

# CATALYTIC HYDROPROCESSING OF LIGNIN IN SUPERCRITICAL ETHANOL

Andreas Martin\*, Pratap T. Patil<sup>§</sup>, Udo Armbruster

Leibniz-Institute for Catalysis  
Albert-Einstein-Str. 29a, D-18059 Rostock, Germany

<sup>§</sup> Institute of Chemical and Engineering Sciences (ICES-A\*Star), Singapore

Email: andreas.martin@catalysis.de

**Abstract.** The use of biomass for the production of alternatives for fossil fuel and chemicals has attracted immense attention in recent years. Lignin is such a raw material; it consists of various oxygenated polyaromatics and reveals no defined primary structure. It could be a renewable basis for fuels, macromolecules, aromatics and phenolic monomers. The main objective of this work was to develop an efficient process using hot compressed water or supercritical ethanol to convert lignin into fuel components or chemicals by using catalysts and hydrogen. The hydroprocessing tests were carried out in an autoclave in presence of supported Pt, Pd, Ru and Ni catalysts. The effect of catalysts and reaction parameters such as nature of supports, temperature, hydrogen pressure, and reaction time on lignin conversion and product distribution is discussed and presented in detail.

Initial lignin hydroprocessing in aqueous medium required high temperature (300 °C) and pressure (120 bar) and resulted in low lignin conversion (<20%); mainly phenols and aromatics were seen. In contrast, lignin was efficiently converted (80-90%) in ethanol medium (90%) at 260 °C and 80 bar resulting in a liquid bio-oil, mainly containing phenol derivatives, some larger lignin fragments and some n-alkanes stemming from fatty acid ethyl esters being present in the parent Organosolv® lignin.

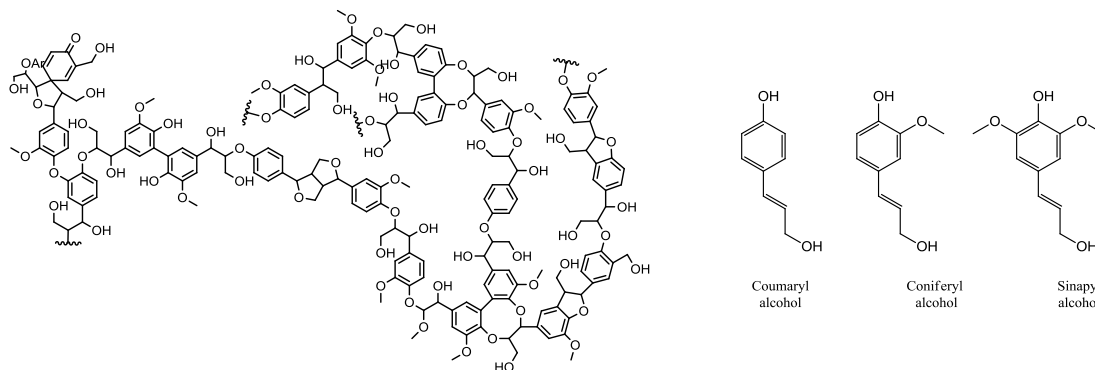
**Keywords :** Bio-oil, Lignin, Hydrodeoxygenation, Catalysts, sc-Ethanol, Hot compressed water

## 1. Introduction

The use of biomass as a renewable feedstock for the production of energy, alternatives for fossil fuel and a wide variety of chemicals and polymers has attracted immense attention in recent years due to the steadily increasing market price and foreseeable shortage of oil & gas. It is absolutely true that “biomass is the only practical source of renewable liquid fuel” [1] but it is also very clear that biomass can't cover the demand, whether today nor in the future. Therefore, our future energy, fuel and chemicals pool will be much more diverse than today.

The complex nature of lignocellulosic biomass (40-50% cellulose, 20-35% hemicellulose and 20-40% lignin) and its stability make its conversion towards specific product classes quite difficult because it necessitates more drastic conditions such as high temperature and pressure. Therefore, several attempts were made to separate first these three main components and treat them apart in specific downstream operations [2]. These separations can be carried out using solvents like ethanol (resulting in Organosolv® lignin [3]), enzymes (sunliquid® process, directly leading to bioethanol from straw [4]) or hot compressed water (Aquasolv® lignin from a hydrothermolytic process [5]).

