

Depolymerization of acetosolv lignin through in-situ catalytic fast pyrolysis

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Resumen. La valorización de corrientes secundarias tal como la lignina Acetosolv es clave en el desarrollo de biorrefinerías de materiales lignocelulósicos. La pirólisis rápida, un proceso termoquímico que convierte biomasa en un producto líquido, actualmente es de particular interés para la producción de compuestos químicos. Sin embargo, la pirólisis rápida convencional de lignina presenta problemas de alimentación, debido a su bajo punto de fusión, aglomeración del lecho y bajo rendimiento de líquidos altamente oxigenados. En este trabajo, se investigó el efecto catalítico de la co-alimentación de CaO y el uso de olivina como material del lecho, para superar estos obstáculos. Se utilizó un sistema de laboratorio de pirólisis rápida con capacidad de alimentación de 0.1 kg/h, para depolimerizar aserrín de pino y lignina Acetosolv a 540 °C. Una caracterización profunda de la fase orgánica utilizando resonancia magnética en estado sólido y líquido proporcionó información estructural más detallada del líquido pirolítico en comparación con las técnicas de caracterización convencionales. Los resultados principales mostraron que la adición de CaO mejoró la alimentación de la lignina dentro del reactor, mientras que se observó un aumento del rendimiento líquido en presencia de olivina. El uso combinado de CaO y olivina pareció ser más beneficioso, ya que mostró el rendimiento más alto de líquido de lignina pirolítica, a pesar de la falta de reproducibilidad.

Palabras Claves: pirólisis rápida, pino, lignina, catálisis

Abstract. The valorisation of secondary streams such as Acetosolv lignin is a key issue in the development of lignocellulosic biorefineries. Fast pyrolysis, a thermochemical process that converts biomass into a liquid product, is currently of particular interest for chemical production. However, conventional fast pyrolysis of lignin presents feeding problems, due to their low fusion point, bed agglomeration and low yield of highly oxygenated liquids. In this work, we investigated the catalytic effect of co-feeding CaO and the use of olivine as bed material to overcome these hurdles.

A laboratory fast pyrolysis system with a feed capacity of 0.1 kg/h was used to depolymerize pine sawdust and its Acetosolv lignin at 540 °C. An in-depth characterization of the tarry phase using solid and liquid-state nuclear magnetic resonance provided a more detailed structural information of the pyrolytic liquid products over conventional characterization techniques. Main results showed that the addition of CaO improved the feeding of lignin into the pyrolytic reactor, while an increase in liquid yield was observed in the presence of olivine. The combined use of CaO and olivine appeared to be the most beneficial, as it displayed the highest liquid yield, despite of the lack of reproducibility. Compared to quartz sand, the use of olivine alone decreased the liquid yield and increased the total amount of aliphatics in the tarry phase at the expense of aromatics. By displaying a high aliphatic content, the composition of liquid product revealed the efficient depolymerization of lignin. It is also important to note that the presence of olivine promoted the deoxygenation of the overall liquid. The catalytic activity of olivine was attributed to the presence of iron, known as a tar destruction agent in gasification.

Keywords: fast pyrolysis, pine, lignin, catalysis

1. Introduction

Urged by a need of diversifying its pool of technologies to produce renewable energy, Chile with its natural dotation of woody biomass- is an attractive place to develop and apply new thermochemical conversion technologies. Consequently, a fast pyrolysis process using a three-stage fluidized bed reactors system with a feed capacity of 25 kg/h was developed at UDT (1). Fast pyrolysis converts biomass mainly into a liquid product, which is currently of particular interest for chemical and energy production (2). If the whole biomass composed of hemicelluloses, cellulose and lignin may be easily converted,

conventional fast pyrolysis of lignin presents feeding problems due to its low fusion point, bed agglomeration and low yield of highly oxygenated liquids (3). Despite these technical hurdles, the few studies that successfully converted lignin using fast pyrolysis indicated the presence of high value compounds such as phenols, guaiacols and aldehydes (Sedat H. Beis 2010). To overcome some of these technical issues, the addition of CaO is currently investigated (4). The authors concluded that the addition of the CaO decreases the oxygen content of bio-oil by reducing the concentration of levoglucosan in favor of acetol.

