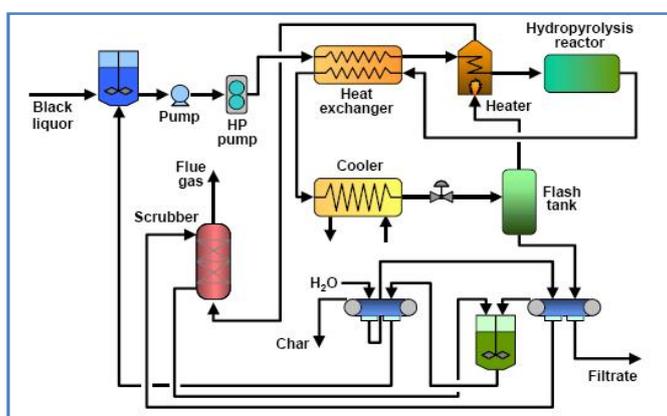
On the basis of the Swedish pulp industry with a total energy input of 42 TWh as black liquor, 7 TWh (at 25% separation of BL lignin) would be initially available and 20 TWh (at 70% separation of BL lignin) would be available in the future for lignin de-polymerization together with 3 TWh lignin generated from wood based future ethanol production (at 3,2 TWh EtOH/year - prognosis for 2020).

Hydrothermal conversion of pulp industry biomass residues

Liquid phase "hydrothermal" conversion condition is normally understood as treatment of e.g. lignin as suspension in a solvent. This solvent is preferably water but could also be ethanol, methanol, liquid CO_2, bio-oil from its own conversion or other solvents depending on its dissolution capability. Mild conditions normally mean temperatures below 400°C. Both homogeneous and heterogeneous catalysts are utilized. Potential homogenous catalysts are K_2CO_3, Na_2CO_3, NaOH, organometallic compounds, phenol, formic acid and many others. A large number of heterogeneous catalysts are known, many of them from petroleum industry where also hydrogen treatment is a common process.

The St. Regis hydropyrolysis process development began in the early 1960s as a search for an alternative to the conventional recovery boiler. Laboratory experiments were conducted between 1968 and 1972 followed by pilot plant testing (16 ton DS/d) in the mid 1970s.

Low dry solids black liquor is pumped to about 193 bar and is heat exchanged with reactor product to about 260°C followed by final heating in a heater to its reactor temperature of 332°C. The hydropyrolysis reaction takes place in a high pressure reactor with a residence time of 20 min where the black liquor is converted to large quantities of char and filtrate, gas and oil. The product is cooled in two steps followed by depressurization in a flash tank and collected gases are utilized for firing of the reactor heater. The suspension is passed to one or more filters in series where char is separated from the solution and washed to remove sodium and sulfur. The char could be used as a fuel in an auxiliary boiler, or could be treated to form activated carbon. The filtrate from the suspension was combined with the char washings and formed the green liquor. Engineering of 530 ton DS/d plant was carried out but was never realized because of low profitability (Timpe, Adams, Gilbert, Whitty, Del Bagno).

Under EU Contract NNE5/393/2001 in a cooperation between SCF Technologies A/S in Denmark and the Karlsruhe research plant the Catliq technology was developed. Initial development and verification of the new technology for catalytic conversion of biomass was done in Karlsruhe in the Carola laboratory set up (capacity 1 kg/h) and in the Verena plant (capacity 100 kg/h) - Larsen (2005).

Since 2007 SCF Technologies A/S has operated a continuous pilot plant (capacity 10–20 l/h) in Herlev, Denmark based on bio-waste conversion in near supercritical H_2O (280-370°C), 25 MPa with K_2CO_3 as homogeneous catalyst and ZrO_2 pellets as heterogeneous catalyst. Promising results with high carbon conversion has been presented by Hammerschmidt et al. (2011) and by Toor et al. (2012). The technology is now, however, sold to Altaca Inc. and the plant has been moved to Turkey.

Through contact with the original inventor Kjeld Andersen this process has inspired to the development of the Chalmers high pressure reactor plant - Andersen (1988, 1993).