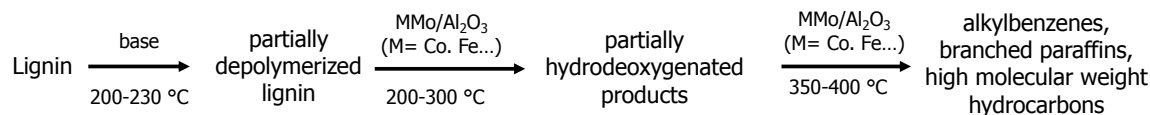
Lignin is a very complex chemical compound most commonly derived from wood. Besides carbon and hydrogen it mainly contains up to 30-40 wt% of oxygen. It is an integral part of the cell walls of various plants and algae, for example. As a natural polymer, lignin is exceptional because of its heterogeneity and lack of a defined monomer structure (Figure 1). The three-dimensional polymeric lignin is structurally composed of a mixture of oxygenated polyaromatics with repeatedly, but randomly cross-linked phenol units which may contain one or two ortho-methoxy groups (Figure 1) [3, 6].



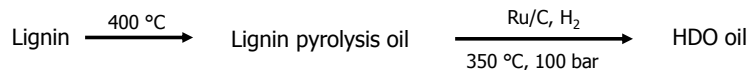
**Figure 1.** Schematic presentation of lignin structure and the main structural units such as coumaryl, coniferyl and sinapyl alcohols [6].

The global production of lignin is around 70 million tons per year mainly originated from pulp industry (“black liquor”) but it is almost exclusively used calorically. The lignin part constitutes up to 40% of the heating value of lignocellulosic biomass [7]. Less than 2%, i.e. ca. 1.1 million metric tons per year of isolated lignin, is at the market mainly stemming from acid sulfite pulping process. This lignin is used in a wide range of low volume niche applications where the form but not the quality is important [8]. It can be also considered as future source for a wide variety of phenols and related compounds [9]. Very recently, a nice review summarized the knowledge on base catalyzed degradation of lignin for manufacture of oxy-aromatic monomers, dimers and oligomers [3]. Several methods are known for the hydroprocessing of lignin into liquid oil [e.g. 10].

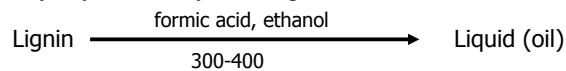
a) Three-step conversion of lignin [11]



b) Pyrolysis/hydrotreatment of lignin [12]



c) Pyrolysis/solvolytic of lignin [13]



Recently, we have reported on first trials of liquefaction of lignin in sub-critical and supercritical conditions of water and ethanol, respectively [14]. In continuation of this work, we are engaged in further tests using autoclaves but we processed first runs of hydrothermal liquefaction of biomass into liquid fuels in a semi-continuous apparatus. Besides lignin, also wheat straw was included as feed in the experiments. Heterogeneous catalysts and hydrogen were used for promoting the depolymerization reaction as well as for hydrotreatment to reduce oxygen content and increase heating value of the resulting bio-oils.

## 2. Experimental

In a typical experiment, commercially available Organosolv® lignin (Aldrich) was converted in an autoclave (25 mL capacity, Parr Instrument Company) in the presence of hydrogen along with a catalyst and a solvent (ethanol, water) at 260 °C for 8 h, in general. The applied Organosolv® lignin always contains significant portions of fatty acid ethyl esters (FAEE) as identified in several feed analyses. Therefore, the liquefaction product always shows FAEE and higher, long-chain alkanes (LCA) as a result of hydrodeoxygenation (HDO). A series of supported Pt, Pd, Ru and Ni catalysts (5 wt% of metal) was synthesized; Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and H-Beta were used as supports. The liquid product analysis was carried out by GC, GC-MS, ESI-MS, NMR & TOC (total organic carbon) analysis; gaseous products were analyzed by on line-GC equipped with FID & TCD. Silylation of raw product for GC-MS analysis was carried out using hexamethyldisilazane (HMDS) and trimethylchlorosilane (TMCS) at 70 °C for 2 h. Residual unconverted solid was always studied by CHN analysis. The conversion of lignin was calculated as given below.

