

Liquid fuels from lignin by hydrothermal liquefaction and deoxygenation (LIGNOHTL)

FINAL REPORT

Title of the research project	Liquid fuels from lignin by hydrothermal liquefaction and deoxygenation
Coordinator of the project	Yrjö Solantausta

BASIC PROJECT DATA

Project period	[1.3.2014-30.06.2017]
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URL of the project	https://www.thuenen.de/en/hf/projects/lignohtl-transportation-fuels-from-woody-residues

FUNDING

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<u>Finland</u> Tekes – the Finnish Funding Agency for Innovation Academy of Finland (AKA)	236 663 EUR
<u>France</u> Ministry of Agriculture, Fisheries and Forestry Resources (MAAF)	92 000 EUR
<u>Germany</u> Agency for Renewable Resources (FNR)	423 174,00 EUR

PROJECT TEAM (main participants)

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DEGREES (if relevant)

Degrees earned or to be earned within this project.

2017	M.Sc.	Male	Alexi Välimäki, 1985 M.Sc. 2017 ,	Aalto University, M.sc. Thesis, supervisor's organization VTT
2018	D.Sc.	Female	Christin Anacker, 1985 D.Sc. 2018	University Rostock, D.Sc.Thesis, supervisor's organization LIKAT
2018	D.Sc.	Male	Jan Ole Strüven	University Hamburg, D.Sc.Thesis,

PROJECT SUMMARY REPORT

The concept developed in this proposal aims at reducing CO₂ emissions of the transportation fuel chain and offering alternative products for European forest-based sector by the production of second generation biofuels from various lignin sources. The concept is based on the combination of hydrothermal liquefaction (HTL) and hydrodeoxygenation (HDO) and co-processing the products therefrom with crude oil distillates in conventional refineries. The study also covered tests on co-upgrading of pulping black-liquor with e.g. biorefinery lignin residues from bioethanol plants.

In the first step the best HTL crude quality was obtained at 360 °C with 34 wt-% dry matter content of black liquor, 12 wt-% NaOH and 59 wt-% of glycerol related to black liquor dry matter amount. After washing the HTL product had low oxygen content (12-15 wt-%) and high heating value on received basis of approximately 30 MJ/kg. Of the feedstock (black liquor, glycerol, NaOH and lignin) energy content more than 50 % of the energy and approximately 25 w-t% of the organics remained in the washed HTL product. Addition of 25 wt-% of soda wheat straw lignin of black liquor dry matter amount to the feed gave similar organic and mass yields than without lignin addition.

Studies with upgraded black liquor showed that the catalyst performance in HDO strongly depends on the nature respective pre-treatment of the black liquor from partner VTT, particularly on sodium removal efficiency. Best HDO results were obtained after iterative adaptation of the HTL step to the needs of the catalyst system with yields > 70% and a degree of deoxygenation ≥ 74 % (“blank test” without catalyst = 9%). Various test series demonstrate a significant impact of temperature and pH-value on the conversion of the reactants. Optimal reaction conditions for HTL were 367 °C and a pH-value of 3 to 4.

Co-processing of upgraded black liquor with mineral vacuum gas oil in a lab-scale fluid catalytic cracking (FCC) unit showed very promising results in terms of yields and product distribution. By this process, renewable gasoline can be incorporated into a conventional refinery product slate.

The process concept seems to be promising from techno-economic point of view and further possibilities for improvement exist especially in the HTL product washing to increase the yield. The most significant factors affecting the techno-economic feasibility were the yield of the HTL product and the price of the olefins produced.

1.1 Introduction

1.1.1 Background

The concept developed in this proposal aims at reducing CO₂ emissions of the transportation fuel chain and offering alternative products for European forest-based sector by the production of second-generation biofuels from various lignin sources. A complementary route to low cost biofuels is identified based on data generated with various lignin sources, preferably black liquor, in this project. The concept is based on the combination of hydrothermal upgrading and hydrodeoxygenation and co-processing the products therefrom with crude oil distillates in conventional refineries. The study also covered tests on co-upgrading of pulping black-liquor with e.g. biorefinery lignin residues from bioethanol plants.

1.1.2 Objectives

In this project, the objectives were first to demonstrate in laboratory scale the production of high-quality transportation fuels, produced by co-processing (catalytic cracking units) of a selected number of upgraded industrial lignin derived feeds from existing pulp mills.

