

# Characteristics of Char produced by means of Slow Pyrolysis of Residual Lignin from Bio-ethanol Production Chain

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## Introduction

The production of ethanol from lignocellulose is growing rapidly, and by looking at the industrial activities in this field steam explosion is by far the most applied pre-treatment technology allowing the delignification of the lignocellulosic feedstock. Formed sugars are further converted by simultaneous saccharification and fermentation to ethanol, and residual lignin is used as energy source. Lignin is a racemic, heteropolymer consisting of three hydroxycinnamyl alcohol monomers differing in their degree of methoxylation: p-coumaryl, coniferyl and sinapyl alcohols. The distribution of the three alcohols in lignin is dependent on the source feedstock. Moreover, lignin chemistry and structure can be modified on dependence of the extraction method from the biomass matrix [1, 2].

The residual lignin from ethanol production is underutilized with about 60 % more lignin generated than is needed to meet internal energy use [3, 4]. The exploitation of this residue for the combined production of biofuels and added value chemicals and materials present a key factor for the increase of the efficiency of the overall ethanol production chain. Pyrolysis can be explored as a possible thermal treatment capable of producing, in the absence of molecular oxygen, a solid residue (char) suitable for application in several fields and a liquid (bio-oil) and gaseous products that can be exploited for energy applications or as a chemicals' source [9].

Review of the literature suggests many possibilities for valorizing char potential for diverse applications such as fuel in traditional and advanced power generation facilities, fertilizer and carbon sink, contaminant adsorbent in wastewater and soil, adsorbent or catalyst for gas cleaning, catalyst for syngas conversion to liquid hydrocarbons and biodiesel production, raw material for supercapacitors and filler in wood and polymer composites [5-8]. The data from previous studies show that pyrolysis chars [10, 11] vary greatly in structure and chemistry due, in part, to the large degree of chemical heterogeneity of the feedstock. At our knowledge char deriving from pyrolysis of residual lignin from ethanol production has received less attention with respect to the liquid product. It has been tested as growth enhancer and as substitute for carbon-black in rubber [12]. In this paper a preliminary study on the solid residue obtained from the thermal treatment of residual lignin spanning from torrefaction to pyrolysis temperature range has been conducted. Torrefaction and pyrolysis tests were performed under slow pyrolysis conditions. Chemical physical analyses were carried out on the solid residues in order to investigate changes in the elemental composition, volatile matter content and porosity characteristics (BET pore volume and pore size distribution) as a function of the temperature.

## Experimental

Lignin samples were pyrolyzed at slow heating rate (7 °C/min) in the temperature range 300 – 700 °C with the experimental apparatus reported in Figure 1.

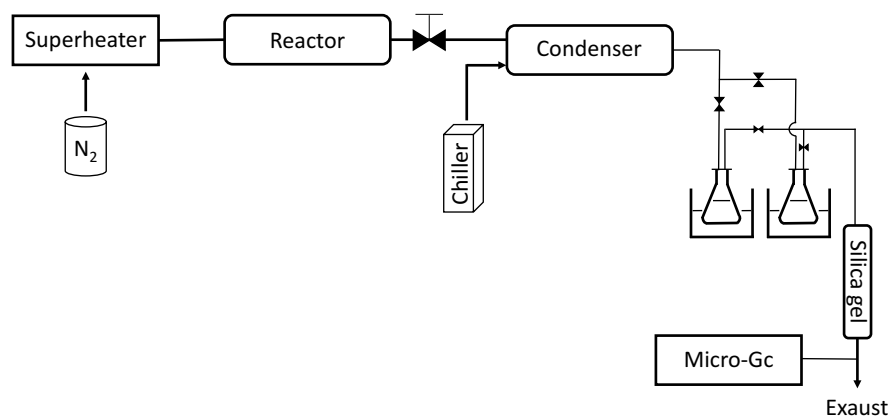


Fig. 1: Schematic diagram of the experimental apparatus.

The pyrolysis reactor described in [12] consists of a prismatic jacketed chamber ( $L = 0.024$  m,  $W = 0.04$  m,  $H = 0.052$  m) into which 6 g of sample are loaded. The sample holder comprises 4 trays allocated uniformly along the rectangular cross section of the inner reaction chamber, where biomass is loaded in thin layers (approximately 1 mm thick). A superheater placed before the jacketed reactor heats the carrier gas to the programmed temperature with the aid of a PID controller. The carrier gas flows into the jacket at a constant gas flow rate (3.09 N L/min). Then the flow is reversed towards the pyrolysis chamber, passing through a ceramic flow straightener before entering in the chamber. The temperature is monitored using N-type thermocouples along the main dimension of the rectangular sample trays. At the end of each experimental test, the char yield was determined gravimetrically, with respect to the fed sample, using a MS105DU (Mettler Toledo) laboratory balance with 0.01 mg resolution. Two replicates of each experiment were conducted and the average values and corresponding standard deviations are reported in the results.