$$X_{\text{lignin}} (\%) = \frac{\text{weight of starting material lignin} - (\text{weight of residue} - \text{weight of catalyst})}{\text{weight of starting material lignin}} * 100$$

In addition, wheat straw was chosen as model biomass for liquefaction coupled upgrading experiments. The liquefaction experiments were carried out semi-continuously in a tubular reactor (Figure 2), i.e. biomass was placed in a tubular reactor between two stainless-steel frits. In some experiments, a catalyst (5 wt% Ru/H-Beta) was placed just below the wheat straw assuming the liquefied bio-oil comes in contact with the catalyst and facilitating the oxygen removal. The feed solution composed of water or ethanol or water-ethanol mixture was passed over the biomass using a high pressure pump at temperatures up to 300 °C and pressures up to 200 bar. The liquid products were collected at the outlet and the gaseous products were analyzed online by GC as described above. The solid and liquid products were separated by filtration prior to analysis. The liquid products were extracted using dichloromethane and two different types of oils, one with high heating value (high-caloric oil - HCO, dichloromethane soluble) and the other with low heating value (low-caloric oil - LCO, water soluble), were obtained after evaporation of the solvent. The HCO and LCO yields were calculated on weight basis based on wheat straw placed in reactor.

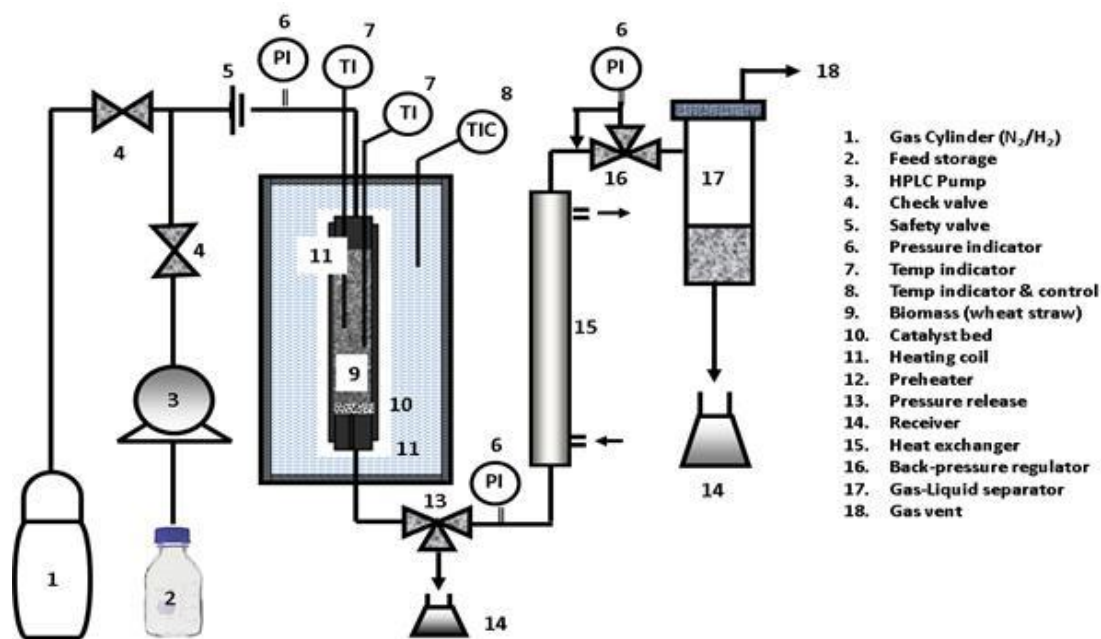


Figure 2. Scheme of experimental set-up for treatment of biomass with hot compressed water.

As an additional characteristic number, the “Higher Heating Value” (HHV) of the bio-oils was calculated by using Dulong’s formula [15].

$$\text{HHV (MJ/kg)} = \left[ 338.2 \times \% \text{ C} + 1442.8 \times \left( \% \text{ H} - \frac{\% \text{ O}}{8} \right) \right] \times 0.001$$

### 3. Results and Discussion

#### 3.1 Lignin hydroprocessing in hot compressed water (HCW)

The used Organosolv® lignin exhibits the following composition as found out by elemental analysis: C = 65.2 wt%, H = 5.9 wt% and O = 28.9 wt% (as calculated by difference). Thus, the parent lignin shows an O: C ratio = 0.33 and an H: C ratio = 1.08; the HHV amounts to 25.31 MJ/kg. First blank tests at temperatures >300 °C showed mainly char formation. This is maybe due to cracking of lignin into smaller fragments becoming water soluble, but these fragments may re-polymerize and form solid polymeric char-like structures. Therefore, the use of catalysts was checked, probably accelerating a deeper hydroprocessing at lower reaction temperatures.