Second objective was to generate mass and energy balance data for the evaluation of the proposed biofuel and -chemical processing chains, and to compare them with other routes using techno-economic assessments. Therefore, yield of organics in each processing stage had to be determined and stable and versatile catalysts had to be found for selected steps. Another objective was to investigate removal of inorganic compounds like alkali metals, which could potentially act as catalyst poisons in the later parts of the process chain.

1.2 Results and discussion

The proposed production chain was demonstrated in laboratory scale and yields for each step (including organics, mass and energy balances) were determined.

WP-1 & WP-4

Different lignin sources were evaluated according to literature. Considering the price of approximately 50 euros /t of black liquor solids (assuming an energy value of 14 €/MWh) and availability, Kraft Black Liquor is the most attractive lignin source. Assuming that 50% of the black liquor could be utilised for transportation fuel production in EU countries, approximately 33 million ton would be available, based on 36.5 Million ton of pulp production in Europe in 2015. Considering the calculated efficiency of the production chain, roughly 7 million tons of transportation fuel could be produced.

Several tests for the hydrothermal liquefaction step were conducted in a 1 l- autoclave and HTL crude product for further tests was produced in a 10 l-autoclave. After varying the reaction temperature, type and amount of alkaline catalyst, dry matter content of black liquor and amount

and type of hydrogen donor, the optimal process variables were identified. In the experiments the best HTL crude quality was obtained at 360 °C with 34 wt-% dry matter content of black liquor, 12 wt-% NaOH and 59 wt-% of glycerol related to black liquor dry matter amount. After washing the HTL product had low oxygen content (12-15 wt-%) and high heating value on received basis of approximately 30 MJ/kg. Of the feedstock (black liquor, glycerol and lignin) energy content more than 50% of the energy and approximately 25 wt-% of the organics remained in the washed HTL crude. Addition of 25 wt-% of soda wheat straw lignin to Kraft black liquor gave similar organic and mass yields compared to only black liquor. In Figure 1 the energy flows are illustrated for a case where 25% of lignin are added to black liquor and the energy flows based on higher heating value are calculated based on experimental results.

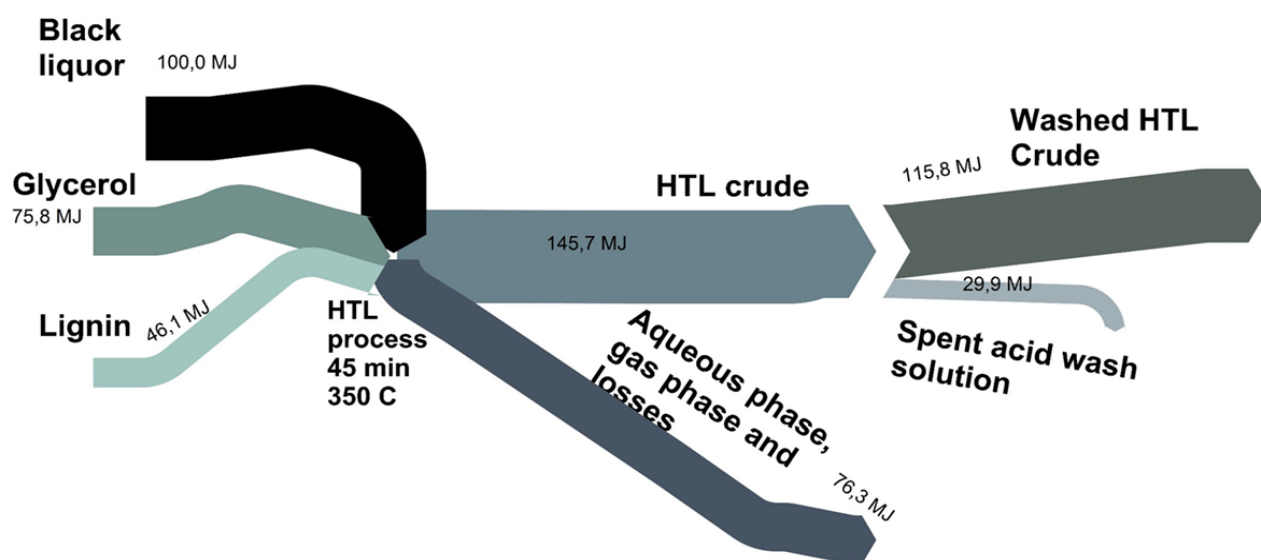


Fig. 1. The energy balances illustrated as a Sankey diagram with 25 wt-% lignin addition to Kraft black liquor.

