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Lignin Solvolysis study **19th International Symposium on the Wood, Fibre and Pulping Chemistry**
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Lignin solvolysis study

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Abstract

Lignin is the only renewable bio-resource of aromatic compounds [2]. Due to the large depletion on fossil resources, develop successful processes which enable to convert lignin into high value chemicals (aromatic chemicals platform) are highly leading [1], [2].

Owing to its complex structure, the challenge is high: it consists in selectively breaking down lignin main bonds between building blocks [1-3] and defunctionalized it to the target products.

The hydroconversion process of wheat straw lignin in presence of tetralin, high pressure of hydrogen (8 MPa) and heterogeneous catalyst was preliminary studied [2]. During the reaction, the lignin was thermally depolymerised and the role of hydrogen, catalyst and solvent partially consisted in saturating the produced radicals. The results showed that the solvent nature had a great impact on reducing condensation reactions and residues formation. However, the lignin behaviour, i.e. its physical or reactive solubilisation in the solvent medium, was not yet elucidated. Moreover, the impact of solvent nature on the first steps of lignin depolymerisation was not fully understood.

To clarify these points an experimental set-up was built up with the support of ANR Lignarocat project [5]. It consisted in a batch reactor (0.5L) which operated at elevated pressure (<130 bar) and high temperature (<400  C). It was equipped with *in situ* on-line ATR (*Attenuated Total Reflectance*) –IR probe which led to detect and follow mass transfer of lignin into solution in the process operating conditions. To simplify the experimental study, lignin depolymerisation was firstly performed in solvolysis conditions, i.e. at lower temperature and without catalyst and gaseous hydrogen addition. The objective was to understand which mechanism dominated (direct solubilisation or reactive depolymerisation) at lower temperature (below 250 C). The system characterization was completed by analytical tools off-line (GPC). Hydroconversion process conditions will be studied lately.

Keywords: lignin/ dissolution/solvolysis/ATR-IR

Introduction

Lignocellulosic biomass is the only available and most abundant renewable carbon resource on earth. Due to the large depletion on fossil resources, converting biomass into fuels and platform molecules is essential to reduce the consumption of non-renewable resources and increase the energetic independence of our country.

Lignin, which contributes around 19-35 % of lignocellulosic weight [1], is a by-product and is currently used as a low-value-fuel to generate electrical energy in the pulp and paper industry. Nevertheless, lignin is the only renewable resource of aromatic compounds in the nature [2]. Hence, it is highly leading to develop successful processes for converting it [3], [4].

Owing to its complex structure, lignin conversion into valuable chemical products is a difficult task. The challenge consists in selectively breaking down lignin main bonds between building blocks (mainly C-O bonds of aryl ethers and carbon-carbon bonds) [2] and defunctionalised it to the target products. Lignin depolymerisation can be undergone in several ways such as the hydroconversion that is the main target of the ANR Lignarocat project. In this study, we focused on the solvolysis way which should allow understanding the first step of lignin hydroconversion. During solvolysis, thermal depolymerisation of lignin is carried out at high temperature in presence of solvent and without addition of catalyst or gaseous hydrogen. In these conditions,

radicals may largely react to form residues by condensation which complicates the understanding of the chemical mechanisms of lignin depolymerisation. The solvent nature (H-donor) has also a great impact on reducing condensation reactions and residues formation. However, its role is not fully understood, especially its capability to solubilise lignin before its depolymerisation. Hence, the lignin behaviour, i.e. its physical or reactive solubilisation in the solvent medium is not yet elucidated. Thus, the study objectives are as follows [2]:

- Understand the lignin behaviour in the solvent, i.e. its physical or reactive solubilisation.
- Understand the impact of solvent nature on lignin thermolysis and solvolysis reactions.