In this work, we investigated the catalytic effect of co-feeding CaO and the use of olivine as bed material to overcome these hurdles. In a first part, the study presents the preliminary work done on a small fast pyrolysis set-up whose experimental conditions have been subsequently applied to the larger scale.

2. Materials and methods

2.1 Feedstocks and preparation

Pinus radiata D. Don sawdust was provided by BSQ Ltda, a forest company located in Concepcion (Chile). The woody material was sieved to obtain a particle size in the range of 0.5-1.5 mm. The moisture content of the woody material was maintained at 10 wt.%. The Acetosolv lignin was prepared from the same *Pinus radiata* wood chips using the so-called Acetosolv process (Berg, Fuentealba & Salazar, 2014). The woody material was delignified using a 87 wt% acetic acid solution at 185 °C for 2 hours. The dissolved lignin was precipitated by diluting the spent pulping liquor with water. The filtered lignin was washed with water. Since the pulping method is sulfur and sodium free, the Acetosolv lignin has low ash and contains almost no covalently bound sulfur in comparison to others extracted lignin originating from the kraft process (5).

The mixture of sawdust and CaO (1:1 wt/wt) was roller-compacted using a Lab Tech Engineering compactor (Model LRM-M-100).

2.2 Catalysts: CaO and bed materials

CaO purchased from Furet (Chile) was dried at 110 °C before use. Two different types of mineral bed materials such as quartz and olivine were respectively purchased from Quipasur (Chile) and Vidrios Lirquen (Chile). Olivine mineral, which is a magnesium-iron silicate, $(\text{Mg}^{+2}, \text{Fe}^{+2})_2 \text{SiO}_4$, is well known to favor the degradation of tar (6). Quartz, which is mainly composed of SiO_2 is in general used as bed material in the fluidized-bed reactor.

2.3 Fast pyrolysis at 0.1 kg/h

The fast pyrolysis (FP) plant (Figure. 1) can be divided into four sections: the biomass-feeding unit, the cylindrical furnace housing the bubbling fluidised bed reactor, one hot-gas filter as separation stage, and the condensation chain. The biomass feeding unit consisted of a hopper with a screw feeder, which introduced biomass (particle size 250–2000 μm) at a feed rate of ± 0.03 -0.06 kg/h into the reactor. The hopper was maintained at a slight N_2 overpressure (± 0.02 bar gauge, gas flow rate of 6 L/min) to prevent hot gas and product vapour pushing back from the reactor into the feeding system. Bed material such as quartz or olivine was used as the heat carrier inside the reactor and fluidized using

a N₂ gas flow rate of 9 L/min. Pyrolysis product vapours left the furnace via a heated pipe (maintained at 400 °C to prevent undesired intermediate condensation) before entering the hot gas filter. The condensation chain consisted of a water-cooling tower followed by an electrostatic precipitator set to 14 kV.

The bio-oil, product of interest, is collected from the condenser tower and precipitator and thus consisted of two single phases corresponding to aqueous and tarry fractions. The char product was recovered from the hot-filter pot, while the non-condensables gases were purged to the atmosphere. Experimental runs were duplicated at 540 °C with a running time between 13 and 60 mins.

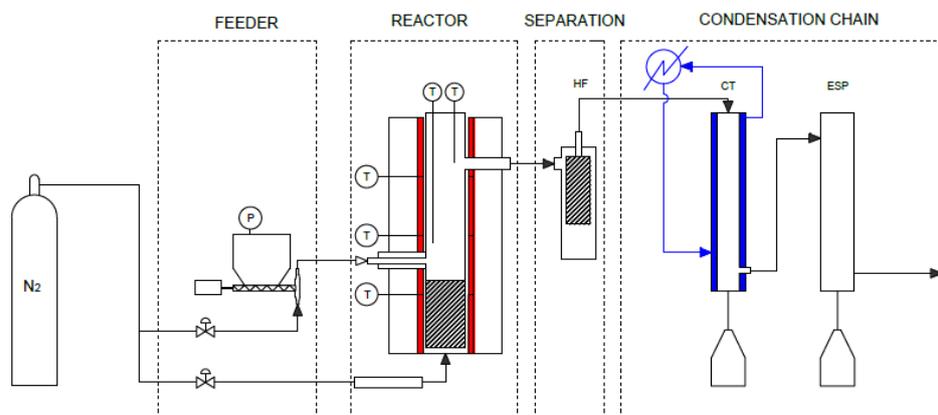


Figure 2. Fast pyrolysis set-up (8).