Low alkali metal content was required for further catalytic processing of the oil in the HDO step. In a single washing step at pH 2.5 with 0.5 M sulphuric acid approximately 1 wt-% alkali metal content was achieved and in two-stage step even HTL crude with <50 ppm alkali metal content was obtained.

The techno-economic analysis of the process revealed that naphtha and olefins could be produced with similar production cost (around 1000 euros per ton per main product) as by routes based on gasification of biomass and synthesis gas thermochemical conversion into fuel by, for example Fischer-Tropsch and Methanol to Gasoline synthesis. Due to the early stage in the development, it is difficult to estimate the techno-economic feasibility accurately at this stage. Nevertheless, the process concept seems to be promising from techno-economic point of view and further possibilities for improvement exist especially in the HTL product washing to increase the yield. The most significant factors affecting the techno-economic feasibility were the yield of the HTL product and the price of the olefins produced. On the other hand, the hydrogen consumption in the hydrotreatment step had only a small effect on the techno-economic performance due to the relatively small amount of hydrogen needed.

The most critical issues for integration of the HTL step into an existing pulp industry were determined. The sodium could be recycled efficiently. However, the washing step with sulfur introduces additional sulfur into the process, which is typically unwanted in Kraft pulp mills, since excess sulfur must be purged from the process and increases the sodium loss. The required sulfuric acid addition calculated was 100-200 kg/ton HTL product, which was less than for the Lignoboost process where typically more than 200 kg sulfuric acid per ton of lignin is used.

WP2:

At LIKAT, a series of redox active catalysts based on nickel supported on materials like ZSM-5, MCM-41, silica and zirconia was prepared. The catalysts were first tested in the HDO of phenol as model reaction in batch experiments. The bimetallic catalyst 10Ni10Co/H-ZSM-5 (synthesized by wetness impregnation method) proved to be very effective for phenol HDO with full conversion and 75% degree of deoxygenation (DOD). Tests on stability and reusability were made to identify the limiting parameters for catalyst lifetime. After stressing the catalyst 10Ni10Co/H-ZSM-5 for 3 days in water with 50 bar N₂ at 250 °C, it still performed in HDO (5 wt% phenol in water, 250 °C, 50 bar H₂, 1 h) like the fresh one (100% conversion and 75% DOD). Analyses of the stressed catalyst reveal low leaching of the metals Ni, Co and Al. Loss of silicon is merely detectable and associated to a decreasing BET surface area at the cost of micropore area. XRD studies confirm the structural transformation of the catalyst. Reusability tests in batch mode on phenol HDO also proved good catalyst stability (conversion ≥ 80% and DOD ≥ 50%) over 3 cycles.

Properties of the catalyst 10Ni10Co/H-ZSM-5

Si:Al-ratio (mol:mol)	12
Nickel and cobalt content (ICP)	9.3 wt% each
Surface area (BET)	275 m ² /g
Microporous area (BET)	224 m ² /g
H ₂ - consumption (TPR)	3.8 mmol/g
Acidity (NH ₃ -TPD)	0.8 mmol/g

In the next stage, more complex model compounds like guaiacol and 2-[2-methoxyphenoxy]-1-phenylethanone were tested in batch HDO with 10Ni10Co/H-ZSM-5. The results revealed that the catalyst is capable to transform other substituents in the feed (nearly complete conversion and DOD ≥ 74%) and thus seems to have a broad application range. In addition, experiments with possibly inhibiting additives (phenol + dimethyl disulfide or sodium-phenolate) were made. The presence of sulfur seems to reduce activity of metallic redox sites (low conversion), and the presence of sodium lowers the catalyst acidity which is needed for deoxygenation.

To move beyond model compounds, tests on HDO of lignin-containing feedstocks with 10Ni10Co/H-ZSM-5 were conducted at optimized reaction conditions (1-5 wt% feed in water, catalyst: feed = 1: 3-1: 20, 250 °C, 50 bar H₂, 2 h) with a refined work-up procedure (using

extraction steps and calculation of DOD based on elemental analysis). Tests with pyrolysis oil and different types of lignin revealed a DOD of 18-32% (blank test = 3-10%) and confirmed the ability of the catalyst to break down large macromolecules independently of the high microporous catalyst volume.

