Effect of Using Regenerated Combined FAU and MOR Zeolites as Catalysts during the Pyrolysis of Kraft Lignin

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The SiO₂/Al₂O₃ mole ratio, pore size, and acid sites are the key parameters of zeolite's activity in lignin pyrolysis. In this study, the comparison of individual Y and M zeolites, the combined 'Y + M' sample after regeneration, and their effect on lignin pyrolysis were studied in five cycles (regeneration and reuse). The results were explained using Brunauer, Emmet, and Teller (BET), micropore surface area (MSA), and total acid sites (TAS) analyses. In comparison with the individual Y or M zeolite sample, the consistent higher catalytic activities of the combined 'Y + M' sample in repeated cycles were observed. Pyrolysis heavy oils were characterized by nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC). The NMR analyses revealed that with increased zeolite regeneration cycles, p-hydroxy phenyl and methoxyl groups increased. Decreases in guaiacyl phenolic hydroxyl were less for the combined 'Y + M' sample than the individual Y and M zeolites. Lower weight average (M_w) of heavy oil for the combined 'Y + M' sample indicated the enhanced cleavage of lignin structures in pyrolysis. These results support the higher catalytic activity of regenerated zeolites for the combined 'Y + M' sample compared with individual Y and M zeolites due to the improved MSA and TAS.

Keywords: Combinations; Kraft lignin; Pyrolysis; Regeneration; Zeolite

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INTRODUCTION

Lignin, a three-dimensional natural polymer, is one of the main constituents in lignocellulosic biomass, and could be an important renewable feedstock for aromatic chemicals (Calvo-Flores and Dobado 2010). Every year in the pulp and paper industry a large amount of pulping spent liquor, known in the industry as black liquor, is produced, which is the main source of kraft lignin, yet only a small fraction of lignin is converted to value-added products (Meier *et al.* 1993). Recently the conversion of lignin to value-added products, including lignin nanoparticles (Dai *et al.* 2019a; Ma *et al.* 2019), bio-oil (Mondal *et al.* 2020), and lignin-based hydrogel (Dai *et al.* 2019b) has received much attention in the research community.

Lignin liquification to produce chemicals and fuels is a subject of high importance for research proposing to develop future renewable supplies. Pyrolysis of lignin using zeolites as a catalyst (Kim *et al.* 2015, 2018) is one of the most promising methods for production of aromatic hydrocarbon such as benzene, toluene, xylene, and phenols (Li *et al.* 2015). When the zeolite catalyst converts lignin to products, coke deposits on the zeolite surface, which blocks the pores and covers the active sites of zeolites, consequently leading to deactivation (Marcilla *et al.* 2007; Hopkins *et al.* 2015). Due to the high price and large amounts of the zeolite catalyst required for use in industry, it is essential to recycle the catalyst and reuse it in a continuously operating plant (Ali *et al.* 2002). One of the most desirable alternatives is their regeneration to recover the lost catalytic activity (Kassargy *et al.* 2019). The regeneration process of zeolite catalyst depends on the process parameters, such as regeneration temperature, pressure, heating rate, heating time, and regeneration media (Jong *et al.* 1998; Ivanov *et al.* 2003; Thompson *et al.* 2005; Tsai 2006; Benamar *et al.* 2009; Khangkham *et al.* 2013).

Ma and Bokhoven (2012) regenerated the catalyst using a calcination process and found that during regeneration the heating rate is an important factor to maintain an intact catalyst structure. Fast heating rates can damage the structure of the zeolite (Ma et al. 2018). Marcilla et al. (2007) investigated different calcination temperatures during regeneration of HZSM5 and HUSY zeolites and found that calcination temperature is an important parameter during regeneration, and it depends on the thermal stability of zeolite structure (Marcilla et al. 2007). Moreover, Gerzeliev et al. (2018) observed no degradation of the zeolite structure by regeneration in hydrogen medium. They used zeolite Y in the PdCaLaH form and the regeneration process was carried out in hydrogen medium with a specific condition (320 °C temperature and 1.2 MPa pressure) and found that mild hydrocracking of hydrocarbon deposits on the catalyst surface occurs during the course of catalyst regeneration in a hydrogen stream. Although Wang et al. (2017) reported that no framework change or damage of the zeolite was caused by the regeneration process, the active acid site decreased when increasing the regeneration cycles (Wang et al. 2017). They studied the calcination process in the presence of oxygen to remove the deposited coke on theZSM-5 zeolite.

Ben and Ragauskas (2012) investigated the pyrolysis of lignin in the presence of various types of zeolites and observed that FAU (Y) and BEA (B) zeolites decomposed methoxyl-aromatic and ether bonds. The MFI (Z), FER (F), and MOR (M) zeolites decomposed the carboxyl groups in the lignin structure, resulting in the production of gasoline range molecular weight oil and low acidic bio oil (Ben and Ragauskas 2012). Aho *et al.* (2008) investigated the pyrolysis of pine using the proton form of different zeolite catalysts, such as beta, Y, ZSM-5, and mordenite as a bed material and found that similar distribution of different groups of chemicals (aldehydes, acids, alcohols, ketones, and phenols) in pyrolysis oil and mordenite formed little quantities of polyaromatic hydrocarbons (PAH) (Aho *et al.* 2008).

The FAU-type zeolite has three-dimensional porosity, 12-membered ring windows with a larger pore diameter (7.4Å), leads with a larger cavity of diameter (12Å), and 1.5 to 2.5 range of Si to Al molar ratio (Algieri *et al.* 2009; Dhainaut *et al.* 2013). Each cavity is surrounded by ten sodalite cages. The pseudo-linear channels of FAU zeolites help to diffuse bulk hydrocarbons and their super cages act as a nano reactor for cracking the hydrocarbons. As a result, they are used for catalytic cracking to convert heavy petroleum crude oils to high value-added products (García-Martínez *et al.* 2012). In contrast, mordenite (MOR) is one of the most industrially important (Vermeiren and Gilson 2009;

Martínez and Corma 2011) zeolites because it is active and shape-selective in many refining and petrochemical catalytic processes (Sie *et al.* 1996; Maxwell and Stork 2001). This is especially attractive on a structural point of view, since it contains two essentially different channels: 1) large 12-membered rings main channels, with an elliptical shape of 6.7×7.0 Å running along the c crystallographic axis; and 2) small 8-membered rings channels, considered side pockets are connected with dimensions of 2.6×5.7 Å (Katada *et al.* 2000; Baerlocher *et al.* 2007). Hydrothermally, MOR is stable (Wright and Pearce 2010). Table 1 indicates the detailed description about Y and M zeolites. The combination of FAU and MOR (the combined 'Y + M' sample) maintained the individual characteristics. No studies have been reported yet to show the catalytic effects of different regeneration times using the combined zeolites and their effect on pyrolysis of lignin. In previous studies, (Huang *et al.* 2014) combined 'Y + M', individual Y and M zeolites were used to catalyze the lignin pyrolysis and the results showed that the combined 'Y + M' sample had a catalytic performance that was in between the individual Y and M zeolites.

Based on previous work (Huang *et al.* 2014), in this paper, a comparative study of regenerating these zeolites (individual Y and M and combined 'Y + M' sample) and their reuse in the catalytic pyrolysis of kraft lignin was carried out. The goals of this study include: 1) to evaluate the effect of regenerating the combined 'Y + M' sample on the key parameters of zeolites in the lignin pyrolysis, such as: Brunauer, Emmet, and Teller (BET) and micropore surface area (MSA) and total acid sites (TAS) of zeolites; and 2) to study the performance of these regenerated zeolites during the subsequent lignin pyrolysis. The experimental techniques are 1D (13 C, 31 P) and 2D, hetero-nuclear single-quantum correlation (HSQC), nuclear magnetic resonance (NMR) spectroscopy, and gel permeation chromatography (GPC) for the analysis of pyrolysis heavy oil. Ammonia-temperature program desorption (NH₃-TPD) techniques were applied for the total acidity measurement of zeolites. Scanning electron microscope (SEM) images and BET analysis were used to observe the surface morphology change and measure the surface area (SA)/pore size (PS) during regeneration of zeolites. For comparison, a blank pyrolysis of kraft lignin without zeolites was performed.

