

SYRINGOL PRODUCTION IN THE PRESENCE OF NiO/H-ZSM-5: INFLUENCE OF LIGNIN ORIGIN AND LIGNIN DEPOLYMERISATION METHOD

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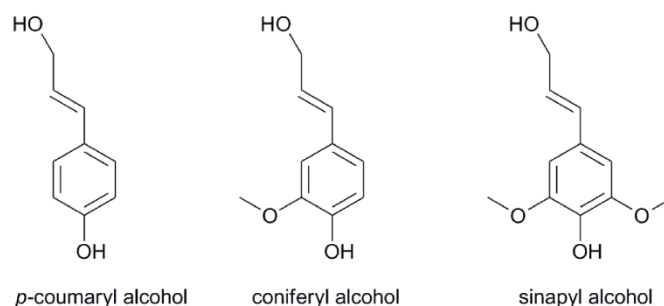
ABSTRACT

The decomposition of two types of hardwood lignins {eucalyptus (EL) and a mixture of birch and aspen woods (BA)} to syringol was studied by a microwave-assisted depolymerisation (MWD) and intermediate pyrolysis (IP) using NiO/H-ZSM-5 zeolite as a catalyst. The catalyst prepared by mechanochemical dry milling (MCDM) method contained bunsenite nano-NiO particles with an average size of 67 nm in concentration of 3.5 wt. % NiO. The results show that the depolymerisation method influenced the bio-oil yield, while the lignin type affected only bio-oil yield from MWD method. The highest bio-oil yield was obtained using BA MWD (20 wt. %). On the other hand, the syringol production showed a highly dependence on both depolymerisation method and lignin type. The highest syringol production (~11 wt. %) was obtained by IP procedure and EL as the feedstock.

Keywords: Lignin, Pyrolysis, Microwave, Zeolite, Syringol

INTRODUCTION

Use of lignocellulosic biomass as feedstock for the production of high added value chemicals, materials and fuels have attracted a significant attention in the last decade. Lignin is the second most important component of lignocellulosic biomass exceeded only by cellulose, representing about 4-35 wt. % of most biomass, 16-25 wt. % of hardwoods and 23-35 wt. % of softwoods^[1]. Lignin is an amorphous, aromatic biopolymer comprised of three different types of phenylpropane building units – monolignols: *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol^[2] (Scheme 1).



Scheme 1. The phenylpropane building units².

The main products of lignin depolymerisation are monophenolic organics, such as phenol, guaiacol or syringol, which are industrial important chemicals. Syringol (2,6-dimethoxyphenol) is a highly value-added chemical used in food and pharmaceutical industries. Lignin depolymerisation is a highly challenging task and numerous efforts have been attempted in order to establish technologies capable to decompose lignin into useful chemicals^[3]. Chemical, biochemical and thermal treatment have been usually applied^[2,3]. Recently, lignin pyrolysis at atmospheric pressure and at moderate temperatures (about 500 °C) has been recognized as a suitable method for the production of biofuels and chemicals^[4,5]. Microwave (MW) heating has also be reported as a promising method providing homogeneous distribution of heat at molecular level and preventing formation of undesired products^[6,7].

Accordingly, the aim of this study was to investigate the influence of lignin origin and lignin decomposition method on the syringol production. EL and BA were used as lignin sources. MWD and IP were used for the lignin depolymerisation in the presence of nano-NiO-containing H-ZSM-5.

EXPERIMENTAL

H-ZSM-5 (Zeolyst International) was modified with Ni(NO₃)₂ • 6H₂O (p.a. Aldrich) using a MCDM method^[2]. A mixture of the Ni(II) salt and H-ZSM-5 was ground during 10 min at 350 rpm in a Retsch PM-100 planetary ball mill using a 125 mL reaction chamber and 10 mm stainless steel balls. The obtained products were then calcined at 400 °C for 4 h under air. The calcined product was characterized by different characterization techniques including X-ray diffraction method (XRD), N₂ physisorption and transmission electron microscopy (TEM). Ni content was determined by an inductively coupled plasma mass spectrometry.

