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

Slutrapport för Ångpanneförenings forskningsstiftelse

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Projektledare: Lars Olausson, lars.olausson@chalmers.se
Institutionen för Energi och Miljö
Värmeteknik och maskinlära
CHALMERS TEKNISKA HÖGSKOLA
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Motor fuels from lignin by catalytic hydro-cracking at near supercritical water conditions

Lars Olausson

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. Simple principal technology based on heating up of a water solution or slurry to 300-400 ^{o}C where the reaction will take place followed by simple separation of oil, water and gas after cooling.

After intense research activities in the field of hydrothermal conversion during 1970-1990 followed by a period of low activity the research has regained interest in the 2000s with better process understanding, new catalysts, supercritical water operation and new materials. Several pilot plant projects have been or are in operation but still no commercial plant has been put into operation.

The valorization potential for hydrocracking of LignoBoost lignin or black liquor to motor fuels or chemicals is very high with a potential contribution comparable to the contribution of the pulp itself. The technology is, however, not yet ready for commercialization and further research has been recommended.

Such research activities has recently been started within a cooperation agreement between Metso and a Chalmers research group with long time experience from catalytic cracking and hydroprocessing of petrochemicals and a high pressure reactor plant has been acquired for catalytic hydrocracking at near supercritical water conditions of LignoBoost lignin to motor fuels or chemicals. Further development of the plant is ongoing with support from ÅForsk which is thankfully acknowledged.

Background

Hydrothermal treatment at near supercritical or 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 slurry to 300-400 ^{o}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 promising and many research projects and some pilot plant 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:

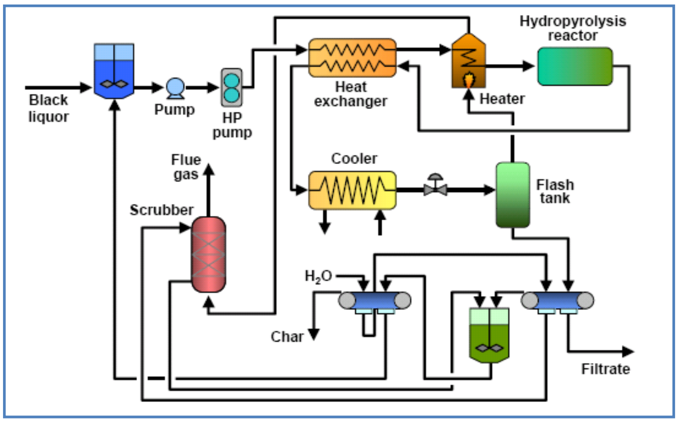
- Water is a readily available and environmentally benign solvent with very special behavior at near supercritical and supercritical conditions (Tester, 2004)
- With catalyst only moderate temperatures are needed for biomass conversion to stable (low oxygen and water) bio-oil with high heating value 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 all these 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 high corrosion rates and demand for special materials.
- 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.

Hydrothermal biomass conversion during 1970-1990

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 slurry 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 slurry 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).

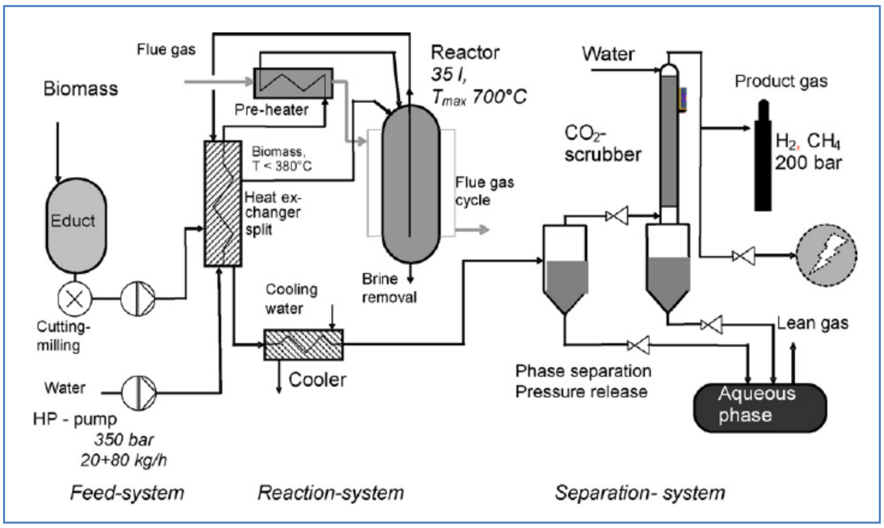
Many other smaller hydrothermal conversion projects during 1970-1990 including lignin and black liquor were carried out but all suffered from general problems with char formation, organic acids generation and operational problems.