Lignin conversion has been studied in many university projects, normally however, only in small scale batch reactors. The very simple case with hydrothermal treatment of lignin in pure water has e.g. been studied by Wahyudiono et al., (2008) at Kumamoto University. They showed very fast lignin depolymerization but also high char formation at studied temperatures of 350 and 400°C. Similar studies published by Pinkowska et al. (2012), and by Tymchyshyn, et al. (2010) at Lakehead University also shows that hydrothermal treatment of lignin in water with alkali or with some H_2 still gives high formation of re-polymerized lignin "pyrolytic lignin" or char. Especially at high temperatures. Lignin also behaves very much different compared to pure biomass (Tymchyshyn).

The effect of different alkali salts as homogenous catalyst has been investigated by Karagoz et al. at Okayama University (2005). The best homogenous catalytic effect was achieved with K_2CO_3.

During the 1990th VTT studied solvent free catalytic conversion of lignin at 400-450°C,10 MPa H_2 – Oasmasa, Alen (1993) and Oasmaa (1993). Kraft pine lignin tested with NiMo(S) on Cr_2O_3/Al_2O_3 or on zeolite gave 61% oil yield (of lignin) - fluid oil, soluble in THF and acetone. Addition of NaOH and water gave much lower yield.

Solvolytic conversion of lignin has been reported from Bergen University – Kleinert and Barth (2008), Kleinert (2009), Öyaas (2012). Non-stirred batch reactors charged with 0,7g lignin, 6ml HFo (as hydrogen donor), 6 ml EtOH, in 380°C during 16-24h. No heterogeneous catalyst. High yield (90%) and low char formation reported.

Catalytic and hydrogen treatment of lignin in supercritical EtOH has been reported from Rostok University – Patil et al. (2011). Batch reactor test with 25 ml, 300°C, 200bar, 20h, 20 bar H_2, Ru/Al_2O_3. High lignin conversion (>90%) reported at very long residence time.

Comprehensive research on lignin conversion to valuable aromatic chemicals is ongoing at several universities in the Netherland. Zakzeski et al. (2010) has presented a comprehensive review of lignin conversion. Bruijnincx et al. (2011) has presented solubility measurement of lignin in water and ethanol/water and lignin model studies in batch reactor, 100 ml, $CoMo(S)/Al_2O_3$, 300 ^{o}C, 50 bar H_2, dodecane solvent. Phenol and cresols are the main products - low yield. Gosselink (2011) reports lignin conversion in CO_2 and acetone – high char formation.

Straight forward hydrogen treatment of lignin is reported by Dumesic et al. Wisconsin Madison. Supercritical water, 40 bar H_2, heterogenous catalyst Pd/C, Rh/C and Pt black. High yield of guaiacyl propanol and syringyl propanol reported.

Organometallic hydrogenolysis of lignin is presented from University of Massachusetts, Amherst - Sergeev and Hartwig (2011) and C&EN (2011). Hydrogenolysis of aromatic C-O bonds in alkyl aryl and diaryl ethers is reported that form exclusively arenes and

alcohols. The process is catalyzed by a soluble nickel carbene complex under just 1 bar of hydrogen at temperatures of 80 to 120°C.

During the last ten years an almost exponential increase in publications in the field of lignin conversion and depolymerization has been recorded including many comprehensive review articles, e.g. Azadi (2013). Almost all as university projects performed in small scale batch reactors. Here a small number of all project have been reviewed showing large variations in the chosen reaction conditions. Our conclusion from all these studies are that a continuous reactor plant arranged for fast heating up to reaction conditions should be preferred. The chosen reactor plant should be able to handle temperatures up to at least 400°C and its corresponding water saturation pressure. Even with water as an ideal solvent the reactor plant must be flexible enough to accept most other solvents and homogeneous catalysts. The heterogeneous catalyst should be easy to exchange both for regeneration and for test of alternative catalysts. Hydrogen is not naturally available in pulp mills and has for that reason not been initially considered in this lignin conversion first test series. It might, however, be necessary to test even hydrogen treatment with means that the reaction plant should be possible to utilize for such operation.
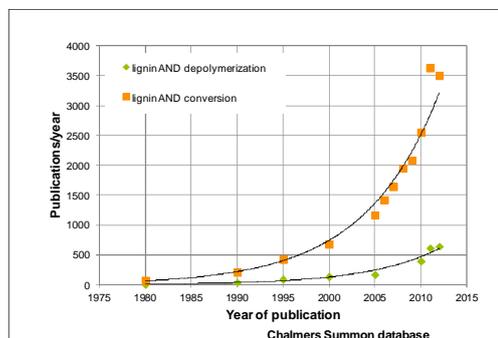
Chalmers high pressure reactor plant

