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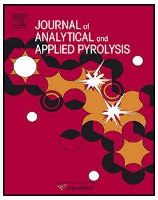

# Influence of HSAPO-34, HZSM-5, and NaY on pyrolysis of corn straw fermentation residue via Py-GC/MS

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## ABSTRACT

The lignin-rich biomass materials can widely be obtained from the resources of black liquor and lignocellulose fermentation residue. The reutilization of the waste lignin-rich biomass material relates to environment, energy, and materials, and thus worth for investigation with great enthusiasm. In this paper, the pyrolysis of corn straw fermentation residue (CSFR) under catalysis of three zeolites of HSAPO-34, HZSM-5, and NaY zeolite were investigated via the instrument of Py-GC/MS. The results showed that the main pyrolytic products were alkoxy phenols, alkoxy aromatics, 2,3-dihydro-benzofuran, alkyl phenols, and alkyl aromatics. Additionally, some acids, long-chain hydrocarbons, and saccharides were also identified. Comparatively alkyl aromatics could be more generated under the catalysis of HZSM-5, while NaY zeolite promoted the formation of phenol more distinctly. HSAPO-34 exerted a weakest influence to all product components with close similarities to the non-catalytic curves. The different catalytic behaviors of the three zeolites could be attributed to their different acidities and textural structures.

## 1. Introduction

Owing to the long time using of fossil fuels and the thereby aroused problems of energy deficit and ecological imbalance, development on renewable energy and reutilization of waste materials for alternative fuels and/or for chemicals are urgently demanded [1–3]. In recently years, thanks to the development of fermentation techniques, lignocellulosic biomass materials were more used for alcohol producing to save starch-rich crops [4,5]. However, how to utilize of the much generated fermentation residue became a big issue, since it cannot be used as livestock feed in large scale like the dried distillers grains (DDGS) [6,7], because of its little nutrition content. Pyrolysis could be a choice beyond combustion, with advantages of multi-products of energy and liquid fuels and/or chemicals, while the researches on fermentation residue related pyrolysis were rather rare at present.

Liang et al. [8] compared the pyrolysis of potato peel waste (PPW) with its fermentation residue (PPW-FR) by PY-GC/MS, and the phenolic derivatives and fatty acids were found more generated in the fermentation residue product system. Yang et al. [9] tested the pyrolysis of wheat straw fermentation residue through a fixed-bed reactor in the temperature range of 250 °C–550 °C under vacuum pressure of 5 mmHg. The water soluble fraction of the pyrolytic oil was analyzed by HPLC, and the result showed that there were plenty of organic acids in this liquid product, and glycolic acid was the major one. Orozco et al. [10] made a comparison between the pyrolysates of coffee pulp and its fermentation residue treated by *Streptomyces* using Py-GC/MS, and the products of monomethoxy and dimethoxy derivatives in the fermented product systems were found in lower contents than that in the untreated systems. We had investigated the pyrolysis of corn straw fermentation residue (CSFR) through a fixed-bed micro reactor under atmospheric pressure, and it was found that the liquid yield had a maximum value at 475 °C, with abundant components of phenols and fatty acids [11]. The pyrolysis of DDGS was investigated as well, and the product oil was found in rich of phenolic derivatives and fatty acids similarly [12,13]; additionally, the formation of phenol and alkyl phenols could be promoted with a reduced content of methoxy phenols under augmented pyrolytic pressures [12], while aromatics and phenol were more generated when catalyzed by CaO [13].

In this paper, the influences of the three zeolites of HSAPO-34, HZSM-5, and NaY on product distribution from pyrolysis of CSFR in the temperature range of 400 °C–800 °C were investigated through the instrument of Py-GC/MS for rapid catalyst evaluation.

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## 2. Materials and experimental

The corn straw fermentation residue was offered by Henan Tianguan Group. Approximate and ultimate analysis of the sample was showed in Table 1. It can be seen that the ash content in CSFR is rather high, even higher than most of conventional biomass materials [14,15].

Nuclear magnetic resonance spectroscopy (NMR) has been broadly used for solid fuel structure characterization [16]. Herein, the sample of CSFR was analyzed by $^{13}$C NMR and the relative contents of major organic groups were listed in Table 2. It can be seen that the material of CSFR is in rich of aromatic structure with abundant alkoxy groups.

The instrument of Py-GC/MS was a pyrolyzer (Model 5200, CDS Pyroprobe) combined with a coupled gas chromatography (Trace GC, Thermo Scientific) and a quadrupole mass spectrometer (ISQ MS, Thermo Scientific). The Py-GC/MS can be operated in two modes, the Py mode and the Trap mode. In the Py mode, the pyrolysate is directly carried away from pyrolyzer to GC/MS for analysis. In the Trap mode, the organic volatiles are first captured by an adsorption trap at 40 °C, and then released by elevated temperature up to 300 °C and carried away by carrier gas to GC/MS. Herein, the Trap mode was applied for test in atmospheric pressure. In each run, a fermentation residue sample (0.8 mg) was first loaded in a quartz tube, and then a catalyst (0.8 mg) was loaded neighbor to the biomass sample separated by a layer of quartz wool. The pyrolysis was carried out under a constant heating rate of 20,000 °C/s and stay at a final temperature ranged from 400 °C to 800 °C for 25 s in Ar atmosphere. The extremely high heating rate is achieved through an electrified electric coil twining round the quartz tube closely. The schematic diagram of the experimental system is showed in Fig. 1.

