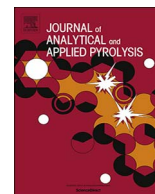




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## Effect of particle size of HZSM-5 zeolite on the catalytic depolymerization of organosolv lignin to phenols

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## ABSTRACT

The effect of particle on the catalytic activity of HZSM-5 zeolite in organosolv lignin to phenols was investigated in the supercritical ethanol-water under the operating conditions of 350 °C and 4 h. Two samples comprising a micro and a nano size HZSM-5 were prepared by reflux and hydrothermal crystallization method, respectively. The catalyst samples were characterized with XRD, SEM, BET and NH<sub>3</sub>-TPD analytical techniques. The effect of crystal size on the lignin conversion to phenols and the structure changes of lignin residue were studied. The nano-HZSM-5 showed higher yield of phenols and lower yield of char as compared to the micro-HZSM-5. The enhanced content of aromatic C-C structures and extenuative content of aromatic C-O and C-H showed that intramolecular dehydration and deoxygenation were occurred with nano- and micro-HZSM-5, and the nano-HZSM-5 activity significantly stronger than micro-HZSM-5.

### 1. Introduction

The utilization of biomass for sustainable fuel production is progressively being regarded as a promising option strategy to contribute to substantial and long-term reductions in net greenhouse gas emissions [1,2]. Among the different thermo-chemical conversion processes, hydrogenolysis have been used to convert the biomass into various biofuel and biochemistry products [3–6]. Lignin is a heterogeneous aromatic biopolymer that accounts for nearly 30% of the organic carbon on Earth and is composed of three main phenylpropanoid units, namely sinapyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) unit and clearly is one of the few renewable sources of aromatic chemicals [7,8]. Organosolv lignin is produced mainly as a byproduct from pretreatments in the bioethanol industry and new biorefinery scheme (i.e., organosolv pulping), it may be a good source of valuable aromatic chemicals if it could be depolymerized into smaller molecular units [3,9,10]. The challenge, however, is that lignin is very difficult to depolymerize and generates very high amounts of solid residue as compared to other components of lignocelluloses [3,11,12]. Therefore, upgrading technologies that efficient depolymerization of lignin to a potential substitution of biochemistry products is necessary. Among these technologies, improving catalyst efficiency for hydrogenolysis reaction during the lignin depolymerization process appears to be pragmatic [13,14].

Many researchers have used solid acid of zeolite to upgrade the effect of lignin depolymerization during the thermo-chemical

conversion processes. For example, Inaba et al. reported that H-Beta [15] and USY [16,17] are effective for the pyrolysis reaction of woody biomass. Singh et al. [18] used one-pot solvolytic depolymerization and hydrodeoxygenation over zeolite HZSM-5 as catalyst and NaOH as co-catalyst to depolymerize Kraft lignin at 220 °C, and they indicated that HZSM-5 with NaOH as co-catalyst in water–methanol was found to be efficient in suppressing char formation and enhancing product quality and quantity. Ben et al. [2] used HZSM-5 zeolites with different SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratios from 23/1 – 280/1 as additives to depolymerize Kraft lignin at 600 °C, and they found HZSM-5 zeolite with a relatively higher SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mole ratio is more effective to improve the cleavage of methoxyl groups, ether bonds, and aliphatic C–C bonds, and dehydration of aliphatic hydroxyl groups. These results can be attributed to different Si/Al molar ratios have effect on surface acidity of HZSM-5 [19]. Consistent with the results of Kim et al. [20] and Aho et al. [21], they suggested that HZSM-5 having higher Si/Al mole ratio favors degrading aromatic C–C bonds as well as preventing recondensation between lignin pyrolysis products and produced more organic compounds. All of these studies indicated that the use of HZSM-5 during depolymerization process that had higher yield of lignin-derived biochemical. Most of the researchers have focused on HZSM-5 as a hydrodeoxygenation catalyst in depolymerization of lignin [18,20–22], while only a few have examined the effect of HZSM-5 itself catalytic activity on the depolymerization of organosolv lignin to phenols. The different Si/Al ratios and load types of HZSM-5 have been shown to

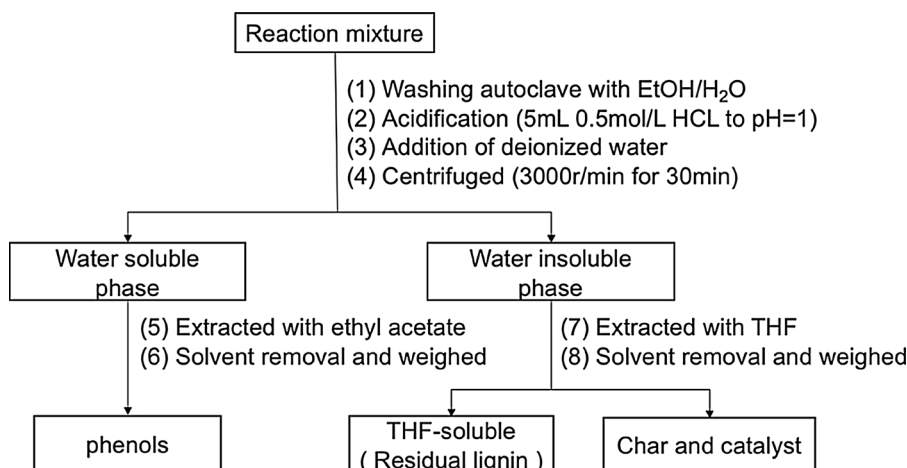
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Scheme. 1. Work-up procedure of reaction product mixture.