An initial evaluation of the hydrocracking technology shows very high potential conversion efficiency in combination with a very high valorisation potential. The hydrocracking technology is, however, not yet ready for commercialization and further research is necessary. To initiate such research a cooperation agreement was made between Metso and a Chalmers research group with long time experience from catalytic cracking and hydroprocessing of petrochemicals.

Within this research cooperation a high pressure reactor plant has been acquired for catalytic hydrocracking at near supercritical water conditions for selective conversion of LignoBoost lignin or black liquor to liquid feedstock for motor fuels and/or aromatic chemicals. The high pressure reactor plant (345 bar, 500°C and 3 l/h capacity) was started up in 2010.

The plant was supplied by Mothes Hochdrucktechnik GmbH, Berlin and built into a safety box. Included in the plant was a 10 l stirred feed tank with heat control, a Lewa diaphragm feed pump, an Endress+Hauser Promass mass flow meter, electrical preheater, a 500 ml Parr 4575 high pressure reactor with magnetically coupled stirrer, reactor heater, burst discs, product cooler, a Samson 3510 pressure relief valve, pressure and temperature meters and a Jumo process control system. Construction material was Inconel Alloy 600 for high temperature parts and stainless steel for other process equipment.

After installation and connection to Chalmers service and ventilation systems the plant was started up and tuning, preparation and feeding of the lignin suspension with the high pressure feed pump was studied in a M.Sc. project by Hedlund (2010). The reactor was then charged with 3 mm catalyst pellets of ZrO_2. A number of experiments with cracking

of lignin suspension (at 5-10% DS) with the reactor operating in continuous stirred tank reactor "CSTR" mode with both a heterogeneous catalyst and a homogeneous catalyst at 360°C have been carried out. Most important findings from this first test period were:

- High pressure feeding of lignin suspension up to 35%DS possible after rebuild of original feed pump valves.
- It was possible to run the reactor with lignin suspension but normal operation time was only 50 minutes which was considered to short *time* for steady-state operation and good performance.
- Process operation of feeding and reactor system had worked well but the discharge system had, in spite of valve rebuild, been sensitive even for low particle concentrations in the product flow.
- Only partial decomposition of the lignin was achieved.

A number of rebuild activities, focused on improving the reactor plant for stable long time operation with improved conversion rate for LignoBoost lignin have been carried out during 2011 and 2012. Most important activities are:

- Installation of a new high pressure high temperature pump for reactor operation in plug flow mode.
- Rebuild of the reactor for plug-flow mode including new recirculation heater, new reactor heater, a second pressure relief valve and control systems.
- Rebuild of the reactor system for inline chemical washing and mechanical high pressure water flushing
- Additional safety measures

The high pressure (HP) reactor plant 2012

Together with the installation and reactor plant tuning activities during 2012 a first test series with LignoBoost lignin has been carried out. Evaluation of these results is under way but a preliminary evaluation is presented in the chapter "Lignin cracking results" below.
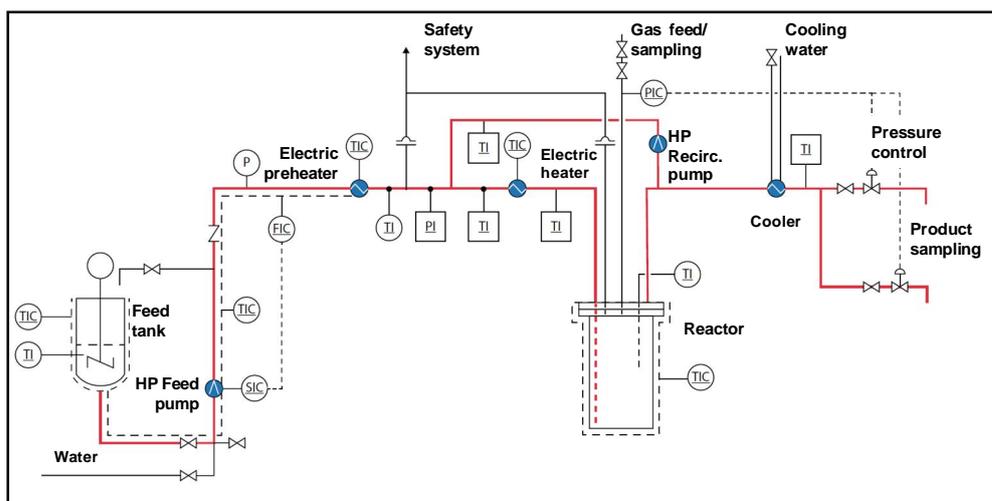
Principal flow sheet of the high pressure reactor plant 2012

