# Lignin catalytic hydroconversion: a semi-continuous experimental study

**Junjie Pu,[a,b] Dorothée Laurenti, [a]* Isabelle Pitault,[b] Mélaz Tayakout, [b] Christophe Geantet [a]**

[a]*Univ. Lyon, IRCELYON, CNRS-UCB Lyon 1, UMR5256, 2 avenue A. Einstein 69626 Villeurbanne cedex, France*

[b]*Univ Lyon, Université Claude Bernard Lyon 1, CNRS, LAGEP UMR 5007, 43 boulevard du 11 novembre 1918, F-69100, Villeurbanne, France*

**Corresponding author: dorothee.laurenti@ircelyon.univ-lyon1.fr*

**Abstract:** The valorization of lignin coming from pulp industry or biorefineries into renewable chemicals is a great challenge to answer to energy transition. We present here a new reactor system consisting in a semi-opened batch reactor on the gas-phase to carry out the catalytic lignin liquefaction. The interest of this equipment is the continuous removing of light products and water from the reacting mixture whereas the hydrogen donor solvent is reintroduced in the reactor via a reflux system. The tested catalysts are metal sulfides and thanks to several analytic tools, the components of the gas and liquid phases were identified and quantified.

**Keywords:** Lignin, sulfide catalysts, GCxGC, NMR.

## 1. Introduction

Because of the fossil fuels depletion and the environmental concerns, transformation of lignocellulosic biomass is becoming a great challenge in order to provide bio-fuels and bio-chemicals in a near future. Lignin which represents almost 30 % of lignocellulosic biomass is the most relevant and abundant ressource to produce aromatics due to its original polymeric structure composed by phenylpropane units with ether linkages[1,2]. However, the 50 million tons lignin co-produced during cellulose extraction are still mainly burned as a low value-fuel. The use of lignin as a precursor of hydrocarbons or phenol type compounds has then gained a strong interest due to its low cost and high availability. In order to find a catalytic way to valorize co-produced lignin, we propose here the catalytic hydroconversion reaction as a mean to liquefy lignin and produce aromatics. The reaction takes place in a H-donor solvent which allows to avoid condensation reactions due to radical reactions between the fragments and also improves hydrogen diffusion into the liquid phase where the catalysis process takes place. A semi-batch reactor, opened on the gas phase with a continuous feeding of $H_2$, is used with a reflux system for keeping the H-donor solvent in the reactor and removing continuously light products and water from the reacting mixture. Various solid catalysts were screened in this set-up which has been demonstrated to be very powerful compared to a simple batch system previously used,[3] as there is no limitation of hydrogen and water and light products are separated avoiding long contact of catalyst with water and over-conversion of lights products to gas.

## 2. Experimental

Lignin (30g) is introduced with tetralin (70g) and $CoMoS/Al_2O_3$ (3 g) in a 0.25 L Parr autoclave reactor opened on the gas phase and equipped with a reflux system maintained at 170°C. The reactor is continuously fed with $H_2$ (40 NL/h) and the temperature is increased up to 350°C under stirring. 8 MPa of total pressure was kept constant during the whole reaction. After reaction and cooling, liquids and solids are separated by centrifugation and solids were extracted with THF. The so-called "lignin residue" is the THF soluble fraction corresponding to partially converted lignin. The overall weight balance was carefully determined and was higher than 96 wt%. Hydrogen consumption and gas production were determined by µGC analysis on-line and a Coriolis flowmeter. For each residence time, the lignin residues were analyzed by GPC and $^{13}C$, $^{1}H$, $^{31}P$ NMR, the monomers in the liquid were characterized by GCxGC-MS for identification and GCxGC-FID for quantification[4].