The lignin samples and the chars produced at different temperature were characterized through proximate analysis using TGA701 LECO using ASTM E870 procedure. Ultimate analysis (carbon, hydrogen and nitrogen content) was performed with an elemental analyzer CHN 2000 LECO analyzer, using EDTA as standard based on CEN/TS 15104. The oxygen was obtained by difference considering the measured C, H, N and ash content calculated on dry basis (db).

The higher heating value (HHV) of the lignin and the chars was calculated, based on their elemental composition on dry basis, using the Dulong formula. The characterization of lignin was reported in Table 1.

Sample	C	H	N	O	HHV	moisture	volatiles	fixed carbon	ash
	wt % db				MJ/kg db	wt % as recieved			
Lignin	38.1	6.8	0.2	46.8	16.9	20.4	55.4	17.8	6.4

Tab. 1 Elemental and proximate analysis of lignin sample.

Characterization of the char samples' pores was carried out by applying gas adsorption porosimetry. Adsorption/desorption isotherms were obtained using  $N_2$  at  $-196$  °C as the adsorbate in an Autosorb-1 (Quantachrome) apparatus. Before analysis, the samples were degassed at  $300$  °C for 5 hours under vacuum conditions. The surface area was evaluated using the BET equation. The determination of micropore volume and area was performed using the t-plot method. The total pore volume of the samples was estimated from a single  $N_2$  adsorbed point at a relative pressure ( $P/P_0$ ) of 0.95. The mesopore volume was calculated using the BJH pore size distribution theory.

## Results

Fig. 2 shows the yields of the pyrolysis products at increasing final temperature. The devolatilization of the most volatile compounds determines the release of permanent gases (gas) and condensable products (liquids) even at low temperature. At 300 °C about 40 wt % of the raw lignin decomposed and was released in form of liquid product whose yield reached about 31 wt%. By increasing the temperature up to 400 °C a significant release of both gaseous and liquid species occurred at the expense of the solid residue (char), whereas at higher temperature only a small decrease of char yield was observed. A different behavior was observed for commercial alkali lignin that shows a significant weight loss up to 700 °C [13]. In the whole temperature range the char yields obtained from the lignin residue are lower than the ones typically obtained from thermogravimetric analysis of commercial alkali lignin [13]. This is probably due to the presence of volatile sugars deriving from not hydrolyzed cellulose and hemicellulose in the lignin rich residue.

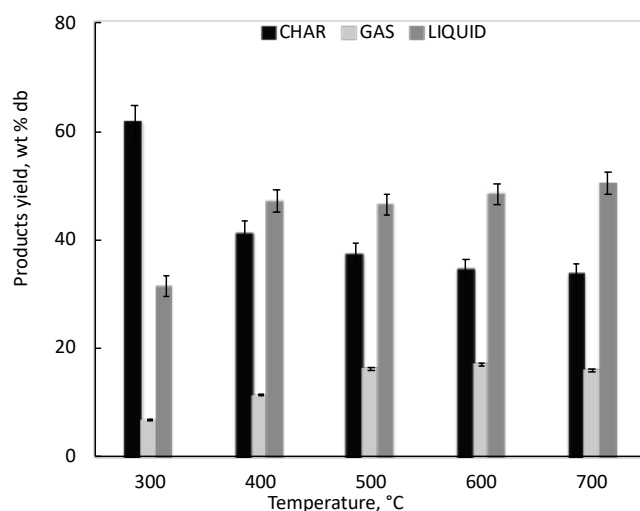


Fig. 2: Pyrolysis products yields at different final temperatures.

The results of elemental analysis, reported in Table 2, show that an increase of temperature determine the reduction of the hydrogen content in the whole temperature range. A corresponding increase of carbon content is observed up to 500 °C, whereas at higher temperature only small variations have been detected.