EXPERIMENTAL

Materials

The ethylenediaminetetraacetic acid disodium salt and sulfuric acid were purchased from VWR International.

	CBV720	CBV21A	References
SiO ₂ /Al ₂ O ₃ Mole Ratio	30	20	(Ben and Ragauskas 2012)
Framework	FAU	MOR	(Ben and Ragauskas 2012)
Code Name	Y	М	(Ben and Ragauskas 2012)
Pore Dimension	3	1	(Ben and Ragauskas 2012)
PS (Å)	7.4 × 7.4	6.5 × 7.0	(Ben and Ragauskas 2012)
Decomposition Temp. (°C)	793	840	(Bhatia 1989; Mohamed <i>et al.</i> 2005)

Table 1. Detailed Description of Zeolites Used in this Study

The dimethyl sulfoxide-*d*₆, chromium acetylacetonate, 2-chloro-4,4,5,5tetramethyl-1,3,2-dioxaphospholane (TMDP), pyridine, chloroform-*d*₁, and tetrahydrofuran were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used in this study without further purification. Isolation of lignin was completed from commercial softwood kraft pulping (Ben and Ragauskas 2012). Two types of zeolites (CBV 720 and CBV 21A) were purchased from Zeolyst, Inc. (Kansas City, KS, USA).

Methods

Lignin separation and purification

Commercial softwood kraft pulping liquor was used as a raw material for the isolation of lignin by following published methods (Ben and Ragauskas 2012). To remove insoluble particles, the cooking liquor was first filtered by filter paper, and then ethylenediaminetetraacetic acid disodium salt (EDTA-2Na⁺, 0.50 g/100.00 mL liquor) was added to the filtrate with continuous stirring for 1 h. The pH of the liquor was maintained at 6.0 *via* addition of 2.0 M H₂SO₄ and stirred vigorously for 1 h. Then, the liquors were acidified further to a pH of 3.0 and frozen at -20 °C. At that time precipitation took place, and after melting, the precipitates (PPTs) were stored on a sintered glass funnel, for transferring the PPTs in the water. The PPTs were washed thoroughly with cold water (three times) and agitated vigorously at 0 °C for 1 h. The PPTs were collected and they were air-dried for Soxhlet extraction in the presence of pentane for 24 h to remove resin. The resulting solid product was air-dried at first, and it was further dried in high vacuum at 45 °C for 48 h. Then, the purified kraft lignin sample was stored at -5 °C until further use.

Preparation of pyrolysis sample

Pyrolysis samples were prepared by thoroughly stirring a mixture of kraft lignin (L) and zeolites with a 1:1 weight ratio. Before using, the zeolites were pre-activated in a pyrolysis tube under N₂ for 6 h at 500 °C. In this manuscript, the individual Y, M zeolites, and combined 'Y + M' sample, were used as catalysts. For comparison of pyrolysis a blank lignin sample (without zeolites) was also prepared. Equal amount of Y and M zeolite were mixed thoroughly to prepare the combination of 'Y+M' sample. A 1:1 weight ratio of the Y, M, and combined 'Y + M' sample was maintained.

Pyrolysis of lignin

For conducting pyrolysis experiments, a quartz pyrolysis tube was used that was heated in a split tube furnace (Ben and Ragauskas 2011b). In general, 6.0 g of sample was used for pyrolysis. Samples were placed into a quartz sample boat that was centered in a pre-heated pyrolysis tube. A thermocouple was dipped in the powder sample to assess the heating rate during pyrolysis. The furnace was pre-heated to 600 °C, and the pyrolysis tube was inserted into the furnace after flushing with N₂ at a flow rate of 500 mL/min. Two condensers were plunged in liquid N₂ so that the outflow directly passed through the furnace and left to cool at normal temperature with continuous N₂ flow. Then, the condensers were removed from liquid N₂ and the pyrolysis products (oil and char) were collected for analysis.

Generally, the liquid portions contained two non-miscible phases of heavy oil and light oil. The light oil was collected by decantation of the upper portion and the reactor was

washed thoroughly with acetone. The heavy oil was collected by evaporation of acetone under low pressure. Char yields and gas formation were calculated by gravimetric and mass difference, respectively.

Regeneration of zeolites

After the pyrolysis, the zeolites were recovered in the muffle furnace overnight at 550 °C. Under this condition, the residual char blocked in the pores of zeolite was oxidized into CO₂, and the activity of zeolite was regenerated. This was an effective process for removing the coke from the surface of zeolite catalyst. Similar procedures have been used by Benito *et al.* (1996) for zeolite catalyst regeneration. The retrieved zeolites were reactivated in the pyrolysis tube under N₂ at 500 °C for 6 h prior to compounding with fresh kraft lignin samples.

SEM characterization of zeolite

The fresh and recovered zeolites were imaged with a scanning electron microscope (LEO-1550; Carl Zeiss, Jena, Germany) with 10 kV acceleration voltages.

Measurement of BET SA of zeolites

The BET, SA, and PS of all the fresh and regenerated zeolites were obtained using a Micrometrics ASAP 2460 series instrument (Atlanta, GA, USA) *via* N₂ adsorption/ desorption isotherm patterns. Prior to the testing, all the samples were preheated at 300 °C for 4 h.

Measurement of the SiO₂/Al₂O₃ ratio of zeolites

The SiO₂/Al₂O₃ ratio of zeolite was evaluated by X-ray diffractometer (Rigaku RINT 2200, Tokyo, Japan) equipped with monochromator based on a literature method (Kosinov *et al.* 2015).

Measurement of total acidity of zeolites

The NH₃-TPD technique is a universal and simple method to evaluate the acid property of solid catalysts (Shao *et al.* 2018). The total acidity of the zeolite was measured using the NH₃-TPD technique, which was performed on a Quantachrome Chem BET Pulsar TPR/TPD automated chemisorption analyzer (Anton Paar, Graz, Austria). In the measurement process, approximately 0.1 g of zeolite was used for pretreatment under a flow of helium (99.9%, 120 cm³/min) at 300 °C for 1 h. Then, anhydrous ammonia was used at 100 °C for 10 min to saturate the zeolite. Afterwards, the zeolite was flushed with helium to remove any absorbed ammonia. Finally, the sample was heated in helium from an ambient temperature to 600 °C with an increasing rate of 10 °C/min and TPD analysis was completed by measuring the desorbed ammonia with a thermal conductivity detector (ChemBET Pulsar-TPR-TPD, Anton Paar, Graz, Austria).

Characterization of Pyrolysis Heavy Oil by NMR

Quantitative ¹³C-NMR

A Bruker Avance/DMX 400 MHz NMR spectrometer (Bruker, Billerica, MA, USA) was used to perform all NMR spectra in this study. For performing quantitative ¹³C-NMR, 100.0 mg of heavy oil was mixed in 450 μ L dimethyl sulfoxide- d_6 (DMSO- d_6) by applying a reverse gated decoupling pulse sequence, 90° pulse angle, a pulse delay of 20 s, and 6000 scans at normal temperature with a line-broadening (LB) of 5.0 Hz. To minimize the

measuring time, 1 mg/mL chromium acetylacetonate, a relaxation reagent, was added in the solutions.