Lignin was processed in HCW using a 5 wt% Ru/H-Beta catalyst at 200, 250 and 300 °C at an initial hydrogen pressure of 35 bar (the final pressures at reaction temperature reached 40, 70 and 100 bar, respectively) and 50 bar (final pressure of 120 bar at 300 °C). Surprisingly, only low lignin conversions were observed (X = 10-20%). Water soluble lignin fragments probably blocked the catalyst pores and/or active sites. Additional tests in the absence of a catalyst were carried out in presence of NaOH (0.5 and 1 M), now showing high conversions of lignin up to values above 90% [14] as revealed by TOC analysis. But neither GC nor GC-MS analysis showed formation of any monomer product. In addition, a similar test but in the presence of 5 wt% Ru/H-Beta catalyst failed, as lignin conversion only reached 33%. It looks that H-Beta pores were blocked and simultaneously Na<sup>+</sup> ions interacted with the Brønsted sites of the zeolitic support changing the acidic properties of the catalyst and the reaction system pH value.

#### 3.2 Lignin hydroprocessing in supercritical ethanol (sc-EtOH)

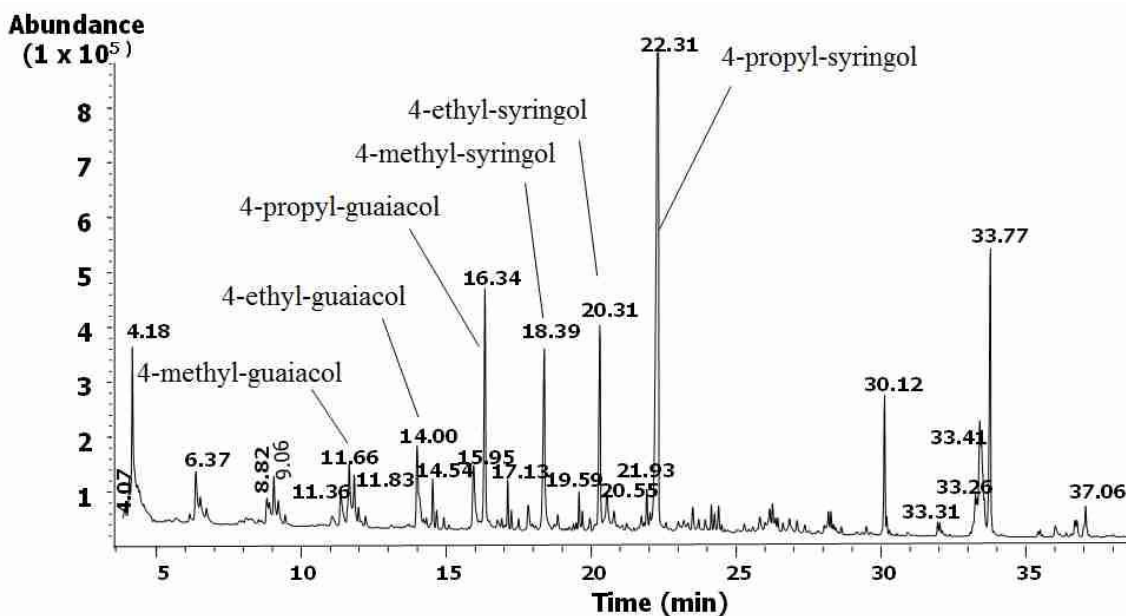
A blank test of lignin conversion in sc-EtOH but in the absence of any catalyst at 260 °C with an initial hydrogen pressure of 20 bar for 8 h lead to a decrease in O: C ratio of ca. 10% and an increase in H: C ratio (1.17) and HHV (27.57 MJ/kg). The reaction was carried out using 0.5 g lignin and 7 mL ethanol; the final pressure reached 85 bar.

