



Understanding the primary and secondary slow pyrolysis mechanisms of holocellulose, lignin and wood with laser-induced fluorescence



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HIGHLIGHTS

- Primary and secondary pyrolysis reactions investigated in a fixed-bed reactor.
- LIF applied to on-line characterization of aromatic species in pyrolysis volatiles.
- Pyrolysis of wood and cellulose and lignin as its two main macromolecules.
- Heterogeneous secondary reactions detected in slow pyrolysis at low temperatures.
- Lignin identified as the main PAHs formation source in wood pyrolysis.

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ABSTRACT

To understand the complex reaction mechanisms involved in biomass pyrolysis, volatile products are characterized on-line by laser-induced fluorescence (LIF), together with on-line measurements of permanent gases by GC-TCD (Gas Chromatograph-Thermal Conductivity Detector) and temperature evolutions in the bed. The focus is to determine the components that emit fluorescence and reactions involved in producing them from wood and from its two main macromolecular components, holocellulose and lignin. A technical-scale fixed-bed reactor is used to identify primary and secondary reactions involved in pyrolysis. The excitation wavelength used for the LIF measurements is 266 nm and the detected species are aromatic compounds (including one-ring phenolics and two-, three- or four-ring polycyclic aromatic hydrocarbons (PAHs)) and species containing carbonyl groups. Holocellulose volatiles show fluorescence that is attributed to the formation of carbonyl compounds and two-ring PAHs during heterogeneous secondary char-forming reactions, which also enhance the production of CO₂. Volatiles from lignin show first fluorescence typical of one-ring phenolics and small (two–three rings) PAHs. Then, due to the enhancement of heterogeneous secondary reactions, fluorescence signal typical of bigger PAHs (three–four rings) is detected. These aromatic species are produced in parallel to gas species like CH₄. The fluorescence that can be observed in pyrolysis of wood comes mainly from the lignin fraction, undergoing also heterogeneous secondary reactions resulting in the formation of bigger PAHs, although a contribution from cellulose is also present.

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1. Introduction

Pyrolysis of biomass is a relevant step in any thermochemical conversion process, such as combustion and gasification, but it is also an important process itself for the production of char (charcoal or biochar) and bio-oil. However, despite its relevance, many aspects of the process still remain a source of controversy. The

reaction mechanism is still largely unknown with respect to its details and widely applicable models to predict the product composition or the enthalpy of the reaction are not yet available [1,2]. There are several factors that increase the complexity in understanding the process, as the complexity and heterogeneity of the feedstocks, the wide range of possible experimental conditions that can be applied and the difficulty, or even impossibility, to characterize some products with conventional techniques such as Gas Chromatography (GC). An example of this is the characterization of the water insoluble fraction called pyrolytic lignin

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produced in pyrolysis of lignocellulosic materials [3]. The combination of several analytical techniques is needed to characterize the products of pyrolysis, which makes it quite time consuming and on-line characterization of the transitory process is very challenging.

In the present work, two on-line measurements are combined to get a deeper understanding of the pyrolysis process. On-line characterization of volatiles is carried out, detecting permanent gases with GC-TCD and condensable volatiles emitting fluorescence with laser-induced fluorescence (LIF). Experiments are performed for wood and its two main macromolecular components, holocellulose and lignin, together with temperature measurements in several positions inside the bed of a technical-scale fixed-bed reactor, to try to understand the behavior of biomass based on the behavior of its main components [4] in conditions close to industrial applications.

LIF has been widely used in combustion for detection of oxygenated compounds, polycyclic aromatic hydrocarbons (PAHs) or particulates (together with Laser-Induced Incandescence (LII)). However, its use in pyrolysis is scarcer. It has been applied to single particle experiments [5,6], detecting mainly PAHs, for the detection of CO and formaldehyde at reactor level in fast pyrolysis [7] and for the characterization of bio-oils produced from fast pyrolysis [8]. The authors of the present paper have also applied LIF with an excitation wavelength of 266 nm to the characterization of volatiles in technical-scale fixed-bed pyrolysis of different wood species at different conditions [9]. The aim of the present study is to get a deeper understanding of the pyrolysis mechanism by analyzing the possible origins of the measured fluorescence and linking its evolution to other produced species, as the permanent gases produced in the pyrolysis process.

2. Experimental

2.1. Materials

Pine-wood chips – approximate average size 3 cm × 2 cm × 0.5 cm – provided by Robeta Holz OHG, Milmersdorf, Germany; holocellulose with high ash content (h.a.c) and holocellulose with low ash content (l.a.c), both obtained from disposable plates cut in pieces – approximate average size 5 cm × 5 cm × 0.2 cm – and powder kraft lignin (Protobind 2000) are used as feedstock in the pyrolysis process. The disposable plates are considered holocellulose and not only cellulose because they can contain significant amounts of hemicellulose [10]. This is due to the fact that pulping removes nearly all the lignin but just partially the hemicellulose, leading to hemicellulose contents that can be higher than 10%. Besides, the pyrolysis mechanism of hemicellulose is very similar to the one from cellulose; therefore the main conclusions from cellulose can be extrapolated to hemicellulose [11]. In Table 1, the proximate and ultimate analysis of the four materials are shown.