In a comprehensive study within the IEA Biomass Agreement Pyrolysis/Liquefaction activity during the late 1980s and early 1990s VTT made an economical assessment of the two processes (Solantausta, Beckman). It was concluded that both processes showed about the same efficiency but AFP “atmospheric flash pyrolysis” was slightly ahead of LIPS “liquefaction of wood in pressurized solvent” with respect to remaining research demand and cost. Following years after this recommendation from 1990 main activities for this type of biomass conversion was within atmospheric flash pyrolysis.

Catalytic hydrocracking for biomass conversion in the 2000th

The hydrothermal technology has regained interest in 2000s with better process understanding, higher heating rate, new catalysts, supercritical water operation and higher temperatures (Savage, 2009).

One comprehensive such research plant adopted for high pressure and temperature hydrothermal processes was the Verena plant in Karlsruhe designed for 350 bar, 700 ^{o}C and a capacity of 100 kg/h of biomass (20% by mass) as reviewed by Kruse (2009).



Karlsruhe - Verena plant

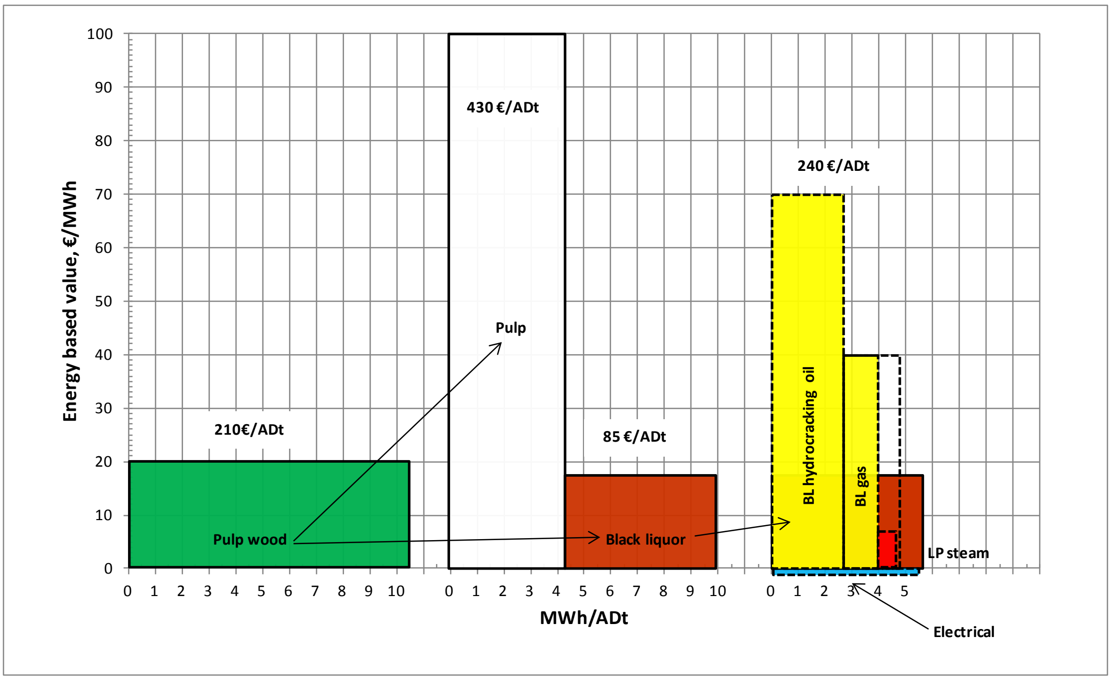
Under EU Contract NNE5/393/2001 in cooperation between SCF Technologies A/S in Denmark and Karlsruhe research plant the Catliq technology was developed. Initial development and verification of the new technology for catalytic conversion of biomass was done in Karlsruhe in the Carola laboratory set up (capacity 1 kg/h) and in the Verena plant (capacity 100 kg/h). Since 2007 SCF Technologies A/S has operated a continuous pilot plant (capacity 10–20 l/h) in Herlev, Denmark (Iversen, 2005).

