



Thermal decomposition of lignocellulosic biomass in the presence of acid catalysts



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HIGHLIGHTS

- The decomposition of lignocellulose is studied by *in situ* and *ex situ* techniques.
- Three fractions, solid, liquid and gas are quantified and characterized.
- The degradation temperature is lowered by 100 °C in the presence of H₃PW₁₂O₄₀.
- At 300 °C with H₃PW₁₂O₄₀, the amount of liquid collected reaches 30 wt.%.
- Traces of furfural was observed from pure wood, with H₃PW₁₂O₄₀ it reaches 2 wt.%.

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ABSTRACT

Transformation of lignocellulosic biomass to biofuels involves multiple processes, in which thermal decomposition, hydrotreatment are the most central steps. Current work focuses on the impact of several solid acids and Keggin-type heteropolyacids on the decomposition temperature (T_d) of pine wood and the characterization of the resulted products. It has been observed that a mechanical mixture of solid acids with pine wood has no influence on T_d , while the use of heteropolyacids lower the T_d by 100 °C. Moreover, the treatment of biomass with a catalytic amount of H₃PW₁₂O₄₀ leads to formation of three fractions: solid, liquid and gas, which have been investigated by elemental analysis, TGA, FTIR, GC–MS and NMR. The use of heteropolyacid leads, at 300 °C, to a selective transformation of more than 50 wt.% of the holo-cellulose part of the lignocellulosic biomass. Moreover, 60 wt.% of the catalyst H₃PW₁₂O₄₀ are recovered.

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1. Introduction

The steady depletion of fossil fuels resources throughout the world as well as ecological and sustainable development issues have turned current research interest for alternative fuel sources (Menon and Rao, 2012). Biomass is considered as renewable energy source. Its contribution to the global warming is negligible compared to fossil fuels, because of its ability to fix CO₂ from the atmosphere. Moreover, employing biofuels is reported to give a positive effect with respect to current greenhouse gas emission (Menetrez, 2012; Pires et al., 2012). Biofuels can be divided into first, second and third generation. First generation comprises liquid biofuels originated from corn, sugarcane, soybean, oil palm, etc. The most common first generation biofuels is bio-ethanol.

However these sources are considered as unsustainable, mainly due to their use of food feed (Poganietz, 2012). Second-generation biofuels originates from non-edible biomass sources, such as lignocellulosic materials, forest residues and wastes. The synthesis of second generation biofuels is indeed independent on the use of crops for food consumption (Poganietz, 2012). However, extensive research efforts are required to make this process economical (Macrelli et al., 2012). The third generation biofuel is known also as Oilgae. It is believed that the cost of their production is low. Moreover, the energy produced as biofuel per acre is higher compared to the land required by other conventional feedstock (Nigam and Singh, 2011). Nevertheless, the production of fuels from microalgae is still at its early stage of development (Fiorese et al., 2013). On the other hand, biorefineries for second generation biofuel production can easily be implemented and size adapted just near the lignocellulosic material, this is not the case for the algae resources.

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The transformation of lignocellulosic materials to biofuel as well as chemical feedstocks, requires thermal or thermocatalytic treatment. The challenge lies in depolymerizing the complex structure of the cellulose, hemicellulose and lignin and ideally further upgrade without decomposition into CO, CO₂ and H₂O. A possibility to circumvent this is to perform the thermolysis at lower temperature. It is reported that during the thermal decomposition process of lignocellulosic biomass, the holocellulose is decomposed first followed by lignin at higher temperatures (Gronli et al., 2002). In the case of the pine wood, it was found that the decomposition of the holocellulose starts at 275 °C and the lignin decomposes at ca. 350 °C (Larabi et al., 2013). Furanic compounds including furfural were released during the decomposition process (Larabi et al., 2013; Sagehashi et al., 2006). Upon hydrotreatment, furfural can be converted to methylfuran (Sitthitha et al., 2011), which is reported to have a high octane number and can be used as additive for conventional fuels (Roman-Leshkov et al., 2007). Some of the thermal reactions such as dehydration, depolymerization and even decarboxylation can be catalyzed by solid acidic catalyst (Chheda and Dumesic, 2007; Wan et al., 2009). Solid acids under oxidative conditions are largely used in the transformation of the wood into paper pulp (Gaspar et al., 2007), and cellulose into chemicals (Deng et al., 2012; Guo et al., 2012; Tian et al., 2010). Herein, we focus on the transformation of pine wood, in the presence of acid catalysts under reductive condition in order to lower the temperature of the thermolysis, to produce valuable chemicals, reduce the formation of CO and CO₂ and the potential cost.

For this purpose, the thermal decomposition of pine wood was performed in batch and dynamic reactors, under hydrogen, at temperature lower than 300 °C in the presence of Keggin heteropolyacid (H₃PW₁₂O₄₀). Keggin type heteropolyacid was chosen for its stability and strong acidity, which is more pronounced than of typically used strong mineral acids (Cui et al., 2011). Moreover, heteropolyacid maintains its property in the liquid phase as well as a solid by precipitation or grafting on supports (Marme et al., 1998; Rao et al., 2005; Shimizu et al., 2009). During this investigation, three main fractions were collected, quantified and characterized, by various techniques including FTIR, GC–MS, elemental analysis and solid state NMR.