Further tests were carried out in the presence of various catalysts. Among the catalysts studied, Ru loaded on alumina support was better in terms of lignin conversion as well as bio-oil yield than other formulations. The increased HHV of the obtained bio-oils compared to non-catalytic test and pure lignin conversion proves a clear catalytic effect on lignin hydroprocessing. Table 1 shows some results with respect to a variation of reaction temperature, pressure and time. It is quite clear that with increasing reaction temperature lignin conversion and bio-oil yield increased. In addition, it can be nicely seen that deoxygenation run more efficiently, and thus a decrease in O: C ratio of ca. 50% and an increase in H: C ratio (1.24) and HHV (33.68 MJ/kg) was observed at 300 °C. The increase in initial hydrogen pressure didn’t show such influence, only at higher pressures additional hydrogenations seemed to run as seen in high bio-oil yield and increased H: C ratio. Additionally, looking to the results at 40 bar, it seemed that increased reaction pressure prevented an effective deoxygenation as revealed by an increased O: C ratio again. However, changes in phase behavior could also play a role due to variation of initial hydrogen pressure and/or hydrogen consumption influencing the rate. In contrast, prolongation of the reaction time at medium reaction pressure was beneficial showing nearly complete conversion and bio-oil yields above 90%, very low O: C ratio (<40% compared to the parent value) and a very high HHV value of ca. 36 MJ/kg, being close to that of diesel fuel (ca. 44 MJ/kg). Some tests carried out with increased catalyst amounts didn’t show significant improvement with respect to deoxygenation efficiency and HHV value.

**Table 1.** Effect of reaction parameters variation on lignin hydroprocessing in sc-EtOH using Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (0.5 g lignin, 0.1 g catalyst (5 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), 7 ml ethanol, <sup>a</sup>lignin conversion calculated based on unconverted lignin after reaction, <sup>b</sup>bio-oil yield measured after careful ethanol evaporation).

T / °C	p / bar	t / h	X <sup>a</sup> / %	Y <sup>b</sup> / %	O: C	H: C	HHV / MJ/kg
220	20	8	68	65	0.3	1.36	28.4
260	20	8	88	73	0.24	1.20	29.9
300	20	8	92	84	0.17	1.24	33.7
260	1	8	80	74	0.25	1.19	30.4
260	20	8	88	73	0.24	1.20	29.9
260	40	8	90	88	0.27	1.50	29.0
260	20	4	76	71	0.28	1.20	28.2
300	20	8	92	84	0.17	1.24	29.9
300	20	20	98	93	0.13	1.40	36.2

Figure 3 shows a representative gas chromatogram from a catalytic run using 5 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. The main components can be assigned to various substituted phenols such as alkyl syringols (e.g., 4-propyl-syringol (22.31 min)) and guaiacols (e.g., 4-propyl-guaiacol (16.34 min)). It seems that the coniferyl and sinapyl alcohols being structural lignin units are the primary products from lignin depolymerization, too. These compounds will be first hydrogenated/dehydrated and subsequently hydrocracked in presence of catalysts leading to propyl, ethyl and methyl derivatives of guaiacol and syringol. Phenolic hydroxyl group and methoxy groups stay intact. In another scenario of producing valuable chemicals like phenols from lignin, it is indeed advantageous that the present catalyst do not produce low valued products such as benzene and cyclohexane by deep hydrodeoxygenation and consecutive hydrogenation, respectively. Additionally, various LCAs are formed from the FAEEs being present in the Organosolv® lignin as already mentioned above. Such FAEEs will be deoxygenated towards LCAs that can be also seen in the chromatogram shown in Fig. 3 (e.g. ethyl octadecanoate (33.77 min)). Moreover, these LCAs will be converted into shorter molecules by catalytic hydrocracking depending on reaction conditions.



**Figure 3.** Gas chromatogram of lignin hydroprocessing products (0.5 g lignin, 0.1 g catalyst (5 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), 7 ml ethanol, 260 °C).

Table 2 summarizes some product distributions of bio-oils obtained from lignin hydroprocessing by using various catalysts. It can be clearly seen that no LCAs are formed in the absence of any catalyst. The bio-oil obtained consist of three equal parts of phenols, FAEEs and oligomers. This picture changes in presence of catalysts. A part of the FAEEs is converted into LCAs and smaller molecules. In addition, Ru/H-Beta shows superior properties with respect to the formation of monomeric phenols.