Feedstock such as manure, sewage sludge, industrial sludge, wet distiller's grain, liquefied waste, saw dust and straw have been tested in Karlsruhe and/or in the Herlev pilot plant. The products are a stable bio-oil (30-60% on feed heating value), some gas (5-10%) and water soluble organics (30-60%). The bio-oil has a heating value of 33-38 MJ/kg and 2-12% oxygen content.

Based on the same scientific basis Grundfos Microrefinery A/S is today also developing similar technology for hydrothermal conversion of waste biomass (Hammerschmidt, 2011).

Lignin and black liquor valorization potential

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

Conditions for the calculations:

- 2,1 ton wood (DS) /ADt, 18 GJ/ton wood (LHV), 20 €/MWh wood
- 1,55 ton BL(DS)/ADt, 13,0 GJ/ton BL(DS) (HHV reduced cond.)
- The black liquor energy value is 18 €/MWh (LHV) corresponding to forest fuel price.
- Pulp energy value is 4,3 MWh/ADt
- Pulp price is 430 €/ADt (600 $/ADt) calculated on a long time average basis.
- Estimated BL hydrocracking yield; 50% oil, 25% HP gas, 10% LP steam (all on a BL HHV basis)
- Estimated bioenergy prices for hydrocracking product and consumables are; 70 €/MWh for BL oil, 40 €/MWh for BL gas, 12 €/MWh for LP steam and 60 €/MWh for electrical power consumption for the hydrocracking plant.

The calculated cost of pulp wood is in total 210 €/ADt. The value of pulp produced is 430 €/ADt which corresponds to 100 €/MWh. The total energy value of black liquor is calculated to 85€/ADt which normally is consumed for operation of the pulp mill.

Based on a hydrocracking plant balance the total value of produced BL oil, BL gas and LP steam minus consumed power has been calculated to 240 €/ADt. Reduced by the total energy value of black liquor of 85 €/MWh the resulting potential gross profit would be 155 €/MWh (by export of black liquor bio-oil) which is in the same magnitude as the pulp contribution if the pulp price (430 €/ADt) is reduced with costs for wood (210 €/ADt) and perhaps also bleaching chemicals.

The impact on the pulp mill energy balance of a black liquor oil export corresponding to the energy value surplus of 155 €/ADt from the hydrocracking plant will leave a surplus of 9,0 GJ/ADt of high pressure biogas and recovered LP steam which is well suited for lime kiln firing, combined cycle power generation and process heat. To reach an energy self sufficient pulp mill, only including normal bark firing, process energy savings going beyond present reference mill studies would be required. One such step could be to develop and implement new evaporation technology with 10+ effects as proposed in other studies (Olausson, 2008).

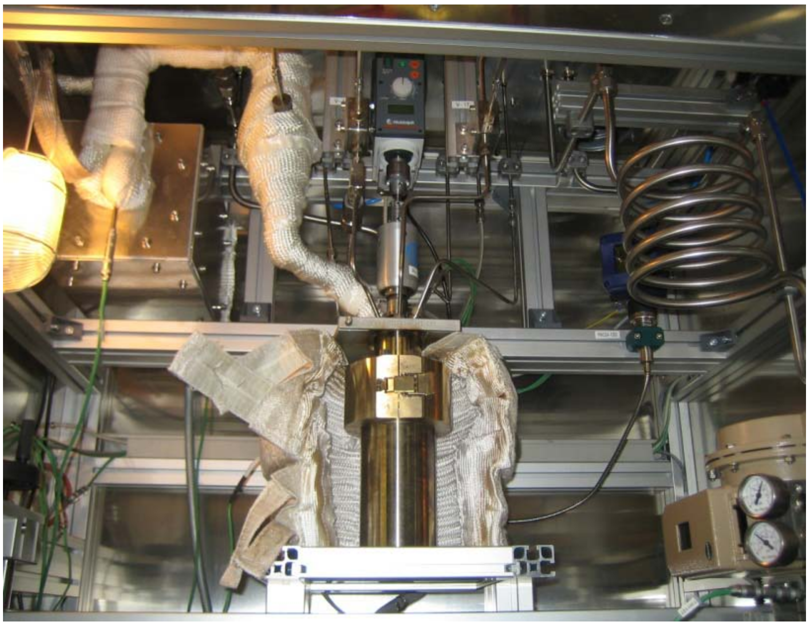
On a less ambitious level the separated lignin from a LignoBoost process or a part flow of black liquor could be treated. Both of these routes would involve less risk and could preferable be associated with a pulp production increase which would give an extended utilization of existing equipment (e.g. recovery boiler).