affect the cracking reactions of lignin during thermo-chemical conversion processes [2,20,23–25]. These reports have been indicated that different Si/Al and load types of HZSM-5 could provide different acidity to improve lignin conversion and inhibit coke formation in depolymerization of lignin. However, almost no researchers have investigated the influence of other physical properties (such as morphology and crystal size) of HZSM-5 on the acid properties and further influence lignin depolymerization products. We therefore hypothesized that the morphology and crystal size of HZSM-5 may also provide a simple and effective way to improve lignin conversion and product selectivity.

To test this hypothesis, two samples comprising a micro and a nano size HZSM-5 were prepared by reflux and hydrothermal crystallization method, respectively. Their detailed characterization studies such as surface area, morphology, crystal size, weak acid, strong acid and total acid were conducted to understand the properties of micro- and nano-HZSM-5. The goal of the influence of micro and nano size of HZSM-5 on the lignin conversion and product selectivity was accomplished by using GC-MS, GC-FID,  $^{13}\text{C}$  NMR and GPC.

## 2. Experimental

### 2.1. Chemicals

The reagent grade chemicals including tetrapropylammonium hydroxide (TPAOH, 20 wt.%), tetraethylorthosilicate (TEOS, 98 wt.%), aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), ethanol (EtOH, 99 wt.%), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ , 99 wt.%), Ethyl acetate (99.8%), anhydrous (99.9%) and solid NaOH were obtained from Sigma-Aldrich.

### 2.2. Lignin extraction from poplar wood

Lignin was extracted from poplar wood by the organosolv technique using ethanol/water as solvent according to our previous report [26]. A mixture of 80 g of poplar wood in 800 mL of ethanol/water (v/v, 60%) was stirred at 205 °C for 2 h. The mixture was cooled, filtered, and washed with solvent (ethanol/water). The ethanol-water soluble portion was concentrated to 200 mL at 50 °C under reduced pressure in a rotary evaporator (RV10 control, IKA Company, Germany) and poured into 600 mL distilled water to precipitate lignin. The precipitates were collected by membrane filtration and washed with acidic water (pH 2.0) for five times. After freeze drying, a dark brown lignin was obtained.

### 2.3. Catalyst preparation

Micro-HZSM-5 was synthesized according to Viswanadham et al.

[27] the procedure given by with some modification as follows: TEOS was used as silica source and NaOH was slowly added to this solution, followed by the addition of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and TPAOH. The components were mixed with constant stirring at room temperature. It is crucial at this point that the solution pH to be above 10. The mixture was stirred at the room temperature to obtain a clear solution before charging it in Teflon lined autoclave for hydrothermal synthesis at 180 °C for 3 days.

Nano-HZSM-5 zeolite was synthesized according to Abrishamkar et al. [28] using a clear solution under atmospheric conditions. Appropriate amounts of  $\text{H}_2\text{O}$ , NaOH, TPAOH and aluminum isopropoxide were mixed and agitated for hours to achieve a clear solution. TEOS was then added dropwise and agitated at room temperature for several hours for complete hydrolysis of TEOS. The achieved mixture was heated in an oil bath at 90 °C under atmospheric pressure (reflux) for 48 h. The product was then recovered by centrifugation for 30 min, washed several times with distilled water, dried overnight at 105 °C and calcined in air at 550 °C for 10 h. To produce HZSM-5 (i.e., with H<sup>+</sup> cation), the obtained zeolites were ion exchanged four times in a large excess of aqueous 1 M solutions of  $\text{NH}_4\text{NO}_3$  at 90 °C and calcined again at 550 °C for 6 h.

### 2.4. Catalytic reactions

The dried lignin (0.5 g) was dissolved in 50 mL ethanol-water (50:50, v/v) and combined with HZSM-5 (0.25 g) catalyst in a 100 mL Parr reactor equipped. The reactor was vacuumed at room temperature then heated to 350 °C under stirring and the desired temperature was established within 50–60 min. When the desired reaction time (4 h) was reached, the reactor was quenched in water. Upon reaching room temperature and the vessel carefully depressurized. The reaction mixture was observed as a yellow solution with gray solids at the bottom of the vessel.

A work-up procedure as shown in Scheme 1 was developed. The products from the reactor were washed with 20 mL ethanol/water (v/v, 50%), acidified to pH 1 and centrifuged at 3000 rpm for 30 min to separate water soluble and solid residue products. The solvent based separation of products was done with ethyl acetate. The solid residue was washed with excess THF over a filter crucible. The filter cake was retrieved, oven dried, weighed and regarded as char and catalyst. The dried cake was calcined in air at 550 °C for 10 h the obtained solid was retrieved, weighed and regarded as catalyst. The THF solvent was removed by rotary evaporation from the THF filtrate, the unconverted lignin and oligomer fragments of lignin were obtained as residual lignin.

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