On the other side, the studies with upgraded black liquor showed that the catalyst performance in HDO strongly depends on the nature respective pre-treatment of the black liquor from partner VTT, particularly on sodium removal efficiency. Best HDO results were obtained after iterative adaptation of the HTL step to the needs of the catalyst system with yields > 70% and a DOD ≥ 74 % (blank test = 9%). Considering all these limiting factors and taking appropriate measures, it is indeed possible to deoxygenate lignin-based material with the help of the catalyst 10Ni10Co/H-ZSM-5.

Studies on larger scale at TI Hamburg revealed that bimetallic NiCo-catalysts on HZSM-5 support were indeed effective catalysts for the hydrodeoxygenation (HDO) of HTL-products from working package 1 (WP1). Various test series demonstrate a significant impact of temperature and pH-value on the conversion of the reactants. Optimal reaction conditions for HDO were 367 °C and a pH-value of 3 to 4 (Catalyst/Biocrude 1:10 by weight, 100 bar H₂ (initial), reaction time: 6 h, stirring velocity: 500 rpm).. The pH-value depends on the pretreatment of the HTL crude product. The HTL crude product was washed with water to remove the acid and increase the pH-value to an optimal range. The composition of monomeric HDO products varies depends on the reaction temperature. Especially at a temperature range from 350 to 400 °C the yields of benzenes increase proportionally to the yields of oxygenates comparable to runs at lower temperatures.. Due to the higher amount of monomers, oligomeric structures remain in solution and a lower viscosity effects a easier pumping of the HDO-product for further process steps. Under these optimized conditions a substantial improvement of elemental composition could be achieved. The amount of carbon and hydrogen were increased with a reduction of oxygen. This results in a DOD of 29% and a degree of hydrogenation of 39%. The results show that a compromise has to be found between a maximum in liquid product yield and its composition, especially the yield of monomers.

As an alternative conversion process, the continuous deoxygenation of black liquor and HTL crude products in subcritical water at a zirconia catalyst was examined. The deoxygenation is caused by an in situ hydrogen production due to water-gas shift reaction (WGS) available for HDO and cleavage of CO and CO₂. It was determined that low molecular weight products like catechol, phenols and nonaromatic oxygenates could be formed during this process. Additional a DOD of 9.7% was reached. During the project several HDO products of various test series were provided for co-processing runs by fluid catalytic cracking with vacuum gas oil (VGO).

WP-3

FCC co-processing consisted of mixing 10-30% upgraded black liquor with 90-70% mineral VGO and treating this mixture in a fluid catalytic cracking (FCC) unit.

Co-processing experiments were carried out with three different upgraded black liquor samples:

Sample 1 : a model feed consisting of a mixture of phenol and Kraft-lignin in a 1:1 ratio, which was hydrotreated at 350 °C for 2.5 h and 100 bar initial hydrogen pressure (cold). The catalyst (11 wt.%) was ZSM-5 with 10 wt.% Ni-loading.

Sample 2 : was from a real black liquor biocrude produced at VTT and then hydrotreated at Thünen Institute. The HDO was carried out at 250 °C in water using 10 wt.% catalyst 10Ni10Co/H-ZSM-5 from LIKAT. This sample was too viscous to be treated in the MAT reactor. Therefore it has been diluted with propanol in a 1:1 ratio. The added propanol will have an impact on the product distribution, especially the light gases.

Sample 3 : To reduce the viscosity of the sample, the black liquor biocrude was acid and water washed before hydrotreating. The HDO was carried out at 367 °C without the addition of solvents using 10 wt.% catalyst 10Ni10Co/H-ZSM-5 from LIKAT.

For the co-processing experiments we have used a typical vacuum gas oil (VGO) with a density of 895.3 kg/m³. An industrial equilibrated FCC catalyst was used. It contains 15 wt% Y-zeolite, 2.5 wt% rare earth oxides, 240 ppm of Ni and 870 ppm of V.

MAT Setup

A standard micro activity test unit (MAT) and protocol were applied to simulate the co-processing of pyrolysis liquid in an FCC unit. The MAT unit has been designed to perform up to four independent and consecutive fixed bed cracking tests following the specifications described by the standard method ASTM D3907-03. The experiments were carried out at 560 °C.

The product distribution is given in terms of groups determined by their boiling point range: dry gas, liquefied petroleum gas, gasoline or naphtha, light cycle oil, bottom fraction and coke. The conversion is defined as the sum of the yields in dry gas, LPG, gasoline and coke.

