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Research paper

Catalytic effect of ZSM-5 zeolite and HY-340 niobic acid on the pyrolysis of industrial kraft lignins

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ABSTRACT

Catalytic pyrolysis studies of industrial Kraft lignins were performed using two acid catalysts: a widely known commercial zeolite (ZSM-5) and a relatively unexplored acid catalyst (HY-340) which has desirable properties, besides having a low cost compared to traditional pyrolysis catalysts. Vapor composition data were determined by a micropyrolyzer coupled to a gas chromatograph and a mass spectrometer (Py-GC/MS). The effects of operational parameters such as pyrolysis temperature and concentration of the catalyst added to the two lignins were also investigated. In addition, for a better understanding of the thermal decomposition kinetics of the studied biomasses, thermogravimetric analyses were also carried out at different heating rates. The results obtained showed that the use of ZSM-5 as a catalyst in the pyrolysis reaction of both lignins promotes the formation of aromatic hydrocarbons. This increase in the selectivity for hydrocarbons reached a maximum area of 91% for lignin 1 and 89% for lignin 2. Whereas the use of HY-340 resulted in an increase in the selectivity for hydrocarbons, mainly alkanes, which reached a maximum area of 92% for lignin 1 and 82% for lignin 2.

1. Introduction

Lignin, which is a macromolecule that confers rigidity to trees and is present in about 25–30% of eucalyptus wood, for example, can become an alternative source of chemical products of high added value for the chemical industry. In the traditional process of pulp production, lignin is one of the components, alongside hemicellulose, of the so-called *black liquor*, a liquid whose burning in boilers is used intensively by the pulp and paper industry for the production of energy. Alternatively, Kraft lignin with the calorific value that corresponds approximately to two thirds of the average fuel oil can be obtained or separated from the black liquor resulting from the cooking process of the timber. Previous studies reported in the literature suggest that lignin has the potential to be used as a carbon source for the production of epoxy resins, adhesives, polymers, phenolic resins, polyolefins, etc. (Stewart, 2008). However, the effective use of lignin for the production of more valuable products is still very limited, mainly due to its structural complexity (Li and McDonald, 2014). It is estimated that less than 2% of the lignin coming from the paper industry is presently being used in production bases or more valuable chemicals (Farag et al., 2014; Gosselink et al., 2004). This information shows that there is a vast field to be explored in the sense of developing new technologies for the conversion of lignin to chemical products with higher added value.

Fast pyrolysis is a technology for the thermal degradation of materials so as to produce a condensable vapor fraction, generally called bio-oil, with yields of up to 75 wt.% (Tumbalam Gooty et al., 2014). This bio-oil can be used directly as a fuel or it can have a variety of more specific applications. Generally, due to the structural complexity of the lignin mentioned above, various kinds of phenols are produced resulting in a bio-oil with a very diverse chemical composition. Additionally, several problems are common in the operation of the continuous reactor of fast pyrolysis of lignin, such as the locking of the screw feeder, excessive agglomeration of the bed particles and subsequent defluidization problems, as well as the formation of preferential channels which affect the fluidization quality of the mixture inside the reactor (Nowakowski et al., 2010; Tumbalam Gooty et al., 2014). Lignin is the most resistant component to heat among the major components of the lignocellulosic biomass. Due to this feature there is a greater residual char formation during the pyrolysis of lignin when compared with other lignocellulosic biomasses (Bu et al., 2014).

Micropyrolysis is a fast and reliable analytical technique which provides useful preliminary information for the development of the complex process of bio-oil production (Oliveira et al., 2015). The micropyrolyser coupled to a gas chromatograph and a mass spectrometer (Py-GC/MS) is widely used to carry out an efficient evaluation of the composition of vapors generated in the pyrolysis of biomass (Carvalho et al., 2015). Consequently, the analytical pyrolysis can provide important information as to the catalytic effect on the decomposition of

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biomass. Py-GC/MS is also used to investigate the influence of catalysts in the production of hydrocarbons and other desirable chemicals before conducting experiments in equipment on a larger scale (Mullen and Boateng, 2010).

Lignin has been intensively investigated as a raw material for the production of chemical products from pyrolysis with higher added value. Several studies reported in literature mention the catalytic effects on the lignin pyrolysis process. According to Wang et al. (2015), there was an increase in selectivity for phenolic compounds in alkaline lignin pyrolysis with addition of KCl, $CaCl_2$ and $FeCl_3$. Ohra-aho and Linnekoski (2015) demonstrated an increase in the formation of aromatic hydrocarbons in pyrolysis of Kraft lignin in the presence of acidic zeolites HZSM-5 and zeolite Kim et al. (2015) investigated the effect of HZSM-5 with different Si/Al mole ratios and the origin of aromatic hydrocarbon from lignin pyrolysis products. The yield of aromatic hydrocarbons increased with increasing catalyst acidity. Shen et al. (2015) evaluated the formation of aromatics in the catalytic pyrolysis of lignin in the presence of five types of zeolite (HZSM-5(25), HZSM-5(50), HZSM-5(210), H-β and H-USY). HZSM-5 was the most effective in promoting the formation of aromatic monomers from lignin pyrolysis at 650 °C, while H-USY increased the selectivity for aromatic hydrocarbons.