The operational capability of the reactor plant has improved tremendously with all measures during 2011 and 2012. One especially important measure is the inline washing rebuild which considerably reduces downtime for cleaning between test runs. Still, however, further improvements areas have been identified;

- New additional high temperature control valve(s) with control system for two step pressure reduction. Pressure control of the high pressure reactor is identified as the most important remaining operational weakness.
- One parallel feed line is available and will be installed during spring 2013. Dual feed will give improved capability for inline washing, higher lignin concentration, separate co-solvent feed and hydrogen gas mixing.
- Hydrogen gas pump and feed mixing vessel if hydrogen treatment will be chosen in future test project
- New high pressure reactor vessel with external bottom feed for improved plug flow capability.

Below is an operation record from a test run with good performance. The normal behaviour shows an initial period for final pressurization and heating up, a short temperature stabilization period followed by start of lignin feed. After some initial pressure variations after start of lignin feed a stable operation period of 3-4 hours normally follows. All temperatures are usually very stable during the whole test run but pressure disturbances might occur with too much unreacted lignin in combination with formation or very high viscosity of produced oil.

About ½-1 hour after ending of the lignin feed a 1-2 hour cooling down and depressurization period follow before the reactor can be opened and removed. Immediately after removal of the reactor, temporary pipes for chemical cleaning and water flushing are connected. The cleaning sequence usually employs THF as first solvent for lignin residues and pyrolytic lignin oil deposited in the reactor plant. Next step is washing with an alkaline isopropanol water solution for oil removal and release of deposited char followed by high pressure water flushing for removal of char and other particles. All pipes and all equipment in contact with the process fluids are cleaned during the cleaning sequence.
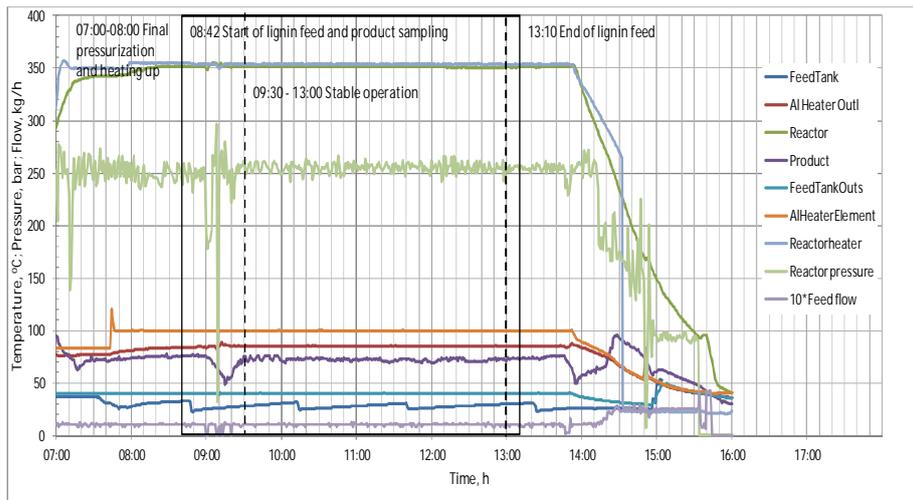
Operation record during test run 9

Funding for development of the plant has been granted through Metso, Chalmers and ÅForsk

Lignin cracking results

With the high pressure reactor plant in improved operation condition the plant has been made available for one Post Doc project and one PhD projects at the Division of Forest Products and Chemical Engineering financed by Chalmers Energy Initiative (CEI) and a Licentiate project at the Division of Heat and Power Technology financed by the LignoFuel project and Metso Power AB. The first results from these joint projects aiming at depolymerization of LignoBoost lignin have been presented at two international bio-refinery conferences (Nguyen, 2013 and Maschietti, 2013) and in one international journal (Nguyen, 2013).

