# Production of Aromatic Hydrocarbons via Catalytic Pyrolysis of Biomass over Fe-Modified HZSM-5 Zeolites

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ABSTRACT: Iron-modified HZSM-5 catalysts were prepared by partial ion exchange of NH_4ZSM-5 with Fe(II) at three different loadings (1.4, 2.8 and 4.2 wt %), and their effectiveness for producing aromatic hydrocarbons from cellulose, cellobiose, lignin and switchgrass by catalytic pyrolysis was screened using a microscale pyrolysis reactor coupled with gas chromatography–mass spectrometry (py-GC/MS). Two different catalyst to biomass ratios of 10/1 and 5/1 (w/w) were studied to determine the varying effects at full and partial conversion of the primary oxygenated pyrolysis vapors. Among the four catalysts screened (including the parent HZSM-5), the one loaded with iron at 1.4 wt % Fe [Fe-HZSM-5 (1.4)] produced the largest increase in production of aromatic hydrocarbons from cellulose, cellobiose and lignin. From cellulose, a carbon yield of selected aromatics (benzene, toluene, o,p-xylenes, ethylbenzene, 1,2,4-trimethylbenzene, naphthalene and 2-methylnapthalene) of ∼18% was achieved with Fe-HZSM-5 (1.4), and for cellobiose the carbon yield of selected aromatics using Fe-HZSM-5 (1.4) was 25%. For switchgrass, Fe-HZSM-5 (1.4) catalyst produced a similar carbon yield of aromatics as the standard HZSM-5 (∼17%) but higher loadings of Fe decreased the yield. However, for all of the starting materials studied, the chemical selectivity of the aromatic products changed with addition of Fe to the catalyst. Benzene and naphthalenes were favored for the iron containing catalysts compared with the standard HZSM-5, while the selectivities for p-xylene, ethylbenzene and trimethylbenzene were decreased with the addition of iron.

KEYWORDS: Catalytic pyrolysis, Biomass, HZSM-5, Aromatics, Hydrocarbons, Iron, Cellulose, Cellobiose, Lignin
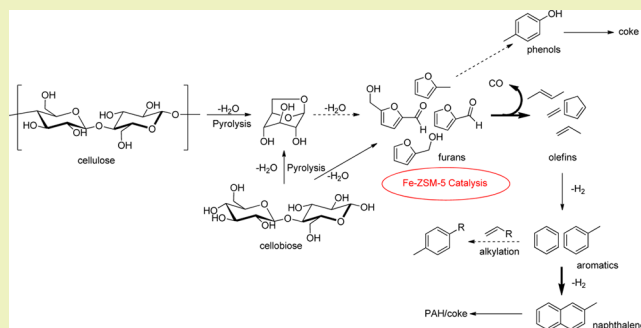
INTRODUCTION

Lignocellulosic biomass is the most abundant renewable resource available for the production of biofuels and biobased chemicals and materials.[1] To use this considerable source of renewable carbon as a feedstock for producing such products using existing infrastructure requires efficient conversion of these materials to stable liquids. Fast pyrolysis processes have shown promise as inexpensive routes to liquefy and densify biomass in high yield; however, the unfavorable properties exhibited because of the high concentration of oxygenated compounds in pyrolysis oils (bio-oil) have hindered its utilization as a fuel, refinery feed or chemical feedstock.[2,3] The most studied method of producing a stable pyrolysis liquid comprising a higher concentration of defunctionalized hydrocarbons has been the production of aromatic hydrocarbons via pyrolysis in the presence of HZSM-5 based catalysts.[4−12] Aromatics are good target products for biomass conversion, because like the biomass itself they have low H/C ratios, meaning they can be produced in relatively high carbon yield without addition of external hydrogen. The bulk partially deoxygenated bio-oil can go on to be upgraded to hydrocarbon fuels with lower hydrogen demand than traditional pyrolysis oil. Alternatively, the aromatic hydrocarbons can be separated and used directly as fuel blendstocks or in chemical applications. For example, toluene and xylenes can be blended into gasoline at high concentrations and in lower concentrations for distillate fuels. Aromatics are also starting materials for many industrial chemicals. For example, p-xylene is in high demand for conversion to terephthalic acid, which is then polymerized to polyethylene terephthalate (PET).[13,14]

