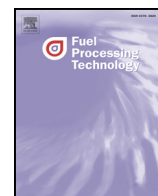




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## FTIR as a simple tool to quantify unconverted lignin from chars in biomass liquefaction process: Application to SC ethanol liquefaction of pine wood

Ngoc Quynh Bui<sup>a,b</sup>, Pascal Fongarland<sup>a</sup>, Franck Rataboul<sup>a</sup>, Cyril Dartiguelongue<sup>b</sup>, Nadège Charon<sup>b</sup>, Christophe Vallée<sup>b</sup>, Nadine Essayem<sup>a,\*</sup>

<sup>a</sup> Institut de Recherche sur la Catalyse et l'Environnement de Lyon, IRCELYON, CNRS, Université Lyon 1, 2 avenue Albert Einstein, F-69626 Villeurbanne, France

<sup>b</sup> IFP Energies nouvelles Rond Point de l'échangeur de Solaize, BP3 F-69360 Solaize, France

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## ABSTRACT

Lignin in solid residues produced from wood liquefaction can be quantified by FTIR analysis. This is applied to investigate pine wood liquefaction in supercritical ethanol in comparison with model lignin and cellulose in order to achieve a thorough description of wood liquefaction in SC ethanol. The proportions of lignin, hemicelluloses, cellulose and chars in the solid residue were quantified by compositional analysis based on acid hydrolysis combined to the quantitative FTIR analysis of the  $\nu\text{C}=\text{C}$  vibration of lignin at  $1514\text{ cm}^{-1}$ . It was shown that SC ethanol is an efficient medium for an easy liquefaction of lignin and hemicellulose from pine wood. Native cellulose in pine wood was only slightly attacked by contrast to microcrystalline cellulose. From pine wood, gas production is limited to 3 wt.% and total yields in liquid products achieved 45 wt.% but only one fourth of liquid products were eluted by GC–MS.

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### 1. Introduction

As a carbon source, biomass has two striking characteristics since it is the only renewable carbon resource and it fixes carbon dioxide from the atmosphere by photosynthesis. Therefore, its use, even for energy issues, does not contribute to the increase of atmospheric  $\text{CO}_2$ . However, the lignocellulosic resource is a complex material involving cellulose, hemicelluloses and lignin as main components. Cellulose is a homopolymer, composed of linear chains of glucose units linked with  $\beta$ -1,4-glycosidic bonds. Hemicelluloses are branched polymers, composed of different monosaccharides. Lignin exhibits a totally different polymer chemical structure with phenyl–propanoyl units in three dimensional amorphous network structures. Cellulose and hemicelluloses are tightly bonded to lignin by hydrogen and covalent bonds making their separation and their hydrolysis to simple sugars difficult. In addition, a strong hydrogen bonds network is responsible for the peculiar resistance of cellulose.

For fuel and chemical production from LCB (Lignocellulosic Biomass), interest is focused on biochemical and thermochemical routes. Biochemical processes involve biogas production by anaerobic fermentation or alcohols and carboxylic acid production via fermentation or enzymatic ways. Thermochemical processes consist in gasification, pyrolysis or solvent liquefaction. The indirect route by gasification requires the highest temperature level and implies the Fisher–Tropsch synthesis as a second step to transform the syngas

into liquid fuels. The most studied way to directly produce liquids from biomass is fast pyrolysis [1], characterized by a rapid heating in an inert atmosphere at relatively high temperature, near  $500\text{ }^\circ\text{C}$ , and at a pressure close to the atmospheric pressure. To date, fast pyrolysis is the only technology performed in demonstration plants and used at industrial level for bio-oil production with a high liquid bio-oil yield of 50–70%, depending on the feedstock [2]. However rough fast pyrolysis bio-oil, with a low heating value, corrosive properties, poor thermal stability and immiscibility to hydrocarbons can only be used for heat and power generation to replace industrial fossil fuels, such as heavy or light fuel oils. Thereby, the fast pyrolysis bio-oil needs to be upgraded to be used as a biofuels in the transport field. Although significant progress has been made in upgrading pyrolysis oils, these multi-step processes, operated at a high pressure of hydrogen, are under development and still quite far from a commercial operation, due to various difficulties such as process scheme complexity, catalyst stability, thermal stability of the bio-oil, feedstock variability or tar formation.