Results

The following 6 co-processing experiments with upgraded black liquor were carried out, where each experiments consist of 7 runs at different Cat/Oil ratios:

1. Processing of pure VGO, which serves as the reference case.
2. Co-processing of 10 wt.% sample 1 + 90 wt.% VGO
3. Co-processing of 18 wt.% sample 2 + 72 wt.% VGO
4. Co-processing of 10 wt.% propanol + 90 wt.% VGO
5. Co-processing of 10 wt.% sample 3 + 90 wt.% VGO
6. Co-processing of 30 wt.% sample 3 + 70 wt.% VGO

The co-processing of sample 3 resulted in slightly lower conversions than pure VGO cracking, while the other co-processing samples give similar to slightly higher conversions. Figure 2 shows the naphtha yield as a function of the conversion. Naphtha is the principal product in FCC. Although the data are scattered, all co-processing feeds show similar naphtha yields as pure VGO cracking. In general, the results are very positive with only small changes in the product distribution. Rather than comparing co-processing of black-liquor to pure VGO cracking, a better comparison is with respect to another bio-liquid such as pyrolysis oil. Figure 1 also shows co-processing of upgraded pyrolysis oil over the same FCC catalysts. Similar trends are observed for both co-processing bio-feeds. This is an important result, as co-processing of pyrolysis oil has been successfully demonstrated at pilot plant level.

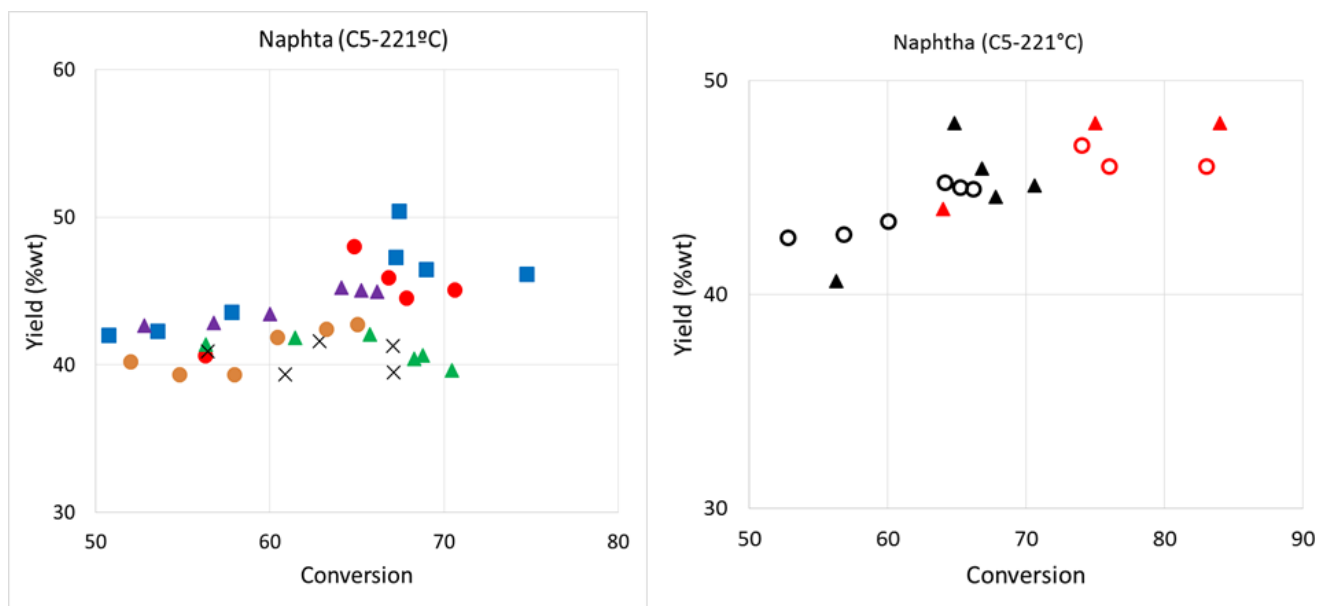


Fig. 2. Left: Naphtha yield for the 6 (co)-processing experiments in a MAT reactor (Symbols red (1), blue (2), green (3), black (4), purple (5) yellow (6)). Right: black: VGO/black liquor, red: VGO/pyrolysis oil.

Co-processing of upgraded black liquor with mineral VGO in a lab-scale FCC unit showed very promising results, in terms of yields and product distribution. By this process, renewable gasoline can be incorporated into a conventional refinery product slate.