**Table 2.** Product distribution (percentages are calculated assuming an average number of each C-H bond present in particular category has a response factor of 1) during lignin hydroprocessing (0.5 g lignin, 0.1 g catalyst, 7 ml ethanol, 20 bar H<sub>2</sub> (initial pressure), 8 h) over various catalysts, <sup>a</sup>long-chain alkanes, <sup>b</sup>fatty acid ethyl esters, <sup>c</sup>oligomers and larger fragments.

catalyst	phenols / %	LCA <sup>a</sup> / %	FAEE <sup>b</sup> / %	others <sup>c</sup> / %
-	37.4	0	25.4	31.2
Ru/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	38.0	6.9	15.6	39.5
Ru/H-Beta	77.7	9.2	3.3	9.8
Ru/TiO <sub>2</sub>	42.2	3.5	9.9	44.4
Ni/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	47.8	7.7	10.6	33.9

### 3.3 Wheat straw liquefaction

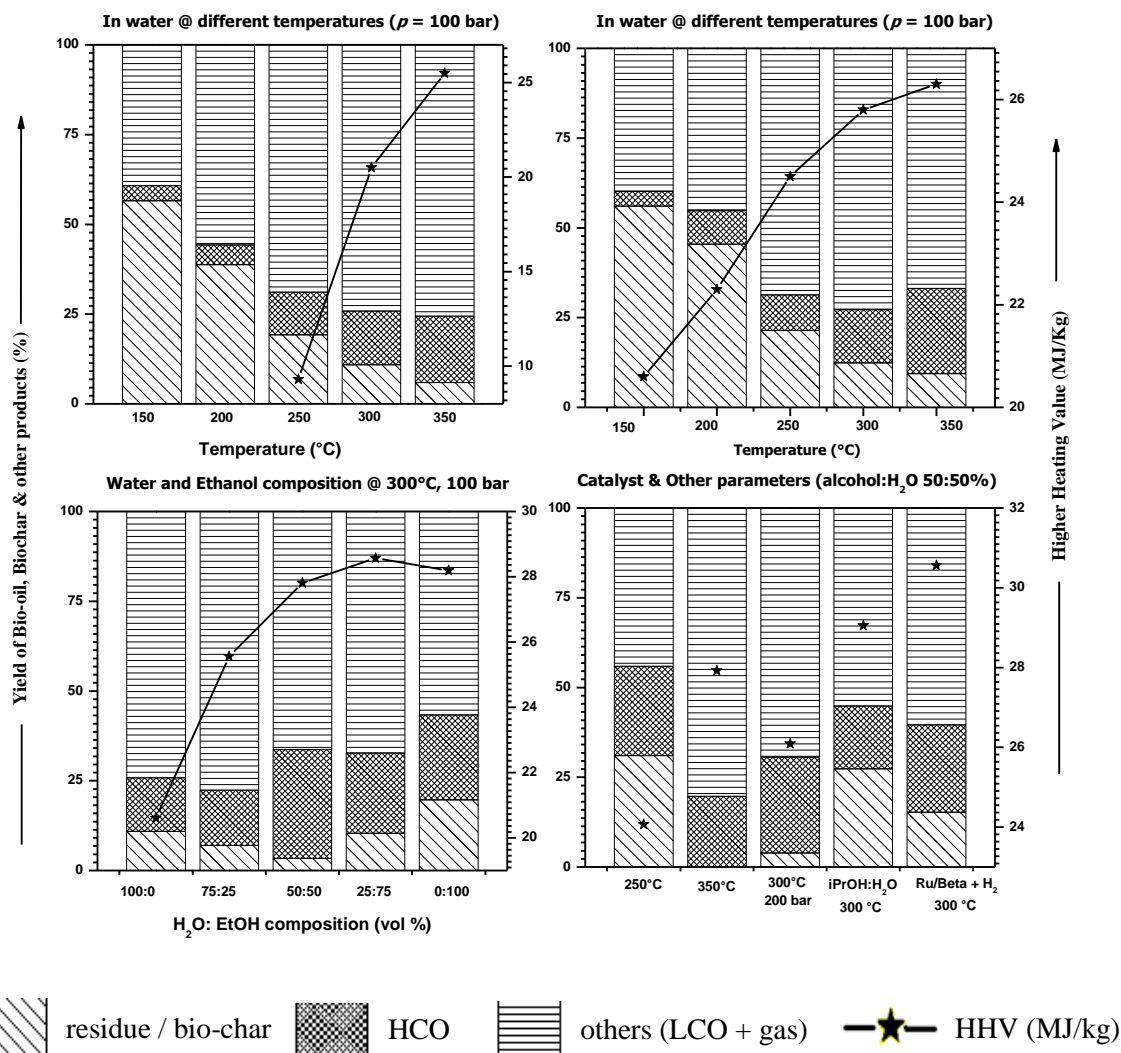
Beside the research in lignin conversion towards smaller units such as substituted phenols it is always a challenge to liquefy biomass into a bio-oil phase as an alternative to gasification or pyrolysis. Due to the results of lignin degradation, we were encouraged to use intact lignocellulosic biomass instead of their single main components such as lignin or cellulose. Doing so, we studied the degradation of wheat straw at different reaction conditions and in presence of Ru/H-Beta catalyst or addition of a base (e.g., K<sub>2</sub>CO<sub>3</sub>). Table 3 shows some results. The used wheat straw reveals a rather low HHV of ca. 14 MJ/kg. This value can be nearly doubled by conversion in sc-EtOH. Straw conversion reached values >80% and a high-caloric bio-oil (HCO) is formed with a yield of ca. 25% related to carbon. The remaining carbon can be found in the gas phase compounds and in water soluble LCO amount. Similar values were obtained using aqueous EtOH. The use of 5 wt% Ru/H-Beta catalyst does not show a beneficial influence. In contrast, the HCO proportion decreased pointing to an increased gas formation.