The valorization potential indicated in the above figure would then be reduced in proportion to the chosen hydrocracking capacity. LignoBoost lignin is in comparison to black liquor a very homogenous product with practically no salt content. Lowest risk is therefore expected with the present research focus on lignin hydrocracking.

Chalmers high pressure reactor plant

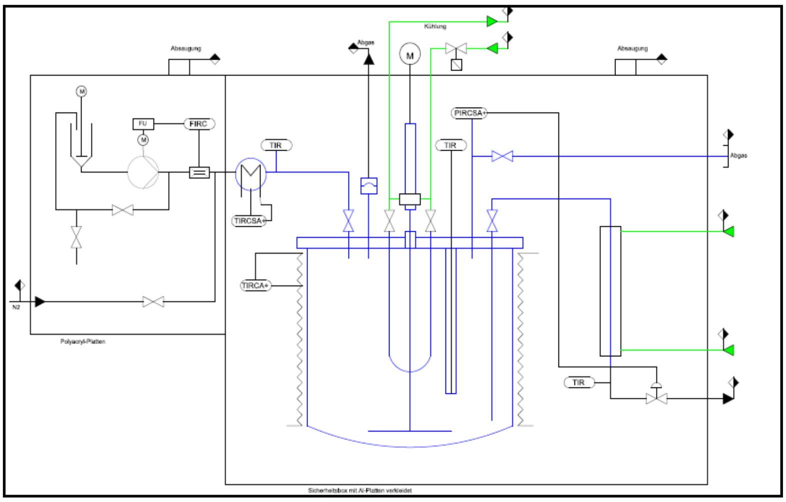
An initial evaluation of the hydrocracking technology shows very high conversion efficiency in combination with a very high valorisation potential. The hydrocracking technology is, however, not yet ready for commercialization and further research is necessary. To initiate such research a cooperation 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 was 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 chemicals. The high pressure reactor plant (345 bar, 500 ^{o}C and 3 l/h capacity) was started up in 2010.



The high pressure reactor plant

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.



Flow sheet of the high pressure reactor plant

Plant development activities

Funding for further development of the plant is available through Metso, Chalmers and ÅForsk. The Licentiate research project that was approved within the LignoFuel project has, however, not yet been released because of conditions related to the start of the Mörrum LignoBoost project.

After installation and connection to Chalmers service and ventilation systems the plant was started up and tuned and preparation and feeding of the lignin slurry 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 the proposed metal oxide. A number of experiments with cracking of lignin slurry (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^{o}C have been carried out. Most important findings from this first test period are:

- High pressure feeding of lignin slurry up to 35%DS possible after rebuild of original feed pump valves.
- It is possible to run the reactor with lignin slurry but normal operation time is only 50 minutes which is considered to short time for steady-state operation and good performance.
- Process operation of feeding and reactor system has worked well but the discharge system has, in spite of valve rebuild, been sensitive even for low particle concentrations in the product flow.
- Only partial decomposition of the lignin has been achieved so far.
- The product from the reactor shows a heavy emission of reduced sulphur components.

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 the fall 2011. 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 and control system, a second discharge valve and high pressure flushing system.

The reactor system has been tuned and is now ready for further research from January 2012 within the LignoBoost Licentiate project and other possible projects under discussion.

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