Quantitative ³¹P-NMR

Prior to analysis of quantitative ³¹P-NMR, samples were prepared as follows: 10.0 mg of heavy oil was *in situ* derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) in a mixture of (1.6:1 v/v) pyridine/CDCl₃, chromium acetylacetonate (relaxation agent), and endo-N-hydroxy-5-norbornene-2,3-dicarboximide (NHND, internal standard). The ³¹P-NMR spectra data was acquired applying an inverse gated decoupling pulse sequence, a pulse angle of 90°, a 25s pulse cycle, and at room temperature 128 scans with a LB of 4.0 Hz.

Characterization of Pyrolysis Heavy Oil by HSQC-NMR

For HSQC-NMR analysis, the same type of sample was used as ¹³C-NMR. The HSQC-NMR were acquired by applying a standard Bruker pulse sequence "hsqcetgpsi.2" with a pulse angle of 90°, a 1.5 s pulse cycle, 0.11 s acquisition time, a ¹*J*_{C-H} of 145 Hz, 48 scans, acquisition of 1024 data points (for ¹H), and 256 increments (for ¹³C). The pulse widths and spectral widths of ¹H and ¹³C were p1 = 11.30 μ s, p3 = 10.00 μ s, and 13.02 ppm, 220.00 ppm, respectively. For the calibration of chemical shift, the central solvent peak was used. MestReNova v7.1.0 software (Mestrelab Research, S.L., Santiago, Spain) was used as a default processing template. By this means, HSQC data processing and plots were accomplished.

Molecular Weight Analysis of Pyrolysis Heavy Oil

The weight average molecular weights (M_w) of the heavy oils after completing each step of pyrolysis were determined by gel permeation chromatography analysis following literature methods (Ben and Ragauskas 2011b). Before injecting the sample to the detector, the heavy oil was dissolved in tetrahydrofuran (1 mg/mL) and the solution was filtered *via* a syringe filter (0.45 µm).

Polymer Standards Service (PSS) WinGPC Unity software (PSS-Polymer, v.1.1, Amherst, MA, USA) data analysis was used to analyze the results. The calibration curve was plotted, and M_w was calibrated against this calibration curve.

RESULTS AND DISCUSSION

Regenerating/Recycling of Zeolite During the Pyrolysis

Figure 1 shows the recycling of 'Y + M' sample after the pyrolysis of kraft lignin. After mixing with kraft lignin samples, the color of fresh 'Y + M' sample (white) turned to gray. After the pyrolysis, the gray 'Y + M' zeolites-lignin mixture turned to dark brown because the char was generated from the kraft lignin. Once the char was burned out in the muffle furnace, the recovered 'Y + M' sample turned to white again. The recovered zeolites were then used for the next cycle of pyrolysis.



Fig. 1. Recycling of 'Y + M' sample after the pyrolysis of kraft lignin (L)

SEM Characterization

The morphological changes of zeolite after pyrolysis are represented in Fig. 2. After each cycle pyrolysis/regeneration and some aggregations of zeolite particles occurred. This phenomenon appeared even after one-time pyrolysis. However, there were no significant morphological differences between the pyrolyzed zeolites (samples 1 through 5). Evidently, the aggregation of zeolite particles decreased the activation points, which degraded the catalytic effects in the pyrolysis. Similar findings were reported in the literature (López *et al.* 2011; Shvets *et al.* 2018). Due to the deposit of coke on the surface of the zeolites, through increasing the number of catalytic cycles, micropore volume of the catalysts decreased to a large extent (López *et al.* 2011; Shvets *et al.* 2018).

Analysis of BET SA of Zeolites

The BET SA and PS of different types of zeolites are presented in Table 2. The BET surface area and acids sites distribution of the spent zeolite after a cycle of usage but before regeneration are also listed in Table 2. In this table, it could be noticed that the total acid sites of the spent zeolites were only 55 to 58% of the starting zeolites. Meanwhile, the BET surface areas of the spent zeolites were about 51% of the starting zeolites. These results indicated the acidity and porosity of zeolites were significantly decreased after the pyrolysis of kraft lignin. However, after the regeneration, the acidity and porosity were recovered to 99%, as indicated in Table 2. In addition, The SA and PS of zeolites gradually decreased *via* increasing the regenerated cycles. The decrease in BET, SA, and PS could

be assigned to the deposition of small quantities of extra framework species in the pores of zeolites (Ma and Bokhoven 2012). It additionally indicated the destruction of crystalline structure of zeolites (Kassargy *et al.* 2019).



Fig. 2. SEM images analysis of zeolites changes after the pyrolysis. Sample 0 to 5 are fresh zeolite without any pyrolysis with kraft lignin, after one time pyrolysis, after two times pyrolysis, after three times pyrolysis, after four times pyrolysis, and after five times pyrolysis with kraft lignin, respectively

Among the repeated cycles, the decreasing rate of BET, SA, and PS for the combined 'Y + M' sample was much slower compared to the individual Y and M zeolites. For example, from the1st to 5th cycles, BET SA decreased approximately 7.61%, 19.99%, and 6.23% for Y, M, and 'Y + M' zeolites, respectively.

Micropore and mesopore SA of zeolites are presented in Table 2. Microporous content is the more important for activity of catalysts during pyrolysis compared to mesoporous content (Imran *et al.* 2018). Through increasing the regeneration cycle, the decrease in the MSA for the combined 'Y + M' sample was less compared to individual Y

and M zeolites. For example, from the 1^{st} to 5^{th} cycles, the MSA decreased 7.81%, 20.23%, and 6.25% for the Y, M, and 'Y + M' samples, respectively. The decrease in the BET, SA, and MSA during the regeneration cycles for combined zeolites were less, indicating the combined zeolites will have better catalytic activity after regeneration compared with individual zeolites (Fuentes-Ordóñez *et al.* 2014).

	Acid Site on	s Distributio NH₃-TPD D	on Based ata	PS Distribution Based on BET Data					
	Weak	Strong	Total	BET SA (m²/g)	MSA (m²/g)	Mesopore SA (m²/g)			
Y + M	0.54	0.42	0.96	615.48	471.36	144.12			
Spent Y + M**	0.30	0.26	0.56	313.89	238.56	75.33			
1 st cycle	0.54	0.41	0.95	609.07	466.45	142.62			
2 nd cycle	0.53	0.41	0.94	602.66	461.54	141.12			
3 rd cycle	0.52	0.40	0.93	596.25	456.63	139.62			
4 th cycle	0.52	0.40	0.92	589.84	451.72	138.12			
5 th cycle	0.51	0.39	0.90	577.01	441.90	135.11			
Y	0.43	0.49	0.92	728.34	502.15	226.19			
Spent Y**	0.22	0.29	0.51	378.74	261.33	117.41			
1 st cycle	0.43	0.48	0.91	720.75	496.92	223.83			
2 nd cycle	0.43	0.47	0.90	712.51	491.23	221.27			
3 rd cycle	0.42	0.46	0.88	696.67	480.32	216.36			
4 th cycle	0.41	0.46	0.87	688.76	474.86	213.90			
5 th cycle	0.40	0.45	0.85	672.92	462.94	208.98			
Μ	0.65	0.35	1.00*	502.62	440.57	62.05			
Spent M**	0.37	0.21	0.58	256.34	225.58	30.76			
1 st cycle	0.62	0.33	0.95	497.38	435.98	61.40			
2 nd cycle	0.60	0.30	0.90	452.36	396.51	55.85			
3 rd cycle	0.58	0.28	0.86	432.25	378.89	53.36			
4 th cycle	0.56	0.27	0.83	417.17	365.67	51.50			
5 th cycle	0.55	0.25	0.80	402.10	351.46	49.64			

Table 2. Acidity from NH₃-TPD and BET SA of Different Zeolite Samples

*: The amount of acidity of fresh M zeolite was assigned as 1.0 and compared with the other samples

**: The spent zeolites were designated as the zeolite after the first-time pyrolysis but before regeneration. Other zeolites were regenerated zeolites.