This work summarizes the first experimental results after the successful development of our experimental set up, with a focus on the IR (*InfraRed*) spectroscopy results obtained with *in situ* and on-line ATR (*Attenuated Total Reflectance*) /IR probe. The experimental work focuses on the system lignin/tetralin, but several other systems will be later performed.

Experimental

Materials

A wheat straw soda lignin (Protobind 1000) was supplied by Green Value (Switzerland). Further information was not provided by the supplier. Lignin was preliminary dried at 60°C during one night to remove the presence of water. ATR (*Attenuated Total Reflectance*) /IR (*InfraRed*) spectrum of the lignin is presented in Figure 2 whereas its weight molecular distribution (measured by Gel Permeation Chromatography (GPC) without acetylation according to procedure described in [7]) is in Figure 5.

1,2,3,4-tetrahydronaphthalene (tetralin) was supplied by Sigma–Aldrich. Its molar purity grade is 99%.

Experimental set up

The apparatus was built up with the support of ANR Lignarocat project [5]. A schematic representation of the experimental set up is depicted in Figure 1.

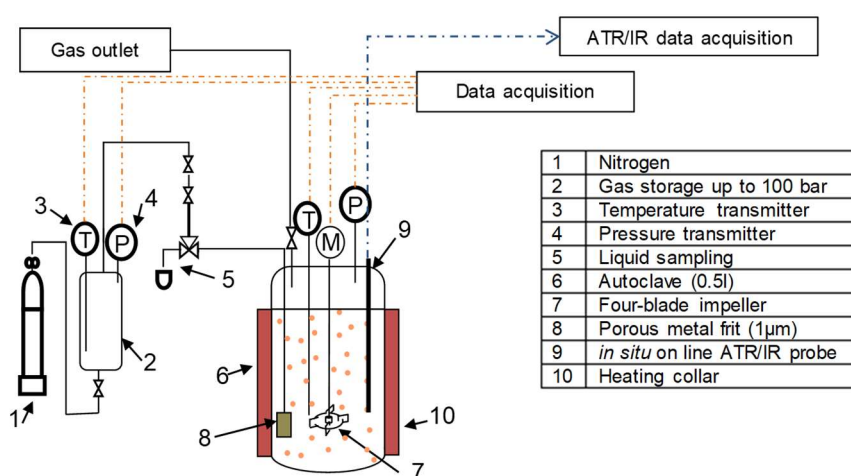


Figure 1. Experimental set up

The experimental set up comprises an autoclave (0.5L) equipped with heating collar which can work at elevated pressure (<130 bar) and high temperature (<400 °C). Temperature and pressure transmitters allow monitoring the system change. A network of manual valves allows gas inlet (nitrogen, supplied by Air products, purity grade: 99%) into the autoclave and gas outlet outside the autoclave. Liquid phase sampling can be performed by means of three-way valve under middle pressure. A porous metal frit (1µm) avoids solid particles into the liquid sampling.

ATR/IR analysis and probe description

InfraRed spectroscopy (IR) allows characterizing functional groups in a sample. Indeed, chemical bonds vibrate at a very specific frequency when irradiated which depends on the atoms of the bond, but also the environment of the bonds (solvent and neighbouring molecules).

The reactor comprises *in situ* on-line ATR-IR probe connected to a FT-IR Nicolet™ iS™ 50 spectrometer. The objective is to provide direct insights into the system and follow physical and/or reactive solubilisation of lignin during the run without sampling. The probe can work under high pressure (20 MPa) and high temperature (250°C). It comprises a diamond conical reflection internal element and is swept with a slight flow of dried air. However, the data acquisition window is limited from 600 to 1900 cm⁻¹.

The use of a high pressure autoclave with ATR-IR probe for on-line *in situ* spectroscopic monitoring of biomass conversion processes was introduced by Zakzeski and Weckhuysen (2011) [6]. Their work focused on solubilisation and aqueous phase reforming reaction of lignin.