In the GC/MS system, a WAX column (30 m–0.25 mm–0.25 μm) was applied. The oven temperature program were set as follows: start at 40 °C holding for 3 min; then increase to 100 °C by 6 °C/min holding for 1 min; then to 180 °C by 6 °C/min for 2 min; then to 240 °C by 6 °C/min for 5 min; finally to 280 °C by 6 °C/min for 1 min. The GC inlet was set as 300 °C. The temperature of the transfer line between GC–MS is 280 °C; the ion source temperature is 250 °C with EI energy of 70 eV and m/e range of 2–500. The components were identified by searching in NIST library [17].

The data reliability of the experimental system was examined by repeated experiments without catalyst at 600 °C, and the maximum relative standard deviation of the contents (area percentages) of major liquid components was no higher than 15%, indicating an acceptable error level for discussion in this paper.

**Table 1**
Approximate and ultimate analysis of CSFR (%).

| $A_d$ | $V_d$ | $FC_d$[a] | $C_d$ | $H_d$ | $N_d$ | $S_d$ | $O_d$[a] |
|---|---|---|---|---|---|---|---|
| 32.34 | 45.39 | 22.27 | 41.07 | 3.97 | 2.13 | 0.21 | 20.28 |

d—dried basis; A—ash; V—volatile matter; FC—fixed carbon.

[a] Obtained by difference.

**Table 2**
$^{13}$C NMR analysis of CSFR.

| Classification | | δ[ppm] | CSFR |
|---|---|---|---|
| Aliphatic | $-\mathbf{C}H_3$ | 0–25 | 5.97 |
| | $-\mathbf{C}H_2$ | 25–51 | 10.78 |
| | $-O-\mathbf{C}H_3$ | 51–67 | 14.12 |
| | R**C**-O-R, R**C**-OH | 67–93 | 7.45 |
| Aromatic | Ar**C**-H | 93–129 | 23.88 |
| | Ar**C**-C | 129–148 | 22.14 |
| | Ar**C**-OH,Ar**C**-OCH$_3$,Ar**C**-O-Ar | 148–171 | 7.45 |
| Carbonyl carbons | −COO- | 171–187 | 3.85 |
| | —**C**=O | 187–235 | 4.36 |

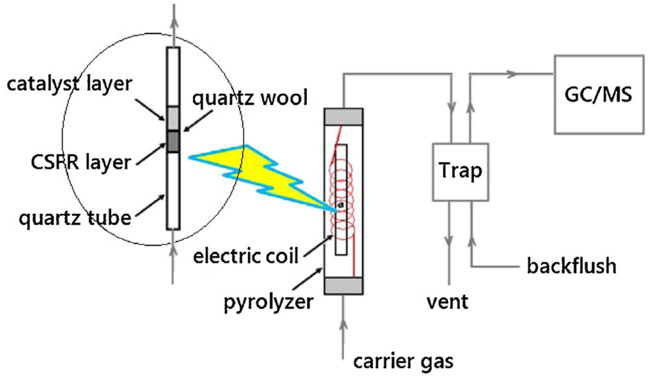

**Fig. 1.** Schematic diagram of the experimental system.

## 3. Results and discussion

### 3.1. TICs and major product components

The total ion chromatograms (TICs) of the pyrolysates obtained at 600 °C were representatively showed in Fig. 2. It can be seen that the main components are alkoxy phenols, alkoxy aromatics, 2,3-dihydro-benzofuran, alkyl phenols, and alkyl aromatics. Additionally, a little amount of acetic acid, *n*-hexadecanoic acid, 5-nonadecene, and D-allose are also identified.

The product distribution obtained under the catalysis of HSAPO-34 exhibited a close similarity to the non-catalytic one with a little bit reduced amount of toluene. When catalyzed by HZSM-5 and NaY, the amounts of toluene and phenol were augmented, and comparatively NaY exerted a more distinct role on phenol promotion, while toluene was more generated under the catalysis of HZSM-5. It indicated that HZSM-5 had a highest deoxygenation effect among the three zeolites, and NaY was in moderate level. The TICs can merely offer a coarse qualitative comparison among the non-catalytic and catalytic cases, so quantitative discussions were conducted in the following sections.

### 3.2. Catalytic effects on alkoxy compounds and alkyl phenols

The amounts (peak areas) of alkoxy compounds including alkoxy phenols and alkoxy aromatics, as well as alkyl phenols, varied with increasing pyrolytic temperature were showed in Figs. 3 and 4 respectively. It can be seen that with increasing temperature, the amounts of all alkoxy compounds exhibited a common regulation of increase first and then fall rapidly, while the amounts of alkyl phenols (including phenol) increased in early stage and then became stable or declined slightly. Alkoxy compounds and alkyl phenols are building blocks of lignin, and thus compose the majority of the products by initial pyrolytic decomposition of the raw structure at low temperatures. The primary products of alkoxy compounds and alkyl phenols may further convert to other components at high temperatures, and thus maximum amounts appeared in middle temperatures. The faster decreasing rate of alkoxy compounds than that of alkyl phenols at high temperatures indicated a higher conversion rate of alkoxy compounds than that of alkyl phenols.

The amounts of alkoxy compounds and alkyl phenols were generally decreased under the catalysis of the three zeolites at temperatures above 500 °C. Comparatively, NaY exerted a most remarkable role in promoting conversions of alkoxy compounds, the effect of HZSM-5 was the moderate, and the influence of