MWD was conducted in a Milestone ETHOS-1 at 180 °C using formic acid as a proton-donor solvent. IP was performed in a fixed-bed reactor under nitrogen at 500 °C^[2,8]. The resulting liquid phase (bio-oil) was analyzed by a GC/MS.

RESULTS AND DISCUSSION

The prepared catalyst contained about 3.5 wt. % of NiO with an average diameter of 67 nm. The PXRD patterns show that the milling did not significantly affect the crystallinity of the ZSM-5 (Figure 1). The pattern of the Ni-containing zeolite displays additional diffractions at $2\Theta = 37.2, 43.3, 62.9$ and 75.4° that correspond to bunsenite (NiO) phase. This is also supported by detailed TEM analysis shown in previous work^[2].

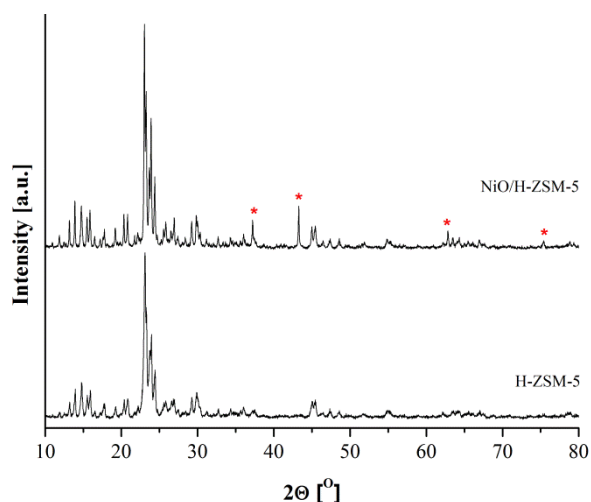


Figure 1. PXRD patterns of H-ZSM-5 and NiO/H-ZSM-5. Diffractions of bunsenite NiO have been marked with asterisks.

Data given in the Table 1 indicate that both NiO formation and the milling procedure slightly affected the textural properties of H-ZSM-5. Both pore diameter and volume increased after the modification.

Table 1. Selected properties of the zeolites used in this study.

Catalyst	Si/Al	NiO (wt. %)	Surface Area (m ² g ⁻¹)	Pore volume (mL g ⁻¹)	Pore diameter (nm)
H-ZSM-5	30	/	330	0.24	2.90
NiO/H-ZSM-5		3.5	330	0.29	3.50

The bio-oil yields (Table 2) obtained by IP showed no dependence on lignin type, being similar for both lignin types (17 wt. %). However, the bio-oil yield obtained by MWD was higher for BA (20 wt. %) than for EL (12 wt. %), showing a significant dependence on lignin type.

Table 2. Yields of bio-oil and syringol.

Decomposition process	Lignin type	Bio-oil Syringol	
		wt. %	
MWD	BA	20	3.4
	EL	12	2.1
IP	BA	17	7.8
	EL	17	10.7

On the other hand, the syringol content in the bio-oils depends on the decomposition method and lignin origin (Table 2). Higher content of syringol was obtained by IP than by MWD. Moreover, EL gave a higher syringol yield than BA by IP method (opposite trend is evident for MWD). The decomposition process and lignin origin influenced the syringol production in the following order: EL IP (10.7 wt. %) > BA IP (7.8 wt. %) > BA MWD (3.4 wt. %) > EL MWD (2.1 wt. %).

CONCLUSION

The obtained results show that the bio-oil yield obtained by intermediate pyrolysis method does not depend on the lignin origin in contrast to that obtained by microwave assisted depolymerisation. Later gave the highest bio-oil yield using the mixture of birch and aspen woods as a feedstock. On the other hand, the highest content of syringol is obtained by the eucalyptus intermediate pyrolysis which leads to conclusion that this method can be considered for syringol production from lignin biomass.

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