Spectrum of lignin (32 scans were collected from 400-4000 cm⁻¹ by means of ATR accessory of the Nicolet spectrometer) is presented in Figure 2. Some main functional groups are out of detection range of the probe (Figure 2) but we can see that a large number of lignin functional groups are still present.

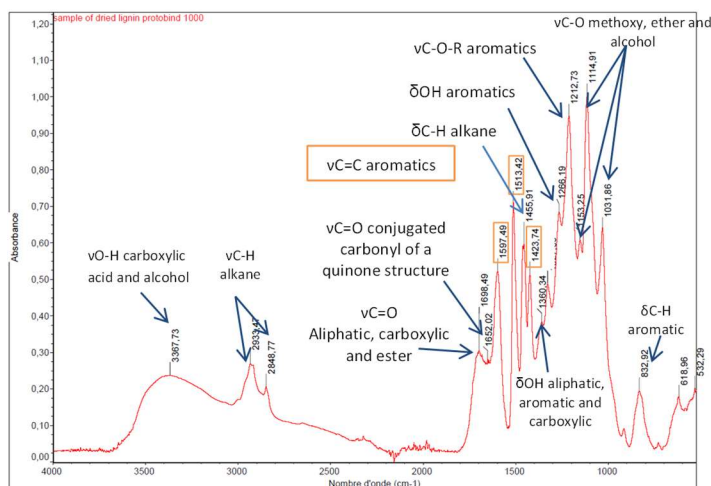


Figure 2. Bands assignment in the mid-infrared region for lignin Protobind 1000 [7]

Experimental procedure

Around 25 g of dried lignin and 275 g of tetralin were poured into the reactor. Then, the autoclave was closed. Nitrogen was bubbled through the liquid along 15 minutes at a pressure near 2 MPa. The reactor was flushed 3 times with nitrogen and finally pressurized to around 0.5 MPa. The system was stirred at 400 rpm. Next the reactor was heated up to the desired temperature. Several ATR/IR spectra of the system lignin/tetralin were collected during the test. After a residence time of several hours, a liquid sample was collected and the run was stopped.

Once ambient temperature was achieved (several hours were required), the reaction mixture was filtered to separate liquid and solid phases. Solid (residual lignin) was dried at atmospheric temperature in presence of extractor hood. "Liquid" phases include the residual solvent (tetralin), a certain amount of solubilised lignin which precipitates over the time (precipitated lignin) and reactive products (which could be in aqueous or in organic liquid phases). Hence, the "liquid" phases were centrifuged to recover precipitated lignin and eventually separate aqueous and organic phases.

Analytical tool off-line

The solid and organic phases were analysed by Gel Permeation Chromatography (GPC) [7]. It allows determining molecular weight distribution of the sample taking the polystyrene as reference.

Results and Discussion

Parameters monitoring and mass balance

Several trials were carried out at different end temperatures (150°C, 240°C) in presence of the same lignin/solvent ratio, at the same initial nitrogen pressure. Figure 3 presents pressure and temperature monitoring during the run "240°C". Experimental procedure steps (from 1 to 5) are fully described in previous section. Several IR spectra were also recorded during the trial. The timing of spectra sampling is also depicted

in Figure 3.