In comparison to gasification and pyrolysis, the reaction conditions of solvent liquefaction (solvolysis) are milder. Liquefaction consists in the thermal degradation of solid biomass in a dense solvent under medium temperature ( $250\text{--}450\text{ }^\circ\text{C}$ ) and high pressure ( $>1\text{ MPa}$ ) for a longer residence time (10–60 min) when compared to fast pyrolysis [2].

This alternative route to convert biomass into liquids of high energy value or platform chemicals is challenging and new strategies such as the liquefaction of LCB by means of supercritical fluids (SCF) have gained growing attention. This can be explained by the tuneable solvent properties associated to SC fluids as well as their ability to modify hydrogen bonds, which make these fluids capable to dissolve materials

\* Corresponding author.

E-mail address: [nadine.essayem@ircelyon.univ-lyon1.fr](mailto:nadine.essayem@ircelyon.univ-lyon1.fr) (N. Essayem).

not soluble in usual liquid solvents [3]. In this field, subcritical/SC water has already attracted intensive research efforts due to its abilities to liquefy LCB. SC water is considered as an environmentally friendly SC solvent but it presents adverse drawbacks such as severe experimental conditions ( $T_c = 374\text{ °C}$ ,  $P_c = 221\text{ bars}$ ), associated to corrosion problems, which makes the scale-up difficult. Besides, this liquefaction route involves the transformation of solubilized biopolymers to shorter liquid products via oxygen removal by dehydration or decarboxylation reactions leading to less polar liquid products which separate into water soluble and insoluble fractions at ambient temperature. Thus, using SC water, the bio-oil recovery is not easy and requires a further extraction step with an organic solvent.

Besides subcritical and SC water, SC organic solvents have also been envisaged, mainly alcohols (i.e. methanol, ethanol, propanol) [4,5] or acetone [6,7]. This is explained by their milder critical coordinates (i.e. ethanol:  $T_c = 241\text{ °C}$ ,  $P_c = 61\text{ bars}$ ) and their better solvent abilities for biomass derivatives [2,8]. Moreover, compared to SC water, enhanced yield in liquid products [6,9] and lower solid residue formation [10,11] were reported using SC alcohols. Methanol and ethanol are, by far, the most studied SC alcohols applied to LCB liquefaction. Note that their critical temperatures are close,  $241\text{ °C}$  and  $239\text{ °C}$  for ethanol and methanol respectively but their critical pressures are distinct, respectively 61 bars and 80 bars. To our knowledge, these two light alcohols were scarcely compared in literature as regards to delignification issues or for woody material liquefaction. Better performances are reported using SC ethanol rather than SC methanol (in batch type reactor and isotherm conditions), explained by its lower dielectric constant [9].

Concerning the abilities of SC ethanol treatment for selective lignin or carbohydrates liquefaction/conversion, the published reports are less clear. Whereas some works reported the efficiency of SC ethanol for the selective lignin removal/liquefaction [12,13], the capability of SC ethanol to remove/liquefy the carbohydrate fraction is rather controversial [14,15]. While some studies reported that SC ethanol attacks only the lignin part, others showed that the carbohydrate fraction was also converted.

These discrepancies may probably result from differences in the experimental conditions: batch vs flow reactor, T and P severity, residence time conditions, and from analysis difficulties. Indeed, in many studies, the solid biomass conversion is determined based on the unconverted solid. The chemical composition of the solid residue is scarcely provided [16]. In fact, the compositional analysis of the solid residue is not trivial. If the cellulose and hemicellulose fractions can be determined by acid hydrolysis protocol (NREL method [17]) for the solid residue, the quantification of the lignin fraction as “Klason Lignin” defined as the  $\text{H}_2\text{SO}_4$  insoluble fraction is not reliable because of the presence of chars which are also  $\text{H}_2\text{SO}_4$  insoluble as previously noticed [12].

In the present work, we paid a peculiar attention to develop reliable experimental procedures and analytic methods, involving lignin quantification by FTIR, and cellulose and hemicellulose analysis by acid hydrolysis in order to achieve an accurate measure of the conversion of each wood component, lignin, cellulose, and hemicelluloses. The objective is to perform a comprehensive study of pine wood liquefaction in SC ethanol in comparison to that of a solvolysis lignin and a microcrystalline cellulose in order to get reliable insights on the mechanism of the wood transformation in SC ethanol. The final goal is to clarify, whether or not, SC ethanol is selective for liquefaction of one of the wood components when used in batch conditions.