T	C	H	N	O+ash
°C	wt % db			
300	58.5	4.6	0.5	36.4
400	63.6	3.2	0.4	32.9
500	69.4	2.4	0.4	27.8
600	69.8	1.7	0.4	28.2
700	71.6	0.9	0.4	27.1

Tab. 2 Elemental analysis of chars at different final pyrolysis temperatures.

A preliminary characterization of chars porosity shows that the char produced at 300 °C has a compact structure, whereas the increase of the final pyrolysis temperature enables the development of an internal porosity corresponding to BET surface values similar to the ones typically obtained for chars obtained from woody and herbaceous feedstocks. The maximum BET surface, 289.6 m<sup>2</sup>/g, was obtained for the char produced at 600 °C. It is worth to be noted that chars obtained from steam assisted pyrolysis of commercial alkali lignin conducted in the same reactor under similar thermal conditions, showed a compact structure even at high pyrolysis temperature [14]. The difference could be ascribed to the higher content of volatiles in the lignin rich residue (c.f. Table 1) with respect to the alkali lignin [15], but also to the

presence of a rigid structure not significantly altered by the enzymatic hydrolysis pretreatment of biomass undergoing fermentation process.

## Conclusions

The study represents a preliminary characterization of chars obtained from slow pyrolysis at different final temperatures of lignin rich residue from bio-ethanol production. The aim is to assess the possibility of valorizing this residue that is only partially utilized for fulfilling the energy requirements of the process. The char yields, the elemental composition and the porosity characteristics allow to deduce that lignin rich residues has a thermal behavior very different from the alkali lignin typically used as reference compound for biomass lignin. The BET values of chars obtained at final temperature in the range 500 -700 °C seems to be promising for char application in processes involving surface phenomena (e.g. adsorption, catalyst support), thus encouraging further analyses on porosity characteristics and surface chemistry.

## References

- [1] Raes, J., Rohde, A., Christensen, J.H., Van de Peer, Y., Boerjan, W., *Plant Physiol.* 133 (2003) 1051–1071.
- [2] Ebringerova, A., Heinze, T., *Macromol. Rapid Comm.* 21 (2000) 542-556.
- [3] Kleinert, M., Barth, T., *Energy Fuels* 22 (2008) 1371-1379.
- [4] Stewart, D., *Ind. Crops Prod.* 27 (2008) 202-207.
- [5] Kambo, H.S., Dutta, A., *Renew. Sustain. Energy Rev.* 2015, 45, 359-378.
- [6] Qian, K., Kumar, A., Zhang, H., Bellmer, D., Huhnke, R., *Renew. Sustain. Energy Rev.* 2015, 42, 1055-1064.
- [7] Lehmann, J., Joseph, S., 2009. *Biochar for Environmental Management*. Earthscan, London.
- [8] Das, O., Sarmah, A.K., Bhattacharyya, D., *Waste Manage.* 2015a, 38, 132-140.
- [9] Ragauskas A. J., Beckham G. T., Biddy M. J., Chandra R., Chen F., Davis M. F., Davison B. H., Dixon R. A., Gilna P., Keller M., Langan P., Naskar A. K., Saddler J. N., Tschaplinski T. J., Tuskan G. A., Wyman C. E., *Science* 2014, 344, 1246843.
- [10] Zanzi, R., Sjoström, K., Bjornbom, E., *Biomass Bioenergy*. 2002, 23, 357-366.
- [11] Lee, Y., Park, J., Ryu, C., Gang, K.S., Yang, W., Park, Y., Jung, J., Hyun, S., *Bioresour. Technol.* 2013, 148, 196-201.
- [12] De Wild, P. J., Huijgen, W. J., & Gosselink, R. J., *Biofuels, Bioproducts and Biorefining*, 2014, 8, 645-657.
- [13] Ferreiro, A.I., Giudicianni, P., Grottola, C.M., Rabaçal, M., Costa, M., Ragucci, R., Unresolved issues on the kinetic modeling of pyrolysis of woody and nonwoody biomass fuels, *Energy Fuels*. 2017, 31, 4035-4044.
- [14] P. Giudicianni, G. Cardone, R. Ragucci, Cellulose, hemicellulose and lignin slow steam pyrolysis: Thermal decomposition of biomass components mixtures, *J Anal Appl Pyrol* 2013, 100, 213-222.
- [15] C. Couhert, J.M. Commandre, S. Salvador, Is it possible to predict gas yields of any biomass after rapid pyrolysis at high temperature from its composition in cellulose, hemicellulose and lignin?, *Fuel*, 2009, 88, 408-417.