As indicated in Table 2, after 5 time of regeneration, the acid sites and BET surfaces areas were slightly decreased (~10%). These findings indicated that the thermal processing destroyed the pores to some extent and the mouths of some pores were chocked with refractory material that could not be removed during the thermal regeneration process. The synthesis of new zeolites with thermal stable pores would be future research directions.

Analysis of the Acidity of Zeolites

The catalytic efficiency of zeolites in the kraft lignin pyrolysis is due to its abundant acid sites in the porous structures. The NH₃-TPD analysis of zeolites from each cycle is shown in Fig. 3. Two characteristic peaks appeared in the range of 100 to 300 °C and 300 to 500 °C, representing the strong and weak acid sites, respectively (Paysepar *et al.* 2018). The strong and weak acid sites for zeolites were decreased gradually by decreasing the peak intensity in the NH₃-TPD curves (Park *et al.* 2010; Veses *et al.* 2015). The acid

strength decreased after each cycle and the intensity difference between the fresh and 1st time regenerated zeolites for individual Y and M samples was higher than for the combined 'Y + M' sample (Fig. 3). The intensity difference between the regeneration cycles for individual zeolites was more than those of the combined 'Y + M' sample. In addition, the acid intensity for individual zeolites decreased more with regeneration cycles compared to the combined 'Y + M' sample.



Fig. 3. NH₃-TPD analysis of zeolites from different regeneration cycles

Included in Table 2 are the results of weak, strong, and TAS (reported as their integrated areas) of zeolites. The amount of acid sites (*i.e.*, acidity) integration of fresh M zeolite was assigned as 1.0 (Gao *et al.* 2008). The acidity values of other zeolites were all based on this value. Initially M zeolites had higher sites compared with Y zeolites and the combined sample's total acid sites were in the middle. The decrease in the TAS for the combined 'Y + M' sample (6.25%) was less compared with individual Y (7.61%) and M (20%) zeolites.

Combination Effect on BET SA, PS, and Acidity of Zeolites in the Pyrolysis of Kraft Lignin

Both the Y and M zeolites had some unique properties (Table 1). The SiO₂/Al₂O₃ mole ratio and PS of Y and M zeolites were different and showed different catalytic activity (Table 3). The SiO₂/Al₂O₃ in the Y zeolite (30) was higher than the M zeolites (20). The measured SiO₂/Al₂O₃ (26) of the combined "Y +M" zeolite was in between zeolite Y and M. The Y and M zeolites are selective towards cleavages of specific bonds/ functionalities in lignin structures during lignin pyrolysis (Table 3). Both the Y and M zeolites have some advantages and disadvantages when used as the catalyst during lignin catalysis. For

example, the Y zeolites have higher MSA, which will have a positive effect on the catalytic performance; in contrast, its lower acidity may lead to a lower catalytic effect. The M zeolites have higher acidity, indicative of better catalytic effect, but smaller MSAs (Table 2) and can lower the catalytic effect (Chen 2004; Bae *et al.* 2010).

For the combined 'Y + M' sample, it exhibited high acidity and big MSAs in lignin pyrolysis. The SiO₂/Al₂O₃ mole ratio and PS in zeolites are important for the catalytic activities in lignin pyrolysis (Ben and Ragauskas 2013), while the PS and acidity are the key parameters for improving their product selectivity (Imran *et al.* 2018). In addition, Ben and Ragauskas (2013) reported that (Fig. 4) in lignin pyrolysis, a higher SiO₂/Al₂O₃ mole ratio and larger PS in zeolites can lead to less decarboxylation and cleavage of more methoxyl groups, ether bonds, aliphatic C–C bonds, and the removal of more aliphatic hydroxyl groups in heavy oils (Ben and Ragauskas 2013).



Fig. 4. Primary chemical reactions/cleavages of chemical bonds in lignin during the pyrolysis (circled by dashed lines in lignin structure) by zeolites. Adapted with permission from (Ben and Ragauskas 2013). Copyright (2013) American Chemical Society.

Table 3. SiO ₂ /Al ₂ O ₃ Mole Ratio and PS of Y and M Zeolites and their Catalytic
Effects on Lignin Pyrolysis (Ben and Ragauskas 2012, 2013)

Zeolite	SiO ₂ /Al ₂ O ₃ Mole Ratio	PS (Å)	Catalytic Effects on Lignin Pyrolysis
Y	30	7.4 × 7.4	 Cleavage of methoxyl-aromatic bonds Cleavage of ether-bonds Dehydration of aliphatic hydroxyl groups Cleavage of C-C bonds
М	20	6.5 × 7.0	Decarboxylation

Pyrolysis Yield

Table 4 shows the yield of different pyrolysis products (light oil, heavy oil, char, and gas) from different pyrolysis processes. When M zeolite was used with lignin, no remarkable change could be observed for the yield of heavy oil and gas, but it led to less light oil and more char. In fact, there were no differences of pyrolysis yields between the repeated cycles with the regenerated M zeolite.

In addition, a previous study supported that the quantity of every pyrolysis product (heavy oil, light oil, char, and gas) for the combination of the 'Y + M' sample catalyzed pyrolysis remained between the individual Y and M zeolites catalyzed pyrolysis (Huang *et al.* 2014). This phenomenon was observed after the regeneration of each cycle.

However, it can be seen from the three processes, combinations of the 'Y + M' sample produced more heavy oil and light oil compared to the individual Y and M. The production rate of gas and char in every process was almost similar. No remarkable variation could be observed in between the repeated cycles even for the zeolite's mixture of 'Y + M' catalyzed pyrolysis.

Table 4. Yields (wt%) of Light Oil, Heavy	Oil, Char (excludes the weight of
zeolite), and Gas for Pyrolysis Treatments	6

	1 st Time Pyrolysis			2 nd Time Pyrolysis			3 rd Time Pyrolysis			4 th Time Pyrolysis			5 th Time Pyrolysis		
	Y + M	Y	М	Y + M	Y	М	Y + M	Y	М	Y + M	Y	М	Y + M	Y	М
Light Oil	18.15	18.95	10.72	18.83	18.90	10.68	19.20	18.82	10.76	19.78	18.78	10.74	18.72	18.77	10.67
Heavy Oil	20.70	16.62	29.03	20.81	16.57	29.12	21.44	16.61	28.84	20.55	17.24	29.21	21.08	16.66	28.59
Char	50.28	54.10	48.93	49.20	53.89	48.66	49.66	53.86	47.86	49.24	53.41	48.24	49.30	53.94	48.87
Gas	10.87	10.33	11.32	11.16	10.64	11.54	9.70	10.71	12.44	10.93	10.57	11.81	1.90	10.63	11.87

Note: Pyrolysis of kraft lignin with 1.0/1.0 ($W_{additive}/W_{lignin}$) of the combined 'Y + M' sample, individual Y and M zeolites as catalysts at 600 °C for 10 min

Quantitative ³¹P NMR Analysis of Pyrolysis Heavy Oil

To find the hydroxyl functional groups in heavy oils, quantitative ³¹P NMR is one of the best processes (Kosa *et al.* 2011; David *et al.* 2012). The integration results of the ³¹P NMR for the heavy oils are summarized in Fig. 5. For all the regenerated zeolite samples, during pyrolysis of kraft lignin the amount of C-5 substituted, catechol, *p*-hydroxy-phenyl, and carboxylic acid -OH decreased. The aliphatic hydroxyl and normal guaiacyl phenolic hydroxyl groups increased gradually with the increase of regeneration cycles.