The chosen operation conditions for the first test series was inspired by the Catliq process conditions as presented by Andersen (1988, 1993). The operation conditions are:

Feed mixture parameters

- LignoBoost kraft lignin from Bäckhammar.
- Lignin DS concentration 5,4 – 5,9 wt%
- Phenol concentration range 0 and 4,0 – 4,4 wt%
- K_2CO_3 concentration range 0,4 – 2,2 wt%
- Water
- Feed flow rate 1 kg/h

Operation parameters

- Pressure 250 bar
- Temperature 290 - 370°C

Catalysts

- Homogenous catalyst; K_2CO_3 and phenol
- Heterogeneous catalyst; ZrO_2 pellets

Test procedure

The reactor plant was operated with water during the initial heating up and pressurization phase. After stable temperature levels were achieved the feed pump was switched to lignin suspension feed which started the test operation period. The temperatures, pressure and feed flow was kept as stable as possible for at least four hours. Liquid product after cooling and depressurization was collected from the start of lignin suspension feed. After sufficient operation time the feed flow was switched back to water or water phenol operation and after ½ - 1 hour displacement operation final cooling down and depressurization started.
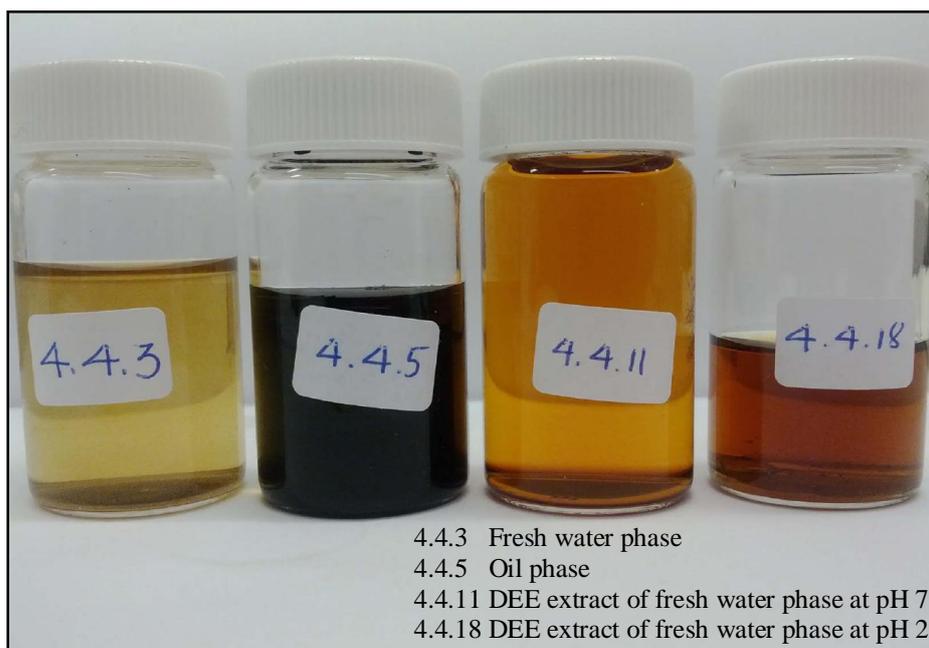
After identification of the stable hydrocracking operation period the liquid product bottles from this period was analysed by Chalmers SIKT and SP. Collected liquid samples as shown in the enclosed picture below goes from brown lignin suspension appearance to oily black appearance. After about two hours the appearance typically stays steady.