2. Experimental

2.1. Materials

The lignocellulosic biomass used is originated from pine wood. It was grounded in a Retsch type RM100 mortar mill, and then sieved to give particle size less than 0.5 mm. In order to distinguish between the water formed during the decomposition process and the physisorbed, the wood dust was pretreated and dried at 110 °C, then stored in the glove box.

γ-Al₂O₃ (Puralox TM 50/150, Sasol), SiO₂–Al₂O₃ (Azko Nobel), ZSM-5 (Sasol), SiO₂ (Evonik aerosil-200), H₃PW₁₂O₄₀·24H₂O (HPW, Phosphotungstic acid hydrate), H₃PMo₁₂O₄₀·24H₂O (HPMo, Phosphomolybdic acid hydrate), H₄SiW₁₂O₄₀·24H₂O (HSiW, Silicotungstic acid hydrate), H₄SiMo₁₂O₄₀·24H₂O (HSiMo, Silicomolybdic acid hydrate), (Aldrich) were used as received. 11-Molybdo-1-vanadophosphoric, H₄SiMo₁₁VO₄₀·24H₂O (HSiMoV), and 10-Molybdo-2-vanadophosphoric H₄SiMo₁₀V₂O₄₀·24H₂O (HSiMoV₂), acids were synthesized according to the literature (Tsigidino and Hallada, 1968; Berndt et al., 1998). Their purity was checked by ³¹P and ²⁹Si liquid-NMR.

2.2. Characterization of product

2.2.1. In-operando DRIFTS-GC/MS

The experiments were carried out in an integrated system comprising mass flow controllers (Brooks), FT-IR adapted high

temperature reaction chamber (Harrick Scientific) and online GC/MS (Agilent GC 6850 MS 5975C). The reaction chamber was equipped with ZnSe windows and fitted into the Praying Mantis optical unit also provided by Harrick. In the glove box, about 15 mg of pine wood were placed onto a porous stainless steel frit in the reaction chamber. A selected gas (argon or hydrogen) was continuously flowing through the pine wood bed. FT-IR spectra were recorded in a Nicolet 6700 spectrophotometer with a MCT detector and 4 cm⁻¹ resolution. The formed compounds were separated by a MS compatible 25 m PORA BOND Q column and analyzed in the online GC–MS.

2.2.2. Nuclear magnetic resonance (NMR) characterization

Solution NMR spectra were recorded on BRUKER AVANCE 300 spectrometer (¹H: 300.1 MHz, ¹³C: 75.4 MHz; ³¹P: 121.5 MHz; ²⁹Si: 59.6 MHz). Chemical shifts were measured relative to 85% H₃PO₄ aqueous solution for ³¹P. ²⁹Si chemical shifts are referenced to Me₄Si in DMSO-*d*₆ using the substitution method.

Solid state NMR spectra were collected on BRUKER AVANCE III 500 spectrometer operating at 202.5 MHz for ³¹P, 125 MHz for ¹³C. The zirconia impeller of 4 mm is filled with the desired product and sealed with a kel-f stopper. It was then transferred into the probe Bruker CP 4 mm spectrometer allowing rotation of the rotor at a speed of 10 kHz. The time between two acquisitions was always optimized to allow complete relaxation of the protons.

2.2.3. Elemental analyses (C, H, and N)

Microanalyses were performed at the Welience – Pôle Chimie Moléculaire Faculté des Sciences Mirande (Dijon, France), using CHNS/O thermo electron flash 1112 Series elemental analyzer.

2.2.4. Ex situ IR analysis

Diffuse reflectance Fourier-transformed infrared (DRIFT) spectra were recorded on a Nicolet 6700-FT spectrometer using a cell equipped with CaF₂ window. Typically, 64 scans were accumulated for each spectrum (resolution 4 cm⁻¹).

2.2.5. IR quantification of the CO and CO₂ analysis

The quantification of evolved CO and CO₂ was performed by transmission FT-IR spectroscopy using a Nicolet 5700-FT spectrometer and infrared cell equipped with CaF₂ windows. Typically, 64 scans were accumulated for each spectrum (resolution 1 cm⁻¹). To estimate the amount of gases (CO, CO₂) in the reactor during the pyrolysis by FTIR technique, the IR detector was calibrated toward CO and CO₂. A calibration curve was obtained by reporting for a given gas pressure the corresponding area related to their asymmetric stretching frequency integrated between 2220–2140 cm⁻¹ for CO and 2400–2250 cm⁻¹ for CO₂. The calibration curve is provided in Fig. S.1.

2.3. Design of experiments

A mixture of grounded wood and a desired amount of heteropolyacids (HPA) was stirred in water at 25 °C for 1 h. After evaporation of water at 60 °C, the impregnated wood was dried 2 h at 80 °C under vacuum (10⁻⁵ mbar), then stored in glove box. A mixture of grounded wood and 10 wt.% of solid acid (SA) was mechanically mixed, dried 2 h at 80 °C under vacuum (10⁻⁵ mbar), then stored in glove box.

2.3.1. Thermogravimetric analysis

Approximately 10 mg of the sample was placed in an Al₂O₃ crucible and heated under 30 mL min⁻¹ of nitrogen. Three independent decomposition studies were performed, (i) the weight loss from room temperature to 700 °C in the presence of 10% in weight of solid acid (SA) or heteropolyacids (HPA) with a heating rate of

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