## 2. Experimental section

### 2.1. Materials

Biomass used in this work is sawdust of pine wood. Wood chips were ground and sieved. Particles smaller than  $500\text{ }\mu\text{m}$  were used.

A solvolysis lignin, provided by CIMV, was used as model lignin and microcrystalline cellulose, purchased from Sigma Aldrich which served as model cellulose. All initial materials (pine wood, lignin, and cellulose) were lyophilized before use in order to keep the cell wall relatively unaltered compared to a conventional drying step done in a furnace. The solid samples, cooled down at  $-20\text{ °C}$  for one night, were dried under vacuum (100 mbar) for 8 h. The same pretreatment was applied to the recovered solid residue before analysis. Ethanol, provided from Sigma Aldrich (99.8% purity) was kept dried by adding molecular sieves. 72 wt.% sulfuric acid (Sigma Aldrich) was used for the acid hydrolysis of solid biomass.

### 2.2. Reaction in SC ethanol media – experimental procedure

#### 2.2.1. Equipment

The batch reactor (Parr) of 74 mL internal volume can be operated at pressure up to 600 bars and temperature up to  $350\text{ °C}$ . The autoclave is equipped with a pressure sensor, a rupture disk, a thermocouple and the purge system. The reactor is equipped with a glass insert of 47 mL which makes the solid and liquid loadings easy.

#### 2.2.2. Experimental procedure

First, 2.5 g of dried biomass and 27 g of anhydride ethanol were introduced in the glass insert. The reactor was closed and cooled down at  $-59\text{ °C}$  in a dry ice–ethanol mixture. Then, the gas part in the autoclave was evacuated to the final pressure of 100 mbar. This procedure insures the sole presence of ethanol and biomass without permanent gas which would modify the critical coordinates of SC ethanol in an uncontrolled way.

The reactor, once warmed up at ambient temperature, was heated up to the reaction temperature  $280\text{ °C}$  with a ramp of  $5\text{ °C/min}$  and kept at this temperature for 1 h. At the reaction end, the reactor was quenched in cooled water bath ( $0\text{ °C}$ ) to enable a rapid temperature decrease to ambient temperature. The product recovery is described in Scheme 1. The gas products were collected by a vessel (95 ml) pre-evacuated at 100 mbar. This vessel is equipped with a manometer in order to measure the residual pressure. The vessel can be isolated and connected to a GC-TCD for identification of the formed gases. The gas yield (wt.%) was calculated assuming that formed light gases contain only one carbon atom with the maximum molecular weight, i.e.  $\text{CO}_2$ . The liquid and solid products were separated using a  $0.45\text{ }\mu\text{m}$  filter. Then, the unconverted biomass and solid products were washed three times with 30 ml of ethanol. The autoclave was also washed with 60 ml of acetone to recover eventual water insoluble solid left on the autoclave wall. Solid recovered by filtration was lyophilized for further analysis and named “solid residue”. The liquid products, liquid from reaction medium plus washing solvents, were first analyzed by GC–MS and then evaporated at  $50\text{ °C}$  under reduced pressure, 200 mbar, in order to eliminate ethanol and acetone. Some light products, previously quantified by GC–MS, were lost during this step. The product fraction, named “light products” in the following corresponds to light liquid products identified and quantified by GC–MS which are lost during the evaporation step applied to recover the bio-oil. They correspond to compounds eluted before 20 min of retention time, the contribution of compounds coming from the solvent degradation being removed such as diethyl ether or ethyl vinyl ether (see Table 2). At the end of this evaporation step, the bio-oil fraction was obtained.

The bio-oil and the light product yields were calculated as follows:

$$\text{Yield bio-oil (wt.\%)} = 100 \times (\text{weight bio-oil}/\text{weight biomass})$$

$$\text{Yield light products (wt.\%)} = 100 \times (\text{weight light products}/\text{weight biomass}).$$

The relative error, obtained by reproducing three times the same experiment, is  $\pm 5\%$ .

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