There have been many recent efforts that aim at modifying the HZSM-5 catalyst to produce aromatic hydrocarbons in higher yield and/or enhance the selectivity to particular target compounds. Efforts to increase the yield of p-xylene include narrowing the openings of the pore structure of HZSM-5, to favor the formation of the p-substituted structure.[14] Other modifications include adding metals to the catalyst either via ion exchange with the acid site or by incorporation into the zeolite framework. Ga addition to ZSM-5 has been reported to be successful at increasing the yields of aromatic hydrocarbons from catalytic pyrolysis of biomass model compounds and pine wood.[15] Other metal-modified zeolites have also been screened for their effect on the process, with at best, marginal improvements in the yield or selectivity of aromatic hydrocarbons.[16−19]

Table 1. Preparation of Catalysts used in this Study

catalyst	NH$_4$ZSM-5 (g)	FeCl$_2$·4H$_2$O (g)	NH$_4$Cl (g)	wt % Fe	acidity (umol/g)[a]
HZSM-5	2.0			0	1022 ± 61
Fe-HZSM-5 (1.4)	2.0	0.1	0.1	1.4	1063 ± 64
Fe-HZSM-5 (2.8)	2.0	0.2	0.2	2.8	958 ± 57
Fe-HZSM-5 (4.2)	2.0	0.4	0.4	4.2	948 ± 57

[a]Measured by isopropylamine temperature-programmed desorption.

Use of iron to modify the HZSM-5 zeolite would be an attractive option because iron is inexpensive and environmentally benign. Iron, because of its stability at both the 2$^+$ and 3$^+$ oxidation states is well-known to facilitate oxygen transfer redox reactions, and in fact FeZSM-5 catalysts are used for both selective oxidations[20,21] and reductions.[22,23] Therefore, iron could find a role in facilitating removal of oxygen in reactions of biomass pyrolysis vapors.

Some have attempted to use the iron oxide containing "red mud" clay as an inexpensive catalyst for the deoxygenation of pyrolysis vapors. However, in these cases only limited success at deoxygenation was achieved, less so than standard HZSM-5 catalyzed pyrolysis.[24,25] There have only been limited reports on the use of Fe-modified HZSM-5 as a catalyst for biomass pyrolysis.[20,26] At a 2 wt % Fe loading, the bio-oil produced from catalytic pyrolysis of willow wood was reported to have lower oxygen content than that produced with HZSM-5 or GaZSM-5 but with lower yields.[26] Another report at higher Fe-loadings (5 wt %) showed a higher level of coke production than with standard HZSM-5.[20] Recently, we reported that there was a correlation between iron present in the biomass and aromatic hydrocarbon yield via catalytic pyrolysis over HZSM-5.[27] The results suggested that in contrast to other active minerals in the biomass, which affect the pathways of the initial thermal depolymerizaton, Fe is active in the catalytic chemistry. We sought to determine if this observation could be exploited to develop better catalysts through simple modification of the HZSM-5 catalyst. To test this hypothesis and to learn more about the iron on the catalytic pyrolysis chemistry, in this contribution we report on the py-GC/MS screening of HZSM-5 catalysts exchanged with Fe(II) at three low loadings, 1.4, 2.4 and 4.2 wt %, for the conversion of cellulose, cellobiose, lignin and switchgrass.

■ MATERIALS AND METHODS

Materials. Cellulose, cellobiose, FeCl$_2$·4H$_2$O, NH$_4$Cl and authentic compounds employed as standards for GC/MS calibration were purchased from Sigma-Aldrich and used as received. NH$_4$ZSM-5 (CBV-2314; 23 SiO$_2$:Al$_2$O$_3$) was purchased from Zeolyst International (Conshohocken, PA). Lignin was purchased from Granit Research and Development SA. Switchgrass was provided by the McDonnel Farm (East Greenville, PA) and finely ground and dried prior to use.

Catalyst Preparation. The ion exchange on ZSM-5 catalysts was performed in a procedure modified from Brandenberger et al.[23] using NH$_4$ZSM-5, FeCl$_2$·4H$_2$O and ammonium chloride. Liquid ion exchange was conducted with various amounts of FeCl$_2$·4H$_2$O and ammonium chloride depending on the desired degree of Fe/Al exchange (Table 1). These compounds and 2 g of NH$_4$ZSM-5 were combined in 200 mL of N$_2$ sparged deionized water. The mixture was stirred overnight under nitrogen at 80 °C. The resulting orange Fe-ZSM-5 powder was rinsed with 200 mL/g deionized water. The powder was dried overnight under an air atmosphere at 80 °C and calcined at 500 °C under nitrogen for 3 h, converting remaining NH$_4$ sites to acid sites.