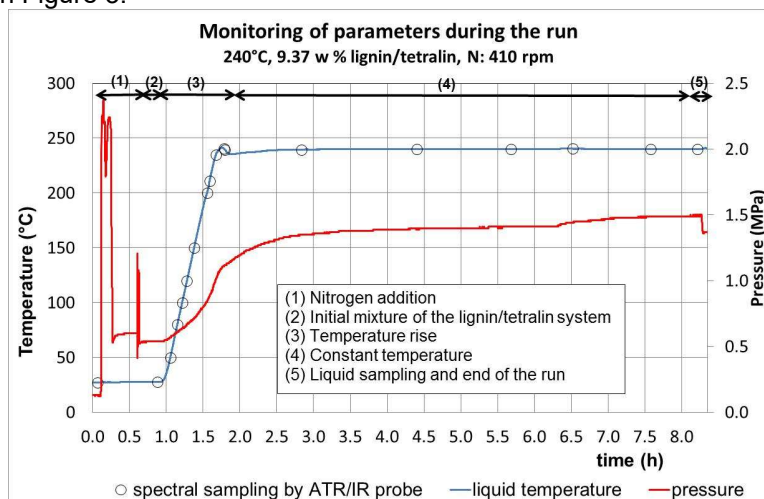


Figure 3. Parameters (pressure, temperature, spectral sampling) monitoring during the run “240°C”.

In Figure 3, we can see that the total pressure of the system has never achieved a constant value. Hence, lignin degradation was suspected at this temperature. During the run “150°C” which is not depicted in Figure 3, the total pressure was constant all along the temperature plateau.

ATR/IR spectra discussion

Several ATR-IR spectra were collected for each run.

For the run “150°C”, specific bands of lignin did not clearly appear in the collected spectra. Indeed, several bands of lignin and tetralin are in the same range of measure and some bands are shared. Hence, it was quite difficult to conclude if the bands intensity variation had to be attributed to lignin solubilisation or to a change of the intensity of bands of tetralin because of the temperature variation. Consequently, we conclude that only tetralin spectrum was noticeable in the medium.

For the run “240°C”, ATR-IR spectra of the medium are depicted in Figure 4a. At ambient temperature and in the first run hours, only tetralin band vibrations were observed and vibrations attributed to the insoluble lignin were not noticed. The change of the ATR/IR spectrum appeared after one hour at 240°C. Some ATR-IR several bands could be attributed without ambiguity to lignin. Indeed, the bands above 1650 cm^{-1} , namely the C=O in stretching mode, and the bands near 1200 cm^{-1} (C-O-R aromatics in stretching mode and OH aromatics in deformation mode) belong to lignin spectrum. Nevertheless, be aware that the variation of intensity of the bands at 1600 cm^{-1} and above 1400 cm^{-1} could also be attributed to aromatic skeleton of tetralin.

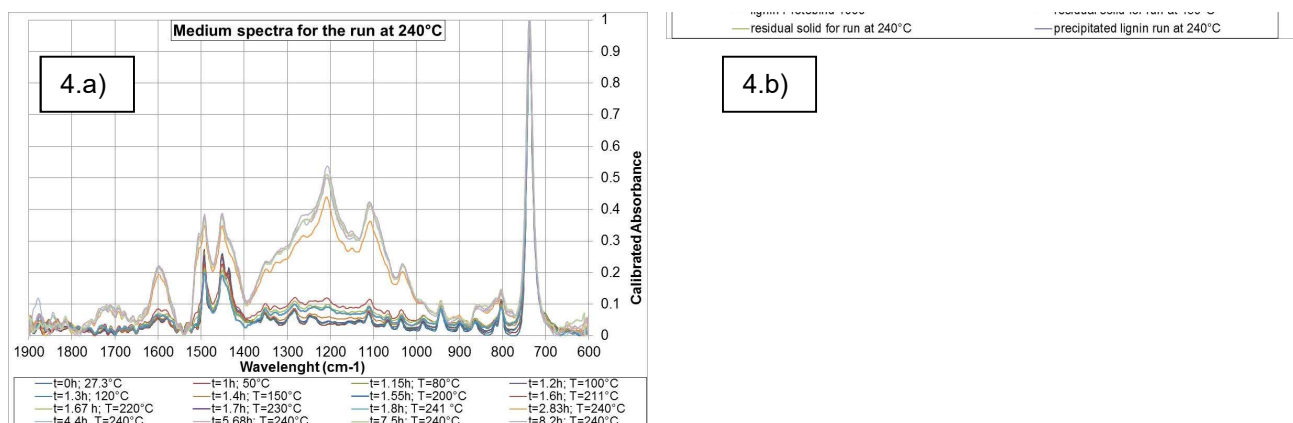


Figure 4. a) *In situ* ATR-IR spectra of the dissolution of Protobind lignin in tetralin for several times and temperature for the run “240°C” 4.b) ATR/IR spectra of initial, precipitated and residual lignin for each run (measured off line in the ATR/IR accessory of the Nicolet spectrometer)