## 3. Results and discussion

We performed the hydroconversion of lignin over $CoMoS/Al_2O_3$ catalyst, at various residence time between 0h and 13h. The catalytic hydroconversion led to four different fractions in the batch reactor: gas, liquid, lignin residue, solids and two phases in the separator: aqueous and organic phase (Figure 1). The evolution of the main gas, $CO_2$ and $CH_4$ coming respectively from decarboxylation of carboxylic functions and from hydrogenation of $CO_2$ (methanation) or demethylation was measured online. We observed that the CO2, CH4 and CO were mainly formed during the increase of the temperature in the first thermal stage of the process and disappeared after 5h of residence time suggesting the total conversion of carboxylic and methoxy functions. For the lignin residue, the depolymerization can be easily followed by the distribution of the molecular masses given by GPC. $^{31}P$ NMR after phosphitylation showed the strong disapperance of aliphatic OH and carboxylic acids during the temperature increase step while the other types of OH are slowly decreasing during the 13h. Regarding the liquid phases, the yield reached 60 wt% after 13h and continue to increase suggesting that depolymerization still occurred. The organic phase recovered in the cold trap mainly contained the deoxygenated products and a few part of phenols. By increasing the reaction time, the total liquid fraction yield (batch and traps) increased and deoxygenation compounds became numerous. The monomers composition in the liquids was investigated by GCxGC. The main families: dimethoxyphenols, methoxyphenols, phenols, alkanes, naphthenes and aromatics (BTX) were quantified for each experiment and the evolution of those showed deoxygenation towards light phenols, BTX and naphthenes recovered in the trap with aqueous phase due to the fractionating system. The C and S in the used catalyst are respectively 12 % and 6 % from 1h to 13h showing that the catalyst was rapidly coked at the very beginning of the process and then keeps its catalytic activity during all the process. Those experimental data allow to propose a complete reaction scheme for the catalytic hydroconversion of lignin and are also used to implement a kinetic model.

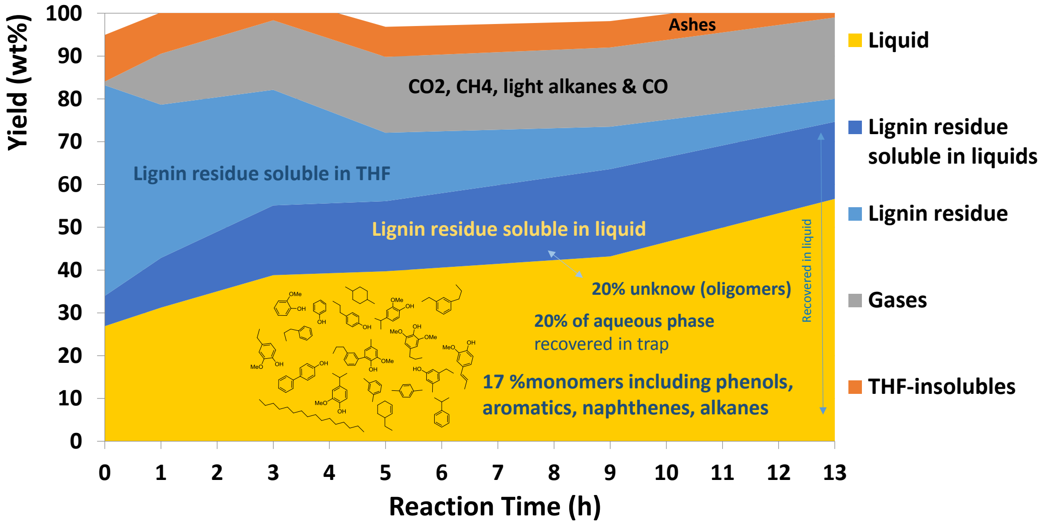

**Figure 1.** Evolution of liquid, lignin residues, solids and gases in function of the reaction time

## 4. Conclusions

The semi continuous system allowed a better description of the reactivity of lignin which was efficiently converted to liquid monomers and oligomers. The characterization of the monomers was performed by GCxGC and showed a continuous increase of phenols, naphthenes and BTX aromatics whereas $CO_2$, $CH_4$ and CO are produced at the early stage of the reaction. The rapid conversion of aliphatic OH and carboxylic groups of the lignin was followed by demethoxylation and deoxygenation of methoxyphenols which are slower processes in those operating conditions. The light deoxygenated components as aromatics and naphthenes are efficiently removed from the mixture with formed water.

## References

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