**Liquid product samples from test run 9 of 2012-11-14**

After cooling down and depressurization the reactor is opened and the catalyst is taken out for regeneration and measurement of formed char. All pipes and equipment of the reactor plant are cleaned in place with organic solvent, alkaline solvent and by high pressure water flushing before the next test run.

The selected liquid sample bottles are prepared for analysis by centrifugation and separation into one aqueous phase and one oil phase. The aqueous phase is extracted with DEE followed by GCMS analysis. Aqueous sample from the different test runs have been sent to SP for TOC analysis.

4.4.3 Fresh water phase
4.4.5 Oil phase
4.4.11 DEE extract of fresh water phase at pH 7
4.4.18 DEE extract of fresh water phase at pH 2

Lignin hydrocracking products after separation

An example of GCMS chromatogram is shown below. 17 water soluble chemicals identified so far from NIST MS Library. Same qualitative behaviour is shown in all runs. The large peak for phenol is a result of its use as co-solvent added to the lignin feed.
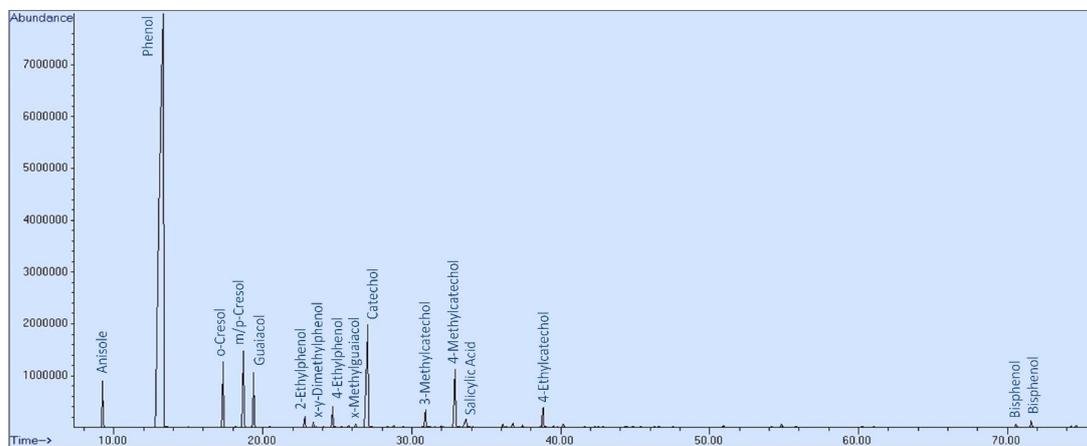
Typical GCMS chromatogram sample from run 9.

The oil fraction is analysed for water by Karl Fisher titration. Oil phase samples from the different test runs have been sent to SP for elemental analysis, ash analysis and heating value measurement.

Some conclusions from the performed test runs are:

- Lignin is converted to a viscous but flowing oil and water soluble aromatic monomers

- About 70 wt% of the lignin feed is converted to oil phase
- About 10 wt% of the lignin feed is recovered as water soluble monomers
- About 20 wt% of the lignin feed is converted to char
- Almost zero gas is released during product sample collection
- Oxygen reduction from 26 to 16%
- Sulfur reduction from 1,9 % to 0,4%
- Heating value increase from 27,7 to 31,9 MJ/kg DS
- Best yield of aromatic monomers is 27% of lignin
- Oil consists of aromatic monomers, dimeres and trimeres

Comments to the result from this first experimental test run and discussions of possible routes for improved conditions:

- The feasibility of the catalytic conversion of LignoBoost Kraft lignin in near-critical water using ZrO_2 + K_2CO_3 as catalytic system and phenol as co-solvent is demonstrated.
- Lignin is depolymerised at a yield of 80% into aromatic mono-, di- and trimeres that are partially deoxygenated, has a moderate increase of carbon content and heat value and a high reduction in sulfur content. It is proposed to test this lignin oil for hydrogen treatment to motor fuels at oil refinery conditions.
- Total yield of aromatic monomers increases with K_2CO_3 - maximum yield 27%
- Depolymerization of lignin in water alone gives a very fast reaction but also a high amount of re-polymerization to "pyrolytic lignin" which results in very high formation of char.
- With additional phenol as co-solvent the char yield is, however, greatly reduced and tests with other co-solvents are pending (eg. methanol, ethanol and lignin oil).
- Further modification of the heterogeneous catalyst is proposed for reduction of the formation of char.
- Addition of hydrogen gas or hydrogen donors has not been considered for these first test runs for the reason that these are expensive and not normally available at pulp mills. For future process comparisons such tests might be necessary. The reactor plant could fairly easy be modified for such operation.