Hence, the appearance of new vibrations in the medium spectra was attributed to the formation of dissolved organic species from the lignin. The ATR/IR spectra of initial lignin, precipitated lignin and lignin residual (see experimental procedure) were also collected and are presented in Figure 4.b. The bonds intensity varies but is small between initial lignin and reactive lignins. The appearance of large bands from 2900-3100 cm^{-1} and from 690 to 780 cm^{-1} may be attributed to the presence of residual tetralin into the sample. The lignin depolymerisation and hence chemical structure variation could not be validated by the IR spectra study in these two runs.

GPC analysis

Figure 5 presents the weight molecular distribution of initial, precipitated and residual lignin for each run.

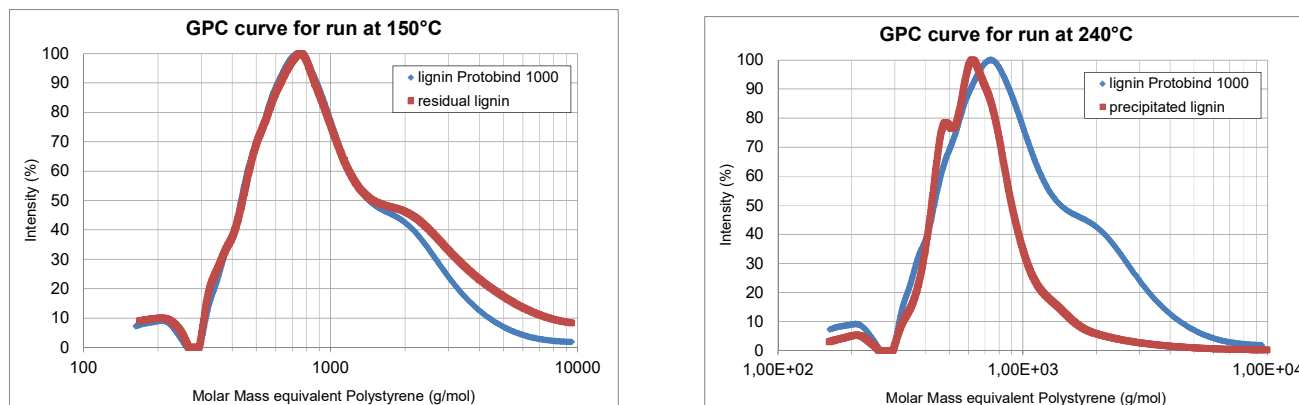


Figure 5. Weight molecular distribution of initial, precipitated and residual lignin for each run

For the run “150°C”, the residual lignin distribution is close to the initial lignin one (Figure 5). Lignin depolymerisation did not occur.

For the run “240°C”, the distribution of the precipitated lignin exhibits a smaller width than the initial lignin one (Figure 5). We can conclude that some solid species solubilise into the organic phase with a different molecular weight distribution. Nevertheless, we cannot conclude clearly on the lignin chemical structure variation. The chemical structure of residual lignin was certainly modified during the process operating conditions: the residual lignin was not soluble into the solvent used for the GPC analysis (tetrahydrofuran).

Conclusions

To conclude, the formation of dissolved solid species from the lignin was evidenced by the *in situ* on-line ATR/IR probe in tetralin at 240°C. Several tools (the total pressure variation all along the temperature plateau at 240°C, GPC analysis) allow validating the chemical modification of lignin during the run. In the future, other solvents will be studied and their effect will be compared.

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