Previous studies have shown that the catalytic pyrolysis of biomass with solid acid catalysts such as zeolite aluminosilicates plays an important role in the thermochemical conversion of biomass. These types of acid catalysts, such as ZSM-5, tend to have desirable physicochemical properties, such as strong Brønsted acidity, greater tolerance to water, tunable acidity and high thermal stability. All these properties are necessary for the production of aromatic hydrocarbon (Engtrakul et al., 2016). The complex porous structure of zeolites is an important physical property that can influence the thermal conversion process in a selective manner (Jae et al., 2011) Medium pore zeolites such as ZSM-5 for example, have a pore size which is considered ideal for converting cellulosic biomass into aromatics with low coke formation (Jae et al., 2011).

Niobium oxide is an insoluble white solid that is stable in air, characterized as inert, including a mesoporous structure (Almeida and Marques, 2016). Brazil is the world's leading producer of niobium, with the production of more than 90% of all world-wide niobium compounds (Nowak, 2012). The niobic acid catalyst ($Nb_2O_5{\cdot}nH_2O$) has been used in various reactions because of its acidic properties. Niobic acid is considered effective as a catalyst for dehydrating alcohols, hydrolysis, oxidation, esterification, alkylation, isomerization and photocatalysis (Nowak and Ziolek, 1999). However, there are few studies as to the use of niobic acid and its derivatives as catalysts in the fast pyrolysis process of biomass. The acidity of niobic acid is high, with Brønsted acid and Lewis acid sites (Carniti et al., 2006), which are desirable properties for catalysts in pyrolysis processes.

Considering the aspects mentioned above, the development of the catalytic pyrolysis of industrial Kraft lignins was studied, aiming primarily at the production of hydrocarbons. For this, ZSM-5 zeolite and hydrated niobium pentoxide (HY-340) were used as catalysts. The novelty of this work is the use of HY-340, a catalyst little explored in pyrolysis process, which has desirable properties, such as the high selectivity to alkanes and the lower cost when compared to commercial zeolites. The composition of the vapor generated in analytical pyrolysis was determined using a gas chromatograph and a mass spectrometer. The effects of operational parameters such as the pyrolysis temperature and the concentration of catalyst added to the two lignins were also investigated. Moreover, to understand better the thermal decomposition kinetics of biomasses studied, thermogravimetric analyses at different heating rates were also performed. The results will be important for the development and improvement of pyrolysis processes of lignin concerning the catalytic pyrolysis for the production of higher added value compounds.

Table 1
Results of elemental analysis, proximate analysis, true and apparent density and higher heating value for the Kraft lignins.

Elemental analysis[a] (%)				
	C	H	O[b]	S
Lignin 1	52.01	5.00	27.84	2.91
Lignin 2	54.60	5.19	31.58	2.51

Proximate analysis[a] (%)				
	Moisture	Volatile matter	Ash	Fixed Carbon
Lignin 1	8.56	52.86	12.24	26.34
Lignin 2	13.09	60.63	6.12	20.16

True density (g/cm^3)		standard deviation (g/cm^3)
Lignin 1	1.4318	0.0006
Lignin 2	1.3908	0.0001

Apparent density (g/cm^3)		standard deviation (g/cm^3)
Lignin 1	1.2239	0.0167
Lignin 2	1.0956	0.0275

Higher heating value[a] (MJ/Kg)		standard deviation (MJ/Kg)
Lignin 1	18.77	0.08
Lignin 2	19.16	0.11

[a] dry basis.
[b] Calculated by 100%-C−H–S-ash.

2. Materials and methods

2.1. Biomass and catalyst

Industrial Kraft lignins of eucalyptus, provided by Suzano Paper and Pulp (Suzano-Brazil), with different levels of ash were used in this study. Lignin 1 has 12.24% of ash, while lignin 2 has 6.12%. Both lignin materials were extracted from the black liquor from a plant of eucalyptus pulp production which uses the Kraft process. Table 1 shows the results of elemental analysis, proximate analysis, true density, apparent density and higher heating value for two Kraft lignins. The lignin and carbohydrate content for similar lignin samples can be found in Dehne et al. (2016). Lignin content determined for this study was 82.8% and carbohydrate content was 1.3%.

Table 2 shows the results of size distribution, performed by laser diffraction on a MALVERN® MASTERSIZER 2000 equipment and the results of particle morphology, carried out by dynamic analysis of images in CAMSIZER L and CAMSIZER XT equipment, both of RETSCH®. In the MASTERSIZER, dry analysis was performed with sample dispersion by means of compressed air at a pressure of 1.4 atm. For analysis using CAMSIZER, due to the wide range of particle size distribution shown by the samples, these were previously sieved and separated into two size ranges and analyzed considering different detection ranges. The retained fraction (> 0.15 mm) was analyzed using CAMSIZER L and that which passed through (< 0.15 mm) was analyzed using CAMSIZER XT X-Flow accessory equipment by dispersion in deionized water.

Table 2 shows the values of D[10], D[50] and D[90], where 10% of the particles have a diameter smaller than D[10], 50% of the particles have a diameter smaller than D[50] and 90% of the particles have a diameter smaller than D[90]. The D[10], D[50] and D[90] values for lignin 1 are larger than those for lignin 2, indicating that the lignin 1 particles are larger.

Table 2 also shows the average values of roundness and aspect ratio