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► To cite this version:

Aurélie Galfré, Isabelle Pitault, Mélaz Tayakout-Fayolle, François Puel, Emilie Gagnière. Lignin solvolyse study. 25th International Symposium on Chemical Reaction Engineering ISCRE25, May 2018, Florence, Italy. 25th International Symposium on Chemical Reaction Engineering ISCRE25. hal-01820538

HAL Id: hal-01820538

<https://hal.science/hal-01820538>

Submitted on 21 Jun 2018

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Lignin solvolysis study

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Highlights

- The lignin physical or reactive solubilization in tetralin is followed by ATR-IR probe.
- The formation of dissolved solid species from lignin was detected in tetralin from 170 C
- The chemical modification of lignin was evidenced by CHONS and GPC.

1. Introduction

Lignin, which contributes around 19-35 % of lignocellulosic weight [1], is the only renewable resource of aromatic compounds in the nature [2]. Due to the large depletion on fossil resources, converting lignin into platform molecules is highly leading [2]. Its structure is a polymer network with cross linking branches. The polymer structure is based on three repetitive units (p-coumaryl, guaiacyl and syringyl units) which differ by the number and the position of the substituted methoxyl groups on aromatic rings [1].

Owing to its complex structure, lignin conversion into valuable chemical products is a difficult task. The challenge consists in selectively breaking down lignin bonding motifs between building blocks (mainly C-O bonds of aryl ethers and carbon-carbon bonds) [2] and defunctionalised it to the target products. Severe conditions (high temperature, high hydrogen pressure and catalyst) are required to carry out lignin depolymerisation. In our project, H-donor solvent was added to the system. The results [3, 4] show that the solvent nature (H-donor) had a great impact on reducing condensation reactions and residues formation. However, several points have to be clarified to complete the reaction scheme [2]. Hence, the lignin behavior, i.e. its physical or reactive solubilization 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 important points, we focus our experimental work on studying lignin depolymerisation in solvolysis conditions (medium temperature, without catalyst or gas hydrogen addition). The experimental set-up comprises *in situ* and on-line ATR (Attenuated Total Reflectance) /IR (Infrared) probe which allows following the first steps of lignin depolymerisation and solubilization in the medium. Several systems (lignin/solvent) would be studied.

2. Methods

The experimental set up consists in an autoclave (0.5L) equipped with heating collar which can work at elevated pressure (<130 bar) and high temperature (<400  C). The reactor comprises *in situ* and on-line ATR-IR probe connected to a FT-IR NicoletTM iSTM 50 spectrometer. The objective is to provide direct insights into the system and follow physical and/or reactive solubilization 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 cm⁻¹ to 1900 cm⁻¹. Spectrum of lignin is presented in Figure 1.a. Some main functional groups are out of detection range of the probe but we can see that a large number of lignin functional groups are still presents.

The ATR/IR results are completed by several analytical tools. Indeed, after the run, the reaction mixture is filtered to separate liquid and solid phases. The chemical structure and composition of the solid residue are analyzed by Nuclear Magnetic Resonance (¹³C and ³¹P, 2 D NMR) and elemental analyses (C, H, O, N, S) [4]. Its molecular weight distribution taking the polystyrene as reference is determined by Gel Permeation

Chromatography (GPC) [4]. The organic liquid phase is analyzed by gas chromatography (GC2D): it allows identifying the main products from lignin degradation [4].

3. Results and discussion

The experiments were performed in presence of wheat straw lignin and tetralin. Several trials were carried out from 150 to 240°C in presence of the same lignin/solvent ratio. To avoid unwanted oxidation reactions, the reaction took place in presence of nitrogen. During the temperature rise and close to 170 °C, the ATR/IR probe had successfully detected the appearance of new vibrations in the medium spectra. The new vibrations corresponded to the lignin ones (Figures 1.b). However, the lignin degradation was not evidenced with the ATR/IR spectra of the medium.

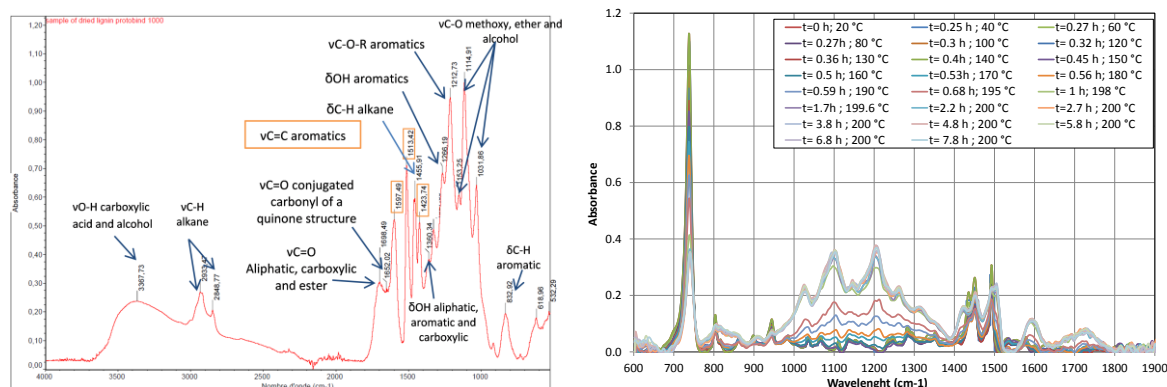


Figure 1.a Bands assignment in the mid-infrared region for lignin Protobind 1000 [3] **Figure 1.b** *In situ* ATR-IR spectra of the dissolution of lignin in tetralin for several times and temperature for the run “200 °C”

The residual solids were characterized with analytical tools off line. The results showed that residual solids had a different weight distribution and a different elemental analysis from initial lignin. Hence, the lignin degradation along the temperature rise was evidenced. Consequently, the appearance of new vibrations in the ATR/IR spectra was attributed to the formation of dissolved organic species from the lignin. RMN analyses would confirm the lignin degradation, would allow evidencing the bonds modification and complete the reaction scheme.

4. Conclusions

To conclude, the formation of dissolved solid species from lignin was evidenced by the *in situ* on-line ATR/IR probe in tetralin from 170°C. The chemical modification of lignin was evidenced by analytical tools off line (CHONS and GPC) which allow confirming the reactive solubilization of the lignin with the temperature rise in the medium. RMN analyses would confirm the lignin degradation. In the future, other solvents will be studied and their effect will be compared.

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Keywords

Lignin ; Dissolution ; Solvolyse ; ATR-IR.