Acknowledgements

Reference list*

- T.D.H. Nguyen et al., 21st EU BC&E, Copenhagen, June 2013
- M. Maschietti, et al., RRB-9 Conference, Antwerp, June 2013
- T.D.H. Nguyen, M. Maschietti, T. Belkheiri, L.-E. Åmand, H. Theliander, L. Vamling, L. Olausson, S.-I. Andersson, "Catalytic Depolymerisation and Conversion

of Kraft Lignin into Liquid Products Using Near-Critical Water", The Journal of Supercritical Fluids (2013), http://dx.doi.org/10.1016/j.supflu.2013.11.022

- Tester J.W., et al., "Salt precipitation and scale control in supercritical water – Part A: fundamentals and research", J. of Supercritical Fluids 29(2004) 265-288
- Timpe and Evers, "The hydropyrolysis recovery process - a new approach to Kraft chemical recovery", Tappi, 1973
- Adams, Jr., W.S., et al, "Hydropyrolysis as an alternative Kraft recovery process", AIChE, 1980
- Gilbert, A.F., and Cooper, D.F., "Hydropyrolysis of Kraft hardwood and softwood black liquor", Can. J. Chem. Eng., 1987(65), Feb., 78-81
- Whitty, K., Verril, C.L., "A historical look at the development of alternative black liquor recovery technologies …..", Int. Chem. Rec. Conf., 2004
- Del Bagno, et al, "On site production of activated carbon from Kraft black liquor", EPA July 1978
- Larsen, T., "CHP plant based on catalytic liquid conversion process - Catliq", Non-confidential technical summary report, EC contract NNE5-393-2001, 2005
- Hammerschmidt et al., "Catalytic conversion of waste biomass by hydrothermal treatment", Fuel 90 (2011) 555-562
- Toor et al., Biomass and bioenergy, 3 6 (2012), 327-332
- Andersen, K., Patent application 1988, DE 3806732 A1
- Andersen, K., "Gasification process", Patent 1993, EP 402 405 B1
- Wahyudiono, Chemical Engng. and Processing ,47(2008), 1609-1619
- Pinkowska, et al., Chem. Eng. J. 187 (2012) 410– 414
- Tymchyshyn, et al. Biores. Techn. 101(2010),2483-2490
- Karagoz et al., Chem. Eng. J., 108(2005), 127-137
- Oasmaa and Alen, Bioresource Technology, 45 (1993) 189-194
- Oasmaa and Johansson, Energy & Fuels 1993, 7, 426-429
- Kleinert and Barth, Energy&Fuels 2008, 22, 1371
- Kleinert et al., NWBC 2009
- Öyaas K., et al., NWBC, 2012
- Patil et al., Energy Fuels 2011, 25, 4713–4722
- Joseph Zakzeski, et al., "Catalytic valorization of lignin for the production of renewable chemicals", Chem. Rev. 2010, 110, 3552–3599
- Pieter. C. A. Bruijnincx, et al.,"Catalytic conversion of lignin and its derivatives for the production of renewable chemicals", Mini-symposium, Wageningen, December 6th 2011
- Gosselink, "Lignin as a renewable aromatic resource for the chemical industry", PhD, Thesis, Wageningen University, 2011
- Dumesic et al., Green Chem., 2012, 14, 1573
- Sergeev and Hartwig, Science Magazine, 22 April 2011, 332 (6028): 439-443
- C&EN, "Chopping up lignin", 89(2011),17,11
- Azadi, et al., " Liquid fuels, hydrogen and chemicals from lignin: A critical review", Renewable and Sustainable Energy Reviews 21 (2013), 506–523
- Hedlund, T., "High pressure and temperature conversion of lignin and black liquor to liquid fuels", M.Sc. Thesis, Chalmers 2010

∗ In order of appearance