Table 1
Proximate and ultimate analysis.

(% mass,d.b.)	Pine chips	Holocel. (h.a.c.)	Holocel. (l.a.c.)	Lignin
Volatiles	85.80	72.87	86.61	74.20
Ash	0.20	15.70	1.17	1.40
F. carbon ^a	14.01	11.43	12.23	24.40
C (%)	49.38 ± 0.40	39.0 ± 0.20	46.17 ± 0.05	63.17 ± 0.06
N (%)	0.05 ± 0.01	0.20 ± 0.01	0.13 ± 0.01	0.75 ± 0.01
H (%)	6.61 ± 0.02	5.57 ± 0.01	6.16 ± 0.06	6.06 ± 0
O ^b (%)	43.78 ± 0.43	39.31 ± 0.25	46.08 ± 0.08	27.50 ± 0.14

^a Fixed carbon is obtained by difference 100% – (Volatiles(%) + Ash(%)).

^b Oxygen content is calculated by difference: 100% – (C(%) + N(%) + H(%) + S(%) + ash(%)).

Due to the ash content that both holocellulose and lignin present, they are expected to behave more similarly to holocellulose and lignin in wood than pure holocellulose or lignin [4].

2.2. Reactor setup and LIF system

The setup used to carry out the experiments has been already presented in detail in a previous work from this group [9]. It consists of a technical-scale fixed-bed reactor of 1 m height and 22 cm internal diameter. The reactor is externally heated with an electrical heater. The heating rates are between 1 and 10 K/min, depending on the process stage. The experiments are performed using 900 g of wood, 500 g of cellulose and 500 g of lignin, previously dried, and a preheated N₂ flow rate of 20 lN/min.

The temperatures are measured inside the reactor at four different heights: 0 (inlet), 5, 10 and 30 cm above the bottom of the reactor. At each height thermocouples are also placed at three radial positions (wall, middle (5 cm to the wall) and center (10 cm to the wall)). The bed heights vary among experiments. For wood, the initial bed height is 15 cm and the final bed height 8–9 cm. For holocellulose, the initial bed height is 26–28 cm and the final bed height 12–14 cm. In the case of lignin, the initial bed height is around 8 cm while the final bed height is lower than 5 cm.

The sampling line used to extract the volatiles and guide them to the characterization system (LIF system) is connected at the top of the reactor and kept above 300 °C until the volatiles enter the measurement cell. Through this cell, in parallel to the volatiles flow, the laser beam (pulsed Nd:YAG laser, 266 nm, 5 mW power, repetition rate of 100 Hz) used to excite the molecules passes through. The fluorescence is collected at 90° with respect to the laser beam and flow direction and guided to a spectrometer. The LIF system has been developed within this research group and further description can be found in [12,9]. After leaving the LIF system, the volatiles are guided to a stainless steel condenser filled with toluene and cooled down to around –15 °C. Afterwards the gases are led to several impingers filled with activated carbon and silica gel to avoid the entrance of solvent or some minor condensable volatiles species into the GC-TCD.

2.3. LIF analysis

The total fluorescence intensity (TFI) evolution is determined as the integral of the fluorescence intensity signal over the wavelengths range under study (266–780 nm) at each time step. This fluorescence is emitted by the species passing through the measuring cell in the LIF system.

To identify which species are emitting fluorescence, single pyrolysis spectra are fitted to spectra of representative pure species which emit fluorescence with an excitation wavelength of 266 nm and may be present in the volatiles stream. These species could be [9]: species containing carbonyl groups, such as ketones and aldehydes; one-ring aromatic compounds, mainly phenolics and two-, three-, and four-ring aromatic compounds.

In Fig. 1 the spectra of representative pure species are shown. These spectra are obtained by analyzing the pure species in vapor phase and in a N₂ atmosphere passing through the cell at 300 °C, except for the case of the carbonyl group. This spectrum has been taken from the initial wood devolatilization spectrum, which is typical of species containing carbonyl groups, such as aldehydes [9,6]. As it can be seen in Fig. 1 phenolic compounds, which have typical fluorescence behavior of one-ring aromatic compounds, emit fluorescence at the lowest wavelengths of all the species analyzed in the present work. Then, the higher the number of rings of the aromatic compound, the more red-shifted the peak of the fluorescence intensity. Compounds including carbonyl groups present the peak of the fluorescence spectrum close to 400 nm.

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