**A study on the adsorption on activated carbons as upgrading technology for Kraft lignin pyrolytic gas**

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**1. Introduction**

Environmental and climate issues deriving from the exploitation of fossil resources led scientists towards the development of more ecological solutions to achieve the carbon neutrality within 2050 [1]. Biochemicals and biofuels production has raised in recent years attempting to reduce carbon dioxide emissions deriving from the combustion of non-renewable resources [2]. Lignocellulosic biomasses can represent one of the most promising alternative feedstocks due to their carbon matrix and their great availability [3]. In particular, from 10 to 30 wt. % of lignocellulosic biomass is represented by lignin, an aromatic-rich compound whose thermal degradation can have a key role in the in the production of bio-based relevant compounds[4]. Among all the different types of commercial lignin, almost 80% is obtained from Kraft process. In this process, Kraft lignin (KL) isolation is obtained by means of a solution of NaS2 and NaOH (black liquor), and for this reason the final lignin still contains 3-4 wt.% of sulfur [5]. In particular, previous results of our group [6] showed that KL pyrolytic gas is rich in CH4, CO, CO2, and H2S with the presence of other sulfur compounds in smaller amount (i.e., CH3SH, CH3-S-CH3, SO2, COS, and CS2). In this work, the thermal degradation in inert environment of KL at 550°C has been studied, and the distribution of sulfur compounds in the gas phase formed during the cracking at high temperature has been investigated. The composition of the gas has been characterized and then compared to the one obtained forcing the gas to pass through a fixed bed of activated carbon with a high selectivity in the adsorption on S-containing compounds. Four different commercial activated carbons were adopted with different adsorption capacities and pore dimensions.

**2. Methods**

In this work, commercial Kraft lignin has been received from StoraEnso® (LineoTM Classic Lignin, Kotka, Finland). Lignin morphology was investigated using scanning electron microscopy (SEM), while the elemental composition in terms of C, Na, S, and O content was determined through energy-dispersive X-ray spectroscopy (EDX). The pyrolysis has been carried out in an inert environment and batch conditions at 550 °C for 3 hours. The total absence of oxygen inside the reactor is guaranteed by a nitrogen purge performed before each test in order to avoid the occurrence of combustion reaction. The setup is characterized by a reaction unit constituted by a furnace where a quartz tubular reactor is collocated. This section is followed by a separation unit constituted by a Liebig condenser where condensable reaction gases are cooled and collected in a flask. Non-condensable gases have been collected in a latex balloon after forcing them to pass in a column packed with different commercial activated carbons. The efficiency of the adsorption process has been evaluated by comparing the results so obtained with those of a control test performed with the same setup without the adsorption bed. Qualitatively, the composition of the produced gas has been investigated using Fourier Transform Infrared Spectroscopy (FT-IR). A quantitative analysis of S-containing compounds was conducted injecting 100 µL of reaction gas every 45 minutes in a gas chromatography–mass spectrometer (GC–MS).

**3. Results and discussion**

In Figure 1 the FT-IR spectra of the pyrolysis gas of the control test (a) and the gas after the adsorption on activated carbons (b, c, d, e) have been reported. Even though most of the sulfur compounds produced during the pyrolysis cannot be detected using FT-IR analysis, the band at 2062 cm-1 can be attributed to the presence of COS. However, this band is only observable in the control test where the gas is not adsorbed on the activated carbon. Moreover, the band around 2364 cm-1 due to the presence of the CO2, has a decreasing intensity signal when adsorbed on the activated carbon bed. An activated carbon with high selectivity towards hydrogen sulfide, would likely interact with CO2 because of its acid character. This results in a gas richer in CH4 whose peaks at 3016 and 1304 cm-1 do not seem to be remarkably affected by the interaction with the bed.



**Figure 1.**FT-IR analysis of pyrolytic gas for control test (a), and after the adsorption on activated carbons (b, c, d, e).

In order to monitor the evolution of sulfur compounds from a quantitative point of view, the GC-MS analysis has been performed and the peak area related to sulfur compounds has been evaluated. H2S resulted the most abundant compound present in the gas phase, with relevant amounts of COS and CH3SH too. Data have been expressed as the ratio between the peak area of the sulfur species normalized with the total area. The concentration of H2S, COS and CH3SH undergoes a remarkable drop after their interaction with the adsorption bed of activated carbon. Preliminary data from GC-MS show a reduction of the relative abundance of H2S from 2.2% to 0.01%. COS and CH3SH, whose relative abundance in control test is 0.2 and 0.8%, respectively, exhibit almost a total adsorption on the activated carbon bed.

**4. Conclusions**

Two different setup configurations have been compared to understand how a coupling of pyrolysis and one pot adsorption could affect the distribution of sulfur compounds in the pyrolytic gas of a commercial Kraft lignin, thus leading to the development of new process outlines. The effect of the adsorption is clearly observed in the disappearing of the band at 2062 cm-1 related to the presence of COS. From a quantitative point of view, a decrease of the peak areas of H2S, COS and CH3SH is revealed from the GC-MS analysis. Other sulfur compounds, i.e CH3-S-CH3, SO2 and CS2 that were also present in conventional test, were not detected in significant amounts after the adsorption on activated carbons. Thus the proposed upgrading process would be feasible for a sulfur rich pyrolytic gas cleaning.

**References**

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