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Fig. 5. Hydroxyl group contents of different heavy oils produced by pyrolysis of kraft lignin

The aliphatic hydroxyl groups in heavy oil were absent after the use of combined the 'Y + M' sample, indicative of its enhanced dehydroxylation of aliphatic hydroxyl groups in lignin. In addition, with the increase of regeneration cycles of the zeolites, C-5 substituted guaiacyl phenolic, catechol, and *p*-hydroxy-phenyl types of hydroxyl groups decreased. Catechol and *p*-hydroxy-phenyl types of hydroxyl groups are the decomposition products of methoxyl aromatic bonds and ether bonds in the lignin (Ben and Ragauskas 2011b,c). Correspondingly, the guaiacyl phenolic hydroxyl groups increased, and catechol and *p*-hydroxy-phenyl decreased with the increase of pyrolysis cycles, indicative of the catalytic activity of zeolites decreased gradually.

Table 5 indicates the increasing percentage of guaiacyl phenolic hydroxyl and decreasing percentage of catechol and *p*-phenyl hydroxyl groups for the combined 'Y + M' sample were less than individual Y and M zeolites. The BET, MSA, and TAS (Table 2) remained higher after each regeneration for the combined 'Y + M' sample compared with individual Y and M zeolites, leading to an increased percentage of guaiacyl phenolic hydroxyl groups and a decreased percentage of catechol and *p*-phenyl hydroxyl groups in the heavy oil.

Table 5. Increased Percentage of Guaiacyl Phenolic Hydroxyl and Decreased Percentage of Catechol and *p*-hydroxy Phenyl Types Hydroxyl Groups in Heavy Oil from the 2nd to 5th Time Pyrolysis in Comparison with the 1st Time Pyrolysis

	2 nd Time Pyrolysis			3 rd Time Pyrolysis			4 th Tim	e Pyrc	olysis	5 th Time Pyrolysis		
	Y + M	Y	Μ	Y + M	Y	Μ	Y + M	Y	М	Y + M	Y	Μ
Guaiacyl	1.6	5.8	2.3	4.4	12.3	4.3	6.6	15.5	6.6	9.3	20.6	9.7
Catechol	1.3	3.5	1.8	2.3	5.2	4.2	3.5	7.7	7.4	5.3	9.6	8.8
<i>p</i> -hydroxy- phenyl	3.8	4.6	7.3	9.5	7.9	14.6	11.4	11.2	22.0	13.3	14.5	26.8

Quantitative ¹³C NMR Analysis of the Pyrolysis Heavy Oil

Quantitative integration results for pyrolysis heavy oils produced from kraft lignin using the combined 'Y + M' sample and individual Y and M as catalysts, are summarized in Fig. 6. The carbonyl groups in the heavy oil for the combined 'Y + M' sample decreased to 85%, which was higher than the individual Y and M zeolite catalyzed pyrolysis oil, indicating the pyrolysis oil was less acidic (Ben and Ragauskas 2013) than the individual Y and M zeolite catalyzed pyrolysis oil. The methoxyl groups content in heavy oil decreased to 74.3% with the combined 'Y + M' sample, indicating the effective demethoxylation, thus increasing catechol type hydroxyl groups, which was consistent of the ³¹P-NMR results (Ben and Ragauskas 2012).

After the use of zeolites, higher amounts methyl aromatic bonds in the heavy oil further indicated the effective cleavage of methoxyl groups (Ben and Ragauskas 2012, 2013). These methyl aromatic bonds in heavy oils are the rearrangement products of methoxyl groups (Ben and Ragauskas 2011b). The amount of aliphatic C–O in heavy oil for the combined zeolites was less when compared with the individual Y and M zeolites, indicating more effective dehydroxylation of aliphatic C–O bonds, due to its relatively high MSA and TAS of the combined zeolites (Ben and Ragauskas 2013), which was supported by the ³¹P-NMR results.



Fig. 6. Quantitative ¹³C NMR integration results for heavy oils produced from kraft lignin; the results are shown as the percentage of carbon

Among the repeated pyrolysis, the increased percentage of methoxyl groups (Table 5), aliphatic C-O bonds, and decreased percentage of methyl aromatic bonds was lower for the combined 'Y + M' sample. In addition, Table 6 represents that in between the repeated cycles, the increased and decreased percentage of different groups in heavy oil was slower for the combined 'Y + M' sample. This was due to its high BET, MSA, and TAS (Tables

2 and 3) of the combined 'Y + M' sample after each regeneration cycle. After each regeneration, the combined 'Y + M' samples showed higher catalytic activity due to retaining its high SA and total acidity, which agreed with the ³¹P-NMR results.

Table 6. Increased Percentage of Methoxyl, Carbonyl, Aromatic C–O, Decreased Percentage of Aromatic C–H and Aliphatic C–C Bonds in Heavy Oil from the 2nd to 5th Time Pyrolysis in Comparison with the 1st Time Pyrolysis

	2 nd Time Pyrolysis			3 rd Tim	ne Pyr	Pyrolysis 4 th Time Pyrolysis					5 th Time Pyrolysis			
	Y + M	Y	М	Y + M Y M		Y+M Y		М	Y + M	Y	М			
Methoxyl Groups	12.44	14.08	6.02	22.67	28.64	17.17	31.11	53.40	23.19	42.67	88.83	30.42		
Carbonyl Groups	15.53	2.99	16.13	17.65	5.97	25.81	18.40	17.91	32.26	41.18	31.34	35.48		
Aromatic C–O	1.38	1.24	0.46	3.52	5.93	1.05	5.91	12.55	1.42	8.03	20.83	2.26		
Aromatic C–H	1.28	0.34	1.30	3.73	3.57	3.67	4.71	5.85	4.89	6.59	9.39	6.08		
Aliphatic C–C	1.41	2.14	1.31	5.51	3.77	2.63	10.35	7.25	4.17	10.80	9.91	7.03		

HSQC-NMR Analysis of Pyrolysis Heavy Oil

Analysis of different C–H bonds in pyrolysis oil by HSQC-NMR (2D NMR) is a modern technique in which more than 30 different C–H bonds can be analyzed (Salanti *et al.* 2010; Samuel *et al.* 2010; Ben and Ragauskas 2011a).



Fig. 7. Aromatic C–H bonds in the HSQC-NMR spectra for the heavy oils using various zeolite catalysts: Samples a-f are L, 1^{st} time L+(Y + M), 2^{nd} time L+(Y + M), 3^{rd} time L+(Y + M), 4^{th} time L+(Y + M), and 5^{th} time L+(Y + M, respectively

Analysis of different C-H bonds in pyrolysis oil using HSQC-NMR is a wellstudied technique, and some limitations of ¹³C NMR can be covered using this. The HSQC-NMR spectra for the heavy oils from various repeated pyrolysis of combinations 'Y + M' zeolites are shown in Figs. 7 through 9. Figure 7 represents the HSQC-NMR spectra of aromatic C–H bonds for the heavy oil from the 'Y + M' sample-assisted lignin pyrolysis. It could be observed that after the use of the zeolite mixture, some PAH was present in the pyrolysis oil. It has been reported that the Y zeolite can form some PAH in heavy oil (Ben and Ragauskas 2013). Y zeolite has large PS and three-dimensional pore channels (Table 1), resulting in small aromatic molecules (Jae *et al.* 2011) going into the pore channels and the zeolites effectively cleaving them (Chantal *et al.* 1985). Among the repeated cycles, the amount of PAH in heavy oil decreased gradually with increasing cycles, indicating that the catalytic active sites decreased with repeated cycles.