**Table 3.** Liquefaction of wheat straw at different reaction conditions (Reaction conditions: wheat straw = 3 g, 300 °C, 100 bar, feed flow rate = 0.5 ml/min. <sup>a</sup> - conversion of biomass, <sup>b</sup> - yield of high-caloric bio-oil (HCO), <sup>c</sup> - higher heating value of the formed HCO, <sup>d</sup> - wheat straw, <sup>e</sup> - in presence of hydrogen).

fluid	catalyst	t / h	X <sup>a</sup> / %	Y <sup>b</sup> / %	HHV <sup>c</sup> / MJ/kg
					14.2 <sup>d</sup>
H <sub>2</sub> O	-	5	89	15	20.5
H <sub>2</sub> O	-	5	88	15	25.8
EtOH	-	2	80	24	28.2
H <sub>2</sub> O: EtOH (1: 1)	-	2	96	31	27.8
H <sub>2</sub> O: EtOH (1: 1)	Ru/H-Beta	2	98	19	22.9
H <sub>2</sub> O: EtOH (1: 1)	Ru/H-Beta <sup>c</sup>	2	98	22	32.5
H <sub>2</sub> O: EtOH (1: 1)	K <sub>2</sub> CO <sub>3</sub> (0.5 M)	2	94	36	25.4

Figure 4 summarizes some additional information on wheat straw conversion in HCW such as temperature dependency at 100 (A) and 200 bar (B) reaction pressure, respectively. The bars show the yield of HCO and LCO/gas phase and char/solid residue portion. In addition, it can be seen in chart C that HHV is increased by using EtOH as fluid. However, HCO proportion does not exceed 20%. An additional experiment using hydrogen (chart D, see also Table 3) revealed a deeper HDO expressed in significantly increased HHV value.





**Figure 4.** Yields of LCO/gas portion (top), HCO (middle) and char/residue (down) with respect to carbon in conversion of wheat straw using HCW, sc-EtOH and their mixture in a temperature range of 150-350  $^{\circ}\text{C}$  and pressures of 100 and 200 bar, respectively (asterisks mark HHV values).

#### 4. Summary and conclusion

The studies have shown that Organosolv<sup>®</sup> lignin can be converted in hot compressed water as well as sc-ethanol. In comparison to HCW, sc-EtOH medium was quite effective, i.e. lignin conversions reached ca. 90% and mainly phenols were formed besides smaller lignin oligomers and long-chain alkanes stemming from the fatty acid ethyl ester portion in the parent lignin. The bio-oils formed showed an increased higher heating value and decreased oxygen content. Hydroprocessing in presence of hydrogen and Ru/alumina catalyst increased efficacy of the process, and a HHV value of ca. 36 MJ/kg was reached. In addition, some tests on the conversion of wheat straw in HCW, sc-EtOH and their mixtures were carried out showing bio-oil portions containing ca. 20% of the originally present carbon in the straw feed. These bio-oils show HHV values of 28-30 MJ/kg.