All product yields (Y_{product}) reported here were calculated on a mass basis (wt.%) of the initial biomass feed (m_{biomass}) as indicated by Equation 1. The liquid yield represents the total liquid product yield without correcting for bio-oil water content.

$$Y_{\text{product}}(\text{wt.}\%) = \frac{m_{\text{product}}}{m_{\text{biomass}}} * 100 \quad \text{Equation (1)}$$

where m_{product} and m_{biomass} are respectively the mass of recovered product and of pyrolyzed biomass.

2.4 Characterization of products

The water content of liquid fractions was determined using a Mettler Toledo V20 volumetric KF Titrator (ASTM E871) using the Combititrant 5 (Merck) as reactive. Ultimate analysis was conducted on both liquid and char products using a Thermo Finnigan Flash EA model (Serie 1112). Ash content of lignin, sawdust and chars was determined in accordance with the ASTM E1131 standard procedure for proximate analysis using a TGA TG209 F3 Tarsus (Netzsch).

Quantitative ¹³C NMR analysis: Chemical functional groups of char and tarry products were determined using nuclear magnetic resonance (NMR), on a Bruker Avance DSZ 400 MHz spectrometer. Quantitative ¹³C NMR were acquired using ~140.0 mg tarry oil dissolved in 900 μL DMSO-d₆ or ~100.0 mg of char dissolved in 900 μL DMSO-d₆ employing an inverse gated decoupling pulse sequence, 90° pulse angle, a pulse delay of 5 s for tarry oils, and 12 s for char. The ¹³C NMR spectra were acquired with a 90° pulse duration of 2.4 μs, and a sweep width of 25,000 Hz and 30,000 Hz for liquids and chars.

Spectra were processed using Bruker TopSpin 3.1. The chemical shift values were calibrated on the solvent peak.

HPLC analysis: The HPLC-RID analyses were performed using a Shimadzu LC-20AT SIL 20A system on two 150 x 7.8 mm columns Phenomenex Rezex ROA- Organic Acid H⁺ in series maintained at 75 °C. The mobile phase composition was sulphoric acid aqueous at 0.0075 M. An aliquot of 0.03 g of tarry phase was diluted in 24 mL of distilled water and 1 mL of methanol (HPLC grade, Sigma-Aldrich), while 500 µL of aqueous product was diluted into 25.0 mL of distilled water. Injection volume of 10 µL of samples was used with the eluent flow rate fixed at 0.6 mL/min.

3. Results and discussion

Overall liquid yields for biomass, 52.3 and 43.5 wt% were respectively obtained in the presence of quartz and olivine at 540 °C. These yields were found lower to the reported literature value of 69.5 wt% for *Pinus sylvestris* sawdust achieved in an equivalent scale (7). Although the compaction and addition of CaO allowed the lignin to be fed into the fluidized bed reactor, only a significant increase from 9.9 to 32.0 wt% in the production of liquids was observed in the presence of olivine. The combined use of CaO and olivine appeared to be the most beneficial as it displayed the highest liquid yield for pyrolysis of lignin. When considering the results and lack of reproducibility, the cracking ability of olivine becomes apparent with decreasing liquid yield in favor of gas yield for pine and lignin conversion.

Total aromatic and aliphatic contents of heavy fractions (Table 1), which are in accordance with literature (8), indicate a substantial decrease of the aromatic fraction using olivine as bed material. Based on ¹³C NMR results between 43.1 and 58.8 % of the carbon from the tarry fraction are aliphatic carbons. This result confirms the capability of olivine to depolymerize lignin, whose catalytic effect could be attributed to the presence of Fe considered as a tar destruction agent in gasifiers (9). In addition, concentrations of hydroxyacetaldehyde (HA), levoglucosan (LG), acetol (AC), formic acid (FA), acetic acid (AA) and glyoxal (GL) originating mainly from degradation of cellulose originally measured by HPLC at levels of ~12, 4, 4.5, 3.0, 1.2 and 0.8 wt % in the aqueous fraction and of ~2.5, 4.2, 1.5, 1.2, 0.8 and 0.6 wt% in the tarry phase for the sawdust pine, respectively declined to 10, 2.4, 2.1, 2.9, 0.8 and 0.7 wt% and to 1.4, 2.3, 1.0, 7.4, 0.5 and 0.2 wt%. These findings confirm a change in conventional degradation pathways of the whole biomass (10) and that the decomposition of lignin and conversion of lignin derivatives are promoted by the olivine as mineral bed material.