The HSQC-NMR spectra for the methoxyl groups in the heavy oils from the 'Y + M' zeolite-assisted lignin pyrolysis are represented in Fig. 8. After the use of the zeolite mixture, methoxyl groups in the heavy oil decreased, which is in agreement with the reduced amount of methoxyl groups observed by ¹³C-NMR. Another good agreement with ¹³C-NMR result was the presence of more methyl aromatic bonds in the pyrolysis oil after using the zeolite. Possible mechanisms for the degradation of methoxyl groups with the zeolite have been reported in published literature (Ben and Ragauskas 2013). Among the repeated cycles, the amount of methoxyl groups in heavy oil increased with increasing cycles, this result was consistent with ¹³C-NMR. This decreasing rate must be slower for the combined zeolites (Table 6).



Fig. 8. Methoxyl groups in the HSQC-NMR spectra for the heavy oils using various zeolites catalysts. Samples a-f are L, 1^{st} time L+(Y + M), 2^{nd} time L+(Y + M), 3^{rd} time L+(Y + M), 4^{th} time L+(Y + M) and 5^{th} time L+(Y + M)

Figure 9 shows the HSQC-NMR spectra for the aliphatic C-H bonds in the heavy oils from combined 'Y + M' zeolite-assisted lignin pyrolysis. The content of long chain aliphatic C-C bonds in upgraded pyrolysis oil was lower than the non-catalyzed pyrolysis oil, which indicated the zeolites improved the cleavage of aliphatic C-C bonds. This result was consistent with the ¹³C NMR results. Possible pathways for the cleavage of C-C bonds in the lignin structure on the zeolite's surface are reported in the literature (Ben and Ragauskas 2013). Among the repeated pyrolysis of kraft lignin with zeolite mixture 'Y + M' the aliphatic C-H bonds in the heavy oils decreased gradually with increasing cycles.



Fig. 9. Aliphatic C–H bonds in the HSQC-NMR spectra for the heavy oils using various zeolite catalysts. Sample a-f are L, 1^{st} time L+(Y + M), 2^{nd} time L+(Y + M), 3^{rd} time L+(Y + M), 4^{th} time L+(Y + M), and 5^{th} time L+(Y + M)

Molecular Weight Analysis of Pyrolysis Heavy Oil

The M_w for the heavy oils produced from different pyrolysis are summarized in Fig. 10. After the use of zeolites, the M_w of pyrolysis heavy oils, in all cases, decreased and afterwards increased gradually when increasing the regeneration cycles. From the Fig. 10, after the use of zeolites the M_w of heavy oil decreased to 53%, 52%, and 7% for combinations of 'Y + M', Y, and M zeolites-assisted pyrolysis oil, respectively. When the M zeolite was used, M_w of heavy oils did not change remarkably and showed nearly stable behavior among repeated cycles. For Y and combinations of 'Y + M' sample, the M_w in heavy oil decreased remarkably and the combinations zeolite show better results (53%) than the individual Y zeolite (52%).

Among the repeated cycles, compared with the 1st time pyrolysis, the increases of the M_w of heavy oil in the 2nd, 3rd, 4th, and 5th time, for combinations of 'Y + M' and individual Y zeolites were 5.4%, 8.7%, 16.1%, and 21.5%; and 7.3%, 15.2%, 23.8%, and 29.1%, respectively. The lower M_w of the zeolite assisted pyrolysis heavy oil of the combinations 'Y + M' sample proved enhanced decomposition of the methoxyl groups,

carboxyl acid, and dehydration of aliphatic hydroxyl groups in the heavy oil (Ben and Ragauskas 2013).

Among repeated cycles, the increments of M_w lowered for the pyrolysis heavy oil using the combined 'Y + M' sample. These results indicated the BET, MSA, and TAS, for the combined 'Y + M' sample, play an important role to enhance the demethoxylation, decarboxylation, and dehydroxylation of the aliphatic hydroxyl groups (Table 3) in heavy oil compared with the individual Y and M zeolites.







Fig. 10. Molecular weight (M_w) of heavy oils produced by pyrolysis of kraft lignin with the combined 'Y + M' and individual Y and M zeolites

CONCLUSIONS

- 1. Regeneration of zeolites as the catalyst and its effect on the kraft lignin pyrolysis were studied for three zeolite samples: the individual FAU (Y), MOR (M) zeolites, and the combined 'Y + M'. Catalytic activity of all of the three zeolites in the lignin pyrolysis decreased when increasing the regeneration cycles, which are due to some aggregations of particle on the zeolite surface, decreased MSA and decreased TAS.
- 2. The NMR analysis of heavy oil revealed the increased percentage of guaiacyl phenolic hydroxyl, methoxyl groups and decreased percentages of catechol and *p*-phenyl hydroxyl groups in heavy oil, were less for the combined 'Y + M' sample than the individual Y and M zeolites.
- 3. The effect of higher catalytic activity of the combined 'Y + M' sample in repeated cycles resulted in lower M_w pyrolysis heavy oil.

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REFERENCESCITED

- Aho, A., Kumar, N., Eränen, K., Salmi, T., Hupa, M., and Murzin, D. Y. (2008).
 "Catalytic pyrolysis of woody biomass in a fluidized bed reactor: Influence of the zeolite structure," *Fuel* 87(12), 2493-2501. DOI: 10.1016/j.fuel.2008.02.015
- Algieri, C., Bernardo, P., Barbieri, G., and Drioli, E. (2009). "A novel seeding procedure for preparing tubular NaY zeolite membranes," *Microporous and Mesoporous Materials* 119(1-3), 129-136. DOI: 10.1016/j.micromeso.2008.10.008
- Ali, S., Garforth, A. A., Harris, D. H., Rawlence, D. J., and Uemichi, Y. (2002).
 "Polymer waste recycling over "used" catalysts," *Catalysis Today* 75(1-4), 247-255.
 DOI: 10.1016/S0920-5861(02)00076-7
- Bae, Y. S., Yazaydın, A. Ö., and Snurr, R. Q. (2010). "Evaluation of the BET method for determining surface areas of MOFs and zeolites that contain ultra-micropores," *Langmuir* 26(8), 5475-5483. DOI: 10.1021/la100449z
- Baerlocher, C., McCusker, L. B., and Olson, D. H. (2007). *Atlas of Zeolite Framework Types*, Elsevier, New York, NY, USA.
- Ben, H., and Ragauskas, A. J. (2011a). "Heteronuclear single-quantum correlation– nuclear magnetic resonance (HSQC–NMR) fingerprint analysis of pyrolysis oils," *Energy & Fuels* 25(12), 5791-5801. DOI: 10.1021/ef201376w