## Acknowledgements

The authors thank Ms. W. Winkler for recording X-ray diffractograms, Dr. C. Fischer for ESI-MS analyses and Mr. R. Eckelt for BET surface measurements. Dr. D. Meier from “Thünen-Institut für Holzforschung” Hamburg is gratefully acknowledged for GC-MS analyses of bio-oils and valuable discussions. We thank the Leibniz-Gemeinschaft for financial support.

## References

- [1] T.E. Bull, Biomass in the energy picture, *Science* 285 (1999) 1209.
- [2] R. Palkovits, K. Taijvidi, A.M. Ruppert, J. Procelewska, Heteropoly acids as efficient acid catalysts in the one-step conversion of cellulose to sugar alcohols, *Chem. Commun.*, 47 (2010) 576-578.
- [3] D. Schmiedl, S. Endisch, E. Pindel, D. Rückert, S. Reinhardt, G. Unkelbach, R. Schweppe, Base catalyzed degradation of lignin for the generation of oxy-aromatic compounds – Possibilities and Challenges, *Erdöl Erdgas Kohle*, 128 (2012) 357-363.
- [4] <http://ethanolproducer.com/articles/8973/sunliquid-cellulose-ethanol-process-reaches-demo-scale-in-germany>
- [5] R. Schweppe, G. Unkelbach, D. Schmiedl, T. Hirth, Lignin in nah- und überkritischen Medien, Fachgespräch „Stoffliche Nutzung von Lignin“, 10. März 2009, Berlin
- [6] J. Zakzeski, P.C.A. Bruijninx, A.L. Jongerius, B.M. Weckhuysen, The catalytic valorization of lignin for the production of renewable chemicals, *Chemical Reviews* 110 (2010) 3552-3599.
- [7] J.E. Holladay, J.F. White, J.J. Bozell, D. Johnson, Top Value-Added Chemicals from Biomass - Volume II-Results of Screening for Potential Candidates from Biorefinery Lignin, 2007, PNNL-16983, Pacific Northwest National Laboratory, Richland, WA. Available from: [http://energyenvironment.pnnl.gov/staff/staff\\_info.asp?staff\\_num=390](http://energyenvironment.pnnl.gov/staff/staff_info.asp?staff_num=390)
- [8] <http://www.nnfcc.co.uk/publications/nnfcc-renewable-chemicals-factsheet-lignin>
- [9] M. Kleinert, T. Barth, Phenols from Lignin, *Chemical Engineering & Technology*, 31 (2008) 736-745.
- [10] T. Barth, M. Kleinert, Motor Fuels From Biomass Pyrolysis, *Chemical Engineering & Technology*, 31 (2008) 773-781.
- [11] J.S. Shabtai, W.W. Zmierczak, E. Chornet, Process for Conversion of Lignin to Reformulated, Partially Oxygenated Gasoline, US patent 6,172,272, 2001.
- [12] P. De Wild, R. Van der Laan, A. Kloekhorst, E. Heeres, Lignin valorisation for chemicals and (transportation) fuels via (catalytic) pyrolysis and hydrodeoxygenation, *Environmental Progress & Sustainable Energy*, 28 (2009) 461-469.
- [13] M. Kleinert, T. Barth, Towards a lignocellulosic biorefinery: Direct one-step conversion of lignin to hydrogen-enriched bio-fuel, *Energy Fuels*, 22 (2008) 1371-1379.
- [14] P.T. Patil, U. Armbruster, M. Richter, A. Martin, Heterogeneously catalyzed hydroprocessing of Organiosolv lignin in sub- and supercritical solvents, *Energy Fuels*, 25 (2011) 4713-4722.
- [15] B. Scholze, D. Meier, Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). Part I. Py-GC/MS, FTIR, and functional groups, *Journal of Analytical and Applied Pyrolysis*, 60 (2001) S. 41-54.