The addition of olivine also decreased the oxygenated aromatic fraction of pine sawdust tarry phase (from 20.2 % to 10.5 % determined by NMR), result corroborated by the elemental analysis that showed a decrease in oxygen content from 59.5 to 48.9 db, wt% and of char from 2.4 db, wt% to none. If limited changes of chemical functionalities were observed for chars from NMR analysis (Table 1), the elemental analysis indicated a substantial increase of the O content using CaO.

Table 1. Effect of bed material and co-feeding of CaO on yields and the quality of bio-oil from fast pyrolysis of Pine sawdust and Acetosolv lignin.

Biomass – Pine	Sawdust		Lignin			
Feed rate (g/min)	1.0 ± 0.1	0.9 ± 0.2	0.5	0.5	0.6 ± 0.4	0.7 ± 0.1
Run time (min)	60	60	15	13	60	60
Bed/catalyst material	Quartz/-	Olivine/-	Quartz/-	Olivine/-	Quartz/CaO	Olivine/CaO
Y _{liquid} (wt%)	52.3 ± 4.0	43.5 ± 0.6	17.3 ± 5.5	9.9 ± 3.6	20.7 ± 2.2	32.0 ± 7.1
Y _{char} (wt%)	8.9 ± 0.3	10.0 ± 2.2	30.2 ± 17.8	11.1 ± 4.3	36.1 ± 5.6	39.5 ± 7.9
Y _{gas} (wt%) ^a	38.8 ± 4.1	46.5 ± 1.7	52.5 ± 12.4	79 ± 0.7	43.2 ± 3.5	28.5 ± 15.0
Total aromatics _{tarry} ^b	58.0 ± 7.5	29.9 ± 19.2	58.10	39.90	75.3 ± 3.5	42.0 ± 12.5
Total aliphatics _{tarry} ^b	29.7 ± 4.3	58.8 ± 31.5	27	52.6	13.9 ± 5.7	43.1 ± 11.7
Total aromatics _{char} ^b	74.0 ± 6.6	64.3 ± 2.6	nd	nd	58.9 ± 16	53.3 ± 16
Total aliphatics _{char} ^b	24.8 ± 4.3	22.4 ± 1.3	nd	nd	32.2 ± 5.9	29.0 ± 4.7
O _{tarry} (db.wt%) ^a	36.3 ± 1.0	44.6 ± 2.6	nd	nd	nd	nd
WC _{tarry} (wt%)	5.6 ± 1.0	13.1 ± 0.4	nd	nd	nd	nd
O _{aqueous} (db.wt%) ^a	73.3 ± 3.5	53.5 ± 4.4	nd	nd	nd	nd
WC _{aqueous} (wt%)	36.3 ± 3.4	28.2 ± 5.8	nd	nd	nd	nd
O _{total-Liquid} (db. wt%) ^a	59.5 ± 2.3	48.9 ± 3.5	nd	nd	nd	nd
O _{total-Char} (db. wt%) ^a	2.4	0	nd	nd	8.84	21.23

^a by difference, ^b obtained by addition of three aromatic fractions measured by NMR, nd: not determined

4. Conclusions

In this study, it has been demonstrated that olivine as a mineral bed material has capability to crack the lignin-derived aromatics into aliphatics during the in-situ catalytic fast pyrolysis of pine sawdust and lignin. The combined use of olivine and CaO, respectively used as catalytic bed and base catalyst co-fed with the feedstock, favored the deoxygenation of the overall liquid. Despite the success of feeding lignin into a fluidized bed reactor, a new reactor design or an alternative co-feeding preparation is required to improve liquid yields obtained from fast pyrolysis lignin.

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