- Ben, H., and Ragauskas, A. J. (2011b). "NMR characterization of pyrolysis oils from Kraft lignin," *Energy & Fuels* 25(5), 2322-2332. DOI: 10.1021/ef2001162
- Ben, H., and Ragauskas, A. J. (2011c). "Pyrolysis of kraft lignin with additives," *Energy* & *Fuels* 25(10), 4662-4668. DOI: 10.1021/ef2007613
- Ben, H., and Ragauskas, A. J. (2012). "One step thermal conversion of lignin to the gasoline range liquid products by using zeolites as additives," *RSC Advances* 2(33), 12892-12898. DOI: 10.1039/C2RA22616B
- Ben, H., and Ragauskas, A. J. (2013). "Influence of Si/Al ratio of ZSM-5 zeolite on the properties of lignin pyrolysis products," ACS Sustainable Chemistry & Engineering 1(3), 316-324. DOI: 10.1021/sc300074n
- Benamar, A., Bechket, Z., Boucheffa, Y., and Miloudi, A. (2009). "Transformation of mxylene over an USHY zeolite: Deactivation and regeneration," *Comptes Rendus Chimie* 12(6-7), 706-715. DOI: 10.1016/j.crci.2008.10.019
- Benito, P. L., Aguayo, A. T., Gayubo, A. G., and Bilbao, J. (1996). "Catalyst equilibration for transformation of methanol into hydrocarbons by reactionregeneration cycles," *Industrial & Engineering Chemistry Research* 35(7), 2177-2182. DOI: 10.1021/ie950493u
- Bhatia, S. (1989). Zeolite Catalysts: Principles & Applications, CRC Press, Boca Raton, FL, USA.
- Calvo-Flores, F. G., and Dobado, J. A. (2010). "Lignin as renewable raw material," *ChemSusChem* 3(11), 1227-1235. DOI: 10.1002/cssc.201000157
- Chantal, P. D., Kaliaguine, S., and Grandmaison, J. L. (1985). "Reactions of phenolic compounds over HZSM-5," *Applied Catalysis* 18(1), 133-145. DOI: 10.1016/S0166-9834(00)80304-8
- Chen, P. (2004). "Catalytic degradation of polystyrene for various zeolites as catalyst," *Journal of Liaoning University of Petroleum & Chemical Technology* 24, 32-35. DOI: 10.3969/j.issn.1672-6952.2004.01.010
- Dai, L., Li, Y., Kong, F., Liu, K., Si, C., and Ni, Y. (2019a). "Lignin-based nanoparticles stabilized pickering emulsion for stability improvement and thermal-controlled release of trans-resveratrol," ACS Sustainable Chemistry & Engineering 7(15), 13497-13504. DOI: 10.1021/acssuschemeng.9b02966
- Dai, L., Zhu, W., Lu, J., Kong, F., Si, C., and Ni, Y. (2019b). "A lignin-containing cellulose hydrogel for lignin fractionation," *Green Chemistry* 21(19), 5222-5230. DOI: 10.1039/C9GC01975H
- David, K., Haoxi, B., Muzzy, J., Feik, C., Iisa, K., and Ragauskas, A. (2012). "Chemical characterization and water content determination of bio-oils obtained from various biomass species using ³¹P NMR spectroscopy," *Biofuels* 3(2), 123-128. DOI: 10.4155/bfs.12.1
- Dhainaut, J., Daou, T. J., Chappaz, A., Bats, N., Harbuzaru, B., Lapisardi, G., Chaumeil, H., Defoin, A., Rouleau, L., and Patarin, J. (2013). "Synthesis of FAU and EMT-type zeolites using structure-directing agents specifically designed by molecular modelling," *Microporous and Mesoporous Materials* 174(3), 117-125. DOI: 10.1016/j.micromeso.2013.03.006
- Huang, F., Ben, H., Pan, S., Pu, Y., and Ragauskas, A. (2014). "The use of combination of zeolites to pursue integrated refined pyrolysis oil from kraft lignin," *Sustainable Chemical Processes* 2(1), Article number 7. DOI: 10.1186/2043-7129-2-7
- Fuentes-Ordóñez, E. G., Salbidegoitia, J. A., Ayastuy, J. L., Gutiérrez-Ortiz, M. A., González-Marcos, M. P., and González-Velasco, J. R. (2014). "High external surface

Pt/zeolite catalysts for improving polystyrene hydrocracking," *Catalysis Today* 227, 163-170. DOI: 10.1016/j.cattod.2013.09.004

Gao, J., Guo, J., Liang, D., Hou, Z., Fei, J., and Zheng, X. (2008). "Production of syngas via autothermal reforming of methane in a fluidized-bed reactor over the combined CeO₂–ZrO₂/SiO₂ supported Ni catalysts," *International Journal of Hydrogen Energy* 33(20), 5493-5500. DOI: 10.1016/j.ijhydene.2008.07.040

García-Martínez, J., Li, K., and Krishnaiah, G. (2012). "A mesostructured Y zeolite as a superior FCC catalyst–from lab to refinery," *Chemical Communications* 48(97), 11841-11843. DOI: 10.1039/C2CC35659G

Gerzeliev, I. M., Temnikova, V. A., Maksimov, A. L., and Khadzhiev, S. N. (2018).
"Regeneration of zeolite catalyst for isobutane alkylation with olefins," *Petroleum Chemistry* 58(10), 827-832. DOI: 10.1134/S0965544118100067

Hopkins, P. D., Miller, J. T., Meyers, B. L., Ray, G. J., Roginski, R. T., Kuehne, M. A., and Kung, H. H. (2015). "Acidity and cracking activity changes during coke deactivation of ultrastable Y zeolite," *Applied Catalysis A: General* 136(1), 29-48. DOI: 10.1016/0926-860X(95)00246-4

- Imran, A., Bramer, E. A., Seshan, K., and Brem, G. (2018). "An overview of catalysts in biomass pyrolysis for production of biofuels," *Biofuel Research Journal* 5(4), 872-885. DOI: 10.18331/BRJ2018.5.4.2
- Ivanov, D. P., Sobolev, V. I., and Panov, G. I. (2003). "Deactivation by coking and regeneration of zeolite catalysts for benzene-to-phenol oxidation," *Applied Catalysis A: General* 241(1-2), 113-121. DOI: 10.1016/S0926-860X(02)00462-3
- Jae, J., Tompsett, G. A., Foster, A. J., Hammond, K. D., Auerbach, S. M., Lobo, R. F., and Huber, G. W. (2011). "Investigation into the shape selectivity of zeolite catalysts for biomass conversion," *Journal of Catalysis* 279(2), 257-268. DOI: 10.1016/j.jcat.2011.01.019
- Jong, S. J., Pradhan, A. R., Wu, J. F., Tsai, T. C., and Liu, S. B. (1998). "On the regeneration of coked H-ZSM-5 catalysts," *Journal of Catalysis* 174(2), 210-218. DOI: 10.1006/jcat.1998.1971
- Kassargy, C., Awad, S., Burnens, G., Upreti, G., Kahine, K., and Tazerout, M. (2019). "Study of the effects of regeneration of USY zeolite on the catalytic cracking of polyethylene," *Applied Catalysis B: Environmental* 244, 704-708. DOI: 10.1016/j.apcatb.2018.11.093
- Katada, N., Kageyama, Y., and Niwa, M. (2000). "Acidic property of Y-and mordenitetype zeolites with high aluminum concentration under dry conditions," *The Journal of Physical Chemistry B* 104(31), 7561-7564. DOI: 10.1021/jp000906r
- Khangkham, S., Julcour-Lebigue, C., Damronglerd, S., Ngamcharussrivichai, C., Manero, M. H., and Delmas, H. (2013). "Regeneration of coked zeolite from PMMA cracking process by ozonation," *Applied Catalysis B: Environmental* 140-141, 396-405. DOI: 10.1016/j.apcatb.2013.04.041
- Kim, J. Y., Heo, S., and Choi, J. W. (2018). "Effects of phenolic hydroxyl functionality on lignin pyrolysis over zeolite catalyst," *Fuel* 232, 81-89. DOI: 10.1016/j.fuel.2018.05.133
- Kim, J. Y., Lee, J. H., Park, J., Kim, J. K., An, D., Song, I. K., and Choi, J. W. (2015). "Catalytic pyrolysis of lignin over HZSM-5 catalysts: Effect of various parameters on the production of aromatic hydrocarbon," *Journal of Analytical and Applied Pyrolysis* 114, 273-280. DOI: 10.1016/j.jaap.2015.06.007