1.3 Conclusions

Potential lignin sources were reviewed and experimental work was done for the chosen lignin sources based on price and availability. The whole production chain from black liquor to transportation fuels was demonstrated in laboratory scale and yields of optimal process conditions and yields of organics were determined for each process step. The critical parameters for the following process such as alkali level content, viscosity etc. steps could be determined.

1.4a Capabilities generated by the project

New process concepts were developed, for example, new methods to reduce the alkali metal content of HTL crude produce and increase its yield. These include for example use of different acids in acid washing, salt separation near the critical point and use of membranes.

The capability to demonstrate and optimise such process chains from pulp mill side products, into fuel processing at the oil refinery was significantly increased.

1.4b Utilisation of results

The plan is to apply for a continuation of the project to develop and optimise further the proven process-chain and demonstrate it in continuous operation mode, which lower the barrier for companies commercialize and demonstrate the technology.

In the nearest future the plan is to produce at least two scientific publications, one on the whole process chain, another on the HTL step results and to present the results in one of the most renowned conferences in the field (tcbiomass2017 in Chicago). The result particularly for the HTL step will also be communicated to some companies in the field in face-to-face meetings.

1.5 Publications and communication

a) Scientific publications

1. Articles in international scientific journals with peer review

2. Articles in international scientific compilation works and international scientific conference proceedings with peer review

Melin K., Välimäki A. Oasmaa A., Lehtonen J., *Proceedings of 7 th Nordic Wood Biorefinery Conference*, Biofuel Production from Black Liquor by Hydrothermal Liquefaction, 28-30th March, Stockholm, Sweden

Melin K., Oasmaa A., Strueven J., Eidam P., Appelt J., Anacker C., Armbruster U., Martin A., Chapelliere Y., Mirodatos C., Schuurman Y., *From black liquor to 2G-transportation fuels*, Accepted for presentation at TCBIOMASS 2017 September 19-21,, Chicago, Usa

3. Articles in national scientific journals with peer review

4. Articles in national scientific compilation works and national scientific conference proceedings with peer review

U. Armbruster, T.M. Huynh, A. Martin
Upgrading of Pyrolysis Oil over Supported Ni/Co Catalysts and Subsequent co-Processing with Atmospheric Residue at FCC Conditions
DGMK-Tagungsbericht 2016-2, Konversion von Biomassen und Kohlen

5. Scientific monographs

Välimäki A. Master Thesis, *Mustalipeän hydrotermisen nesteytyksen vaikutus bioöljyn laatuun (Improving bio-oil quality in hydrothermal liquefaction of black liquor)*, Espoo, 2017, Aalto University

6. Other scientific publications, such as articles in scientific non-refereed journals and publications in university and institute series

IEA Newsletter Task 34, Direct Thermochemical Liquefaction
<http://task34.ieabioenergy.com/wp-content/uploads/2017/04/PyNe-Issue-40-March-2017.pdf>

a) Other dissemination

Presentation of the LignoHTL project at invited lectures:

Scientific colloquium at Karlsruhe Institute of Technology (KIT), 30.01.2017, Karlsruhe (Dr. J. Appelt)

Scientific colloquium at 86th session of German Society for Petroleum and Coal Science and Technology (DGMK), 31.03.2017; Dortmund (Dr. J. Appelt)

U. Ambruster, Upgrading of Pyrolysis Oil over Supported Ni/Co Catalysts and Subsequent co-Processing with Atmospheric Residue at FCC Conditions, lecture; DGMK-Fachbereichstagung „Konversion von Biomassen und Kohlen“, 10.05.2016, Rotenburg a.d. Fulda

C. Anacker, U. Armbruster, A. Martin

Hydrodeoxygenation of pre-treated black liquor on a bimetallic catalyst: evaluation of catalyst performance

Lecture; EUBCE 2017, 12.06.2017, Stockholm

C. Anacker, U. Armbruster, A. Martin, Hydrodeoxygenation of pre-treated black liquor on a bimetallic NiCo/HZSM-5 catalyst, Poster; 50. Jahrestreffen deutscher Katalytiker, 15.-17.03.2016, Weimar

1.6 National and international cooperation

Stora Enso has supplied raw material (the black liquor from their industrial pulping mills). Timo Pekka Veijonen has been interested in the results of the project and Alexi's Master Thesis. The Poster in Nordic Wood Biorefinery Conference attracted interested among industrial companies in the Field. Especially Renfuels in Sweden converting Kraft lignin into fuel in Preem's refineries was highly interested. In addition, the Swedish company Suncarbon was interested in the technology and the Finnish Pöyry consulting company.