Pyrolysis Experiments. Micropyrolysis was performed by a Frontier Lab Double-Shot micropyrolyzer PY-3030iD with a Frontier

Lab Auto-Shot Sampler AS-1020E attached to a gas chromatograph, Shimadzu GC-2010.[10] Detection of products was achieved using a Shimadzu GCMS-QP2010S mass spectrometer. The interface temperature of the micropyrolyzer was set to 300 °C and the furnace was set to 500 °C. A 1:10 or 1:5 ratio biomass to catalyst ratio was used for catalytic pyrolysis. A sample size of ~0.3 mg biomass and ~1.5 or ~3.0 mg catalyst was subjected to a single-shot pyrolysis at 500 °C for 30 s using stainless steel cups (disposable eco-cup LF; Frontier Laboratories) followed by separation on the GC. The biomass was added to the cup first and then the catalyst was added directly on top of the biomass. The pyrolysis vapors therefore diffused through the catalyst to exit the cup. Analysis of condensable gas was performed on a RTX-1701 60 m × 0.25 mm GC fused silica capillary column with a 0.25 μm film thickness. The oven for the GC column was set at an initial temperature of 45 °C for 5 min followed by a ramp rate of 3 °C min^{-1} to 280 °C and held for 20 min for a total run time of 102 min. The injector temperature was at 250 °C with a split ratio of 90:1 and a helium flow rate of 1 mL min^{-1}. For the analysis of noncondensable gases, identical experiments were performed with a different column and GC method. A split ratio of 100 and a CP-PoraBOND Q 25 m × 0.25 mm fused silica capillary column was used (Varian, Palo Alto, CA). The oven for the GC column was set at 35 °C for 3 min followed by a ramp rate of 5 °C min^{-1} up to 150 °C then 10 °C min^{-1} to 250 °C and held for 45 min for a total run time of 81 min. Quantitative analysis of the yield of individual chemical products was done by the external standard method, using authentic samples to generate calibration curves. Analyses were performed in triplicate and compared statistically using analysis of variance (ANOVA).

■ RESULTS AND DISCUSSION

The variation of the overall production of aromatic hydrocarbons (represented by eight of the most abundantly produced: benzene, toluene, o- and p-xylene, ethylbenzene, 1,2,4-timethylbenzene, naphthalene and 2-methylnaphtalene), with the loading of Fe on HZSM-5, for a 10/1 mass ration of biomass to catalyst is shown in Figure 1. As expected, aromatic
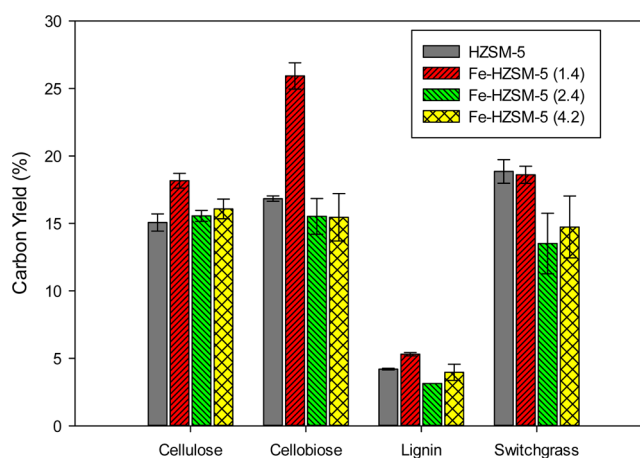
Figure 1. Aromatic hydrocarbon production from each biomass feedstock with different catalysts at (catalyst/feedstock = 10 w/w). Average of three replicates; error bars are one standard deviation.

Table 2. Carbon Yields and Aromatic Selectivities for Pyrolysis of Cellulose (Catalyst/Cellulose = 10 w/w)

catalyst	none	HZSM-5	Fe-HZSM-5 (1.4)	Fe-HZSM-5 (2.8)	Fe-HZSM-5 (4.2)
carbon yield (%)					
BTEX[a]	0.04	12.03[A]	12.64[A]	11.47[A]	11.24[A]
naphthalenes[b]	0.01	2.65[D]	5.35[A]	4.00[C]	4.74[B]
phenols[c]	0.05	0.49[A]	0.22[B]	0.01[C]	0.04[C]
acetic acid	0.15	0.06[A]	0.01[A]	0.00[B]	0.00[B]
levoglucosan	28.78	0.00[A]	0.00[A]	0.00[A]	0.01[A]
HMF[d]	1.69	0.00[A]	0.00[A]	0.00[A]	0.00[A]
other oxygenates[e]	1.41	0.00[A]	0.00[A]	0.02[A]	0.02[A]
CO	0.95	9.25[B]	10.99[A]	11.12[A]	10.65[AB]
CO_2	1.18	4.78[B]	5.39[A]	5.55[A]	5.21[AB]
olefins[f]	0.08	2.68[A]	1.62[C]	2.26[B]	1.82[C]
aromatic hydrocarbon selectivity (%)					
benzene		11.74[B]	14.65[A]	14.13[A]	14.23[A]
toluene		41.86[A]	39.18[B]	41.82[A]	39.75[A]
p-xylene		19.15[A]	12.45[C]	14.03[BC]	12.05[C]
o-xylene		1.72[BC]	2.01[ABC]	2.37[AB]	2.80[A]
ethylbenzene		5.34[B]	1.26[A]	1.35[A]	1.11[A]
1,2,4-trimethylbenzene		2.61[A]	1.00[B]	0.59[C]	0.58[C]
naphthalenes[b]		17.59[C]	29.45[A]	25.72[B]	29.49[A]

[a]BTEX = benzene, toluene, ethylbenzene and xylenes. [b]naphthalenes = naphthalene and 2-methylnapthalene. [c]Phenols = phenol, p-,o-,m-cresols, 2,4-dimethylphenol, 4-ethylphenol. [d]HMF = 5-hydroxymethylfurfural. [e]Other oxygenates = acetol, furfural, furfuryl alcohol, 2,3-butandione. [f]Olefins = ethylene, propene. Values in a row that do not share a superscript capital letter are statistically different based on ANOVA of three replicates.

Table 3. Carbon Yields and Aromatic Selectivities for Pyrolysis of Cellobiose (Catalyst/Cellobiose = 10 w/w)

catalyst	none	HZSM-5	Fe-HZSM-5 (1.4)	Fe-HZSM-5 (2.8)	Fe-HZSM-5 (4.2)
carbon yield (%)					
BTEX[a]	0.03	12.71[B]	18.20[A]	11.34[B]	11.28[B]
naphthalenes[b]	0.02	3.77[B]	7.50[A]	4.13[B]	4.12[B]
phenols[c]	0.03	0.82[A]	0.14[B]	0.16[B]	0.09[B]
acetic acid	0.24	0.32[A]	0.03[B]	0.06[B]	0.00[B]
levoglucosan	10.32	0.00[A]	0.00[A]	0.71[A]	0.57[A]
HMF[d]	19.35	0.00[A]	0.00[A]	0.00[A]	0.00[A]
other oxygenates[e]	2.12	0.61[A]	0.13[C]	0.25[BC]	0.20[BC]
CO	1.60	9.10[B]	12.03[A]	9.99[A]	10.25[A]
CO_2	2.98	6.81[A]	7.44[A]	7.96[A]	8.04[A]
olefins[f]	0.10	1.88[A]	1.92[A]	1.94[A]	1.85[A]
aromatic hydrocarbon selectivity (%)					
benzene		10.93[B]	12.12[B]	14.73[A]	15.76[A]
toluene		41.13[B]	39.42[B]	44.05[A]	42.84[A]
p-xylene		17.30[A]	14.08[B]	11.29[C]	11.39[C]
o-xylene		1.79[B]	3.24[A]	1.55[B]	1.68[B]
ethylbenzene		4.34[A]	1.31[B]	1.42[B]	1.32[B]
1,2,4-trimethylbenzene		2.15[A]	0.89[B]	0.38[B]	0.38[B]
naphthalenes[a−f]		22.36[C]	28.94[A]	26.58[B]	26.63[B]

[a−f]See Table 2 footnote for definitions. Values in a row that do not share a superscript capital letter are statistically different based on ANOVA of three replicates.

hydrocarbons are more readily produced from cellulose and cellobioise than from lignin.[10,28,29] When an actual biomass sample (switchgrass) was pyrolyzed, overall the catalysts performed similarly to the carbohydrates in terms of total carbon yield of aromatic hydrocarbons produced. This is consistent with the results of the model components because switchgrass contains only about 10−20% lignin.[30] The pyrolysis of cellulose and cellobiose responded the most to the presence of iron in the catalyst, with the catalyst having the lowest loading of iron (1.4 wt %) resulting in a significant increase in the production of aromatics for each of those feedstocks, with an especially large increase yield increase from cellobiose, up to

25% carbon yield. For cellulose, the carbon yield of aromatics increased to about 18% from about 15% with the standard HZSM-5 catalyst.

Table 2 presents a more detailed breakdown of the variation in product carbon yields and selectivities for the aromatic hydrocarbons for the conversion of cellulose. The major product of the initial pyrolytic breakdown of cellulose (as shown by the noncatalytic results in the first column of the table) is levoglucosan; it along with most of the other oxygenates are completely converted for all catalysts at this catalyst:biomass (10/1) ratio. The chemical pathway to aromatics from levoglucosan involves acid catalyzed dehydra-