- Kosa, M., Ben, H., Theliander, H., and Ragauskas, A. J. (2011). "Pyrolysis oils from CO₂ precipitated Kraft lignin," *Green Chemistry* 13(11), 3196-3202. DOI: 10.1039/C1GC15818J
- Kosinov, N., Auffret, C., Borghuis, G. J., Sripathi, V. G., and Hensen, E. J. (2015).
 "Influence of the Si/Al ratio on the separation properties of SSZ-13 zeolite membranes," *Journal of Membrane Science* 484, 140-145. DOI: 10.1016/j.memsci.2015.02.044
- Li, C., Zhao, X., Wang, A., Huber, G. W., and Zhang, T. (2015). "Catalytic transformation of lignin for the production of chemicals and fuels," *Chemical Reviews* 115(21), 11559-11624. DOI: 10.1021/acs.chemrev.5b00155
- López, A., De Marco, I., Caballero, B. M., Adrados, A., and Laresgoiti, M. F. (2011).
 "Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes," *Waste Management* 31(8), 1852-1858. DOI: 10.1016/j.wasman.2011.04.004
- Ma, M., Dai, L., Si, C., Hui, L., Liu, Z., and Ni, Y. (2019). "A facile preparation of super long-term stable lignin nanoparticles from black liquor," *ChemSusChem* 12(24), 5239-5245. DOI: 10.1002/cssc.201902287
- Ma, Z., and Bokhoven, J. A. V. (2012). "Deactivation and regeneration of H-USY zeolite during lignin catalytic fast pyrolysis," *ChemCatChem* 4(12), 2036-2044. DOI: 10.1002/cctc.201200401
- Ma, Z., Ghosh, A., Asthana, N., and Van Bokhoven, J. (2018). "Visualization of structural changes during deactivation and regeneration of FAU zeolite for catalytic fast pyrolysis of lignin using NMR and electron microscopy techniques," *ChemCatChem* 10(19), 4431-4437. DOI: 10.1002/cctc.201800670
- Marcilla, A., Beltrán, M. I., and Navarro, R. (2007). "Application of TG/FTIR to the study of the regeneration process of husy and HZSM5 zeolites," *Journal of Thermal Analysis and Calorimetry* 87(2), 325-330. DOI: 10.1007/s10973-005-7322-3
- Martínez, C., and Corma, A. (2011). "Inorganic molecular sieves: Preparation, modification and industrial application in catalytic processes," *Coordination Chemistry Reviews* 255(13-14), 1558-1580. DOI: 10.1016/j.ccr.2011.03.014
- Maxwell, I., and Stork, W. (2001). "Hydrocarbon processing with zeolites," in: *Studies in Surface Science and Catalysis*, Vol. 137, Elsevier, New York, NY, USA, pp. 747-819.
- Meier, D., Berns, J., Grünwald, C., and Faix, O. (1993). "Analytical pyrolysis and semicontinuous catalytic hydropyrolysis of organocell lignin," *Journal of Analytical and Applied Pyrolysis* 25(93), 335-347. DOI: 10.1016/0165-2370(93)80053-3
- Mohamed, M. M., Nohman, A. K., and Zaki, M. I. (2005). "Development of catalytic properties of mordenite zeolite *via* chemical modification," *Catalysis* 4, 79-99. DOI: 10.1002/chin.200638241
- Mondal, A. K., Qin, C., Ragauskas, A. J., Ni, Y., and Huang, F. (2020). "Preparation and characterization of various Kraft lignins and impact on their pyrolysis behaviors," *Industrial & Engineering Chemistry Research* 59(8), 3310-3320. DOI: 10.1021/acs.iecr.9b06690
- Park, H. J., Heo, H. S., Jeon, J. K., Kim, J., Ryoo, R., Jeong, K. E., and Park, Y. K. (2010). "Highly valuable chemicals production from catalytic upgrading of radiata pine sawdust-derived pyrolytic vapors over mesoporous MFI zeolites," *Applied Catalysis B: Environmental* 95(3-4), 365-373. DOI: 10.1016/j.apcatb.2010.01.015
- Paysepar, H., Rao, K. T. V., Yuan, Z., Shui, H., and Xu, C. C. (2018). "Improving activity of ZSM-5 zeolite catalyst for the production of monomeric

aromatics/phenolics from hydrolysis lignin *via* catalytic fast pyrolysis," *Applied Catalysis A: General* 563, 154-162. DOI: 10.1016/j.apcata.2018.07.003

- Salanti, A., Zoia, L., Orlandi, M., Zanini, F., and Elegir, G. (2010). "Structural characterization and antioxidant activity evaluation of lignins from rice husk," *Journal of Agricultural & Food Chemistry* 58(18), 10049-10055. DOI: 10.1021/jf102188k
- Samuel, R., Pu, Y., Raman, B., and Ragauskas, A.J. (2010). "Structural characterization and comparison of switchgrass ball-milled lignin before and after dilute acid pretreatment," *Applied Biochemistry & Biotechnology* 162(1), 62-74. DOI: 10.1007/s12010-009-8749-y
- Shao, S., Zhang, H., Xiao, R., Li, X., and Cai, Y. (2018). "Controlled regeneration of ZSM-5 catalysts in the combined oxygen and steam atmosphere used for catalytic pyrolysis of biomass-derivates," *Energy Conversion and Management* 155, 175-181. DOI: 10.1016/j.enconman.2017.10.062
- Shvets, O. V., Konysheva, K. M., and Kurmach, M. M.(2018). "Morphology and catalytic properties of hierarchical zeolites with MOR, BEA, MFI, and MTW topology," *Theoretical and Experimental Chemistry* 54(2), 138-145. DOI: 10.1007/s11237-018-9557-7
- Sie, S., De Vries, A., Mesters, C., Boone, A., Bottenberg, K., and Trautrims, B. (1996). "Development and industrial performance of a zeolite-based xylene isomerization catalyst," *Erdöl, Erdgas, Kohle* 112(11), 463-466.
- Thompson, D. N., Ginosar, D. M., and Burch, K. C. (2005). "Regeneration of a deactivated USY alkylation catalyst using supercritical isobutane," *Applied Catalysis A: General* 279(1-2), 109-116. DOI: 10.1016/j.apcata.2004.10.018
- Tsai, T. C. (2006). "Reactivation of acidic sites in mordenite used in toluene disproportionation," *Applied Catalysis A: General* 301(2), 292-298. DOI: 10.1016/j.apcata.2005.12.011
- Vermeiren, W., and Gilson, J. P. (2009). "Impact of zeolites on the petroleum and petrochemical industry," *Topics in Catalysis* 52(9), 1131-1161. DOI: 10.1007/s11244-009-9271-8
- Veses, A., Puértolas, B., Callén, M. S., and García, T. (2015). "Catalytic upgrading of biomass derived pyrolysis vapors over metal-loaded ZSM-5 zeolites: Effect of different metal cations on the bio-oil final properties," *Microporous & Mesoporous Materials* 209, 189-196. DOI: 10.1016/j.micromeso.2015.01.012
- Wang, J., Lin, B. C., Huang, Q. X., Ma, Z. Y., and Yan, J. H. (2017). "Aromatic hydrocarbon production and catalyst regeneration in pyrolysis of oily sludge using ZSM-5 zeolites as catalysts," *Energy & Fuels* 31(11), 11681-11689. DOI: 10.1021/acs.energyfuels.7b01855
- Wright, P. A., and Pearce, G. M. (2010). "Structural chemistry of zeolites," in: Zeolites & Catalysis: Synthesis, Reactions and Applications, Wiley-VCH Verlag GmbH & Co., Berlin, Germany, pp. 171-207. DOI: 10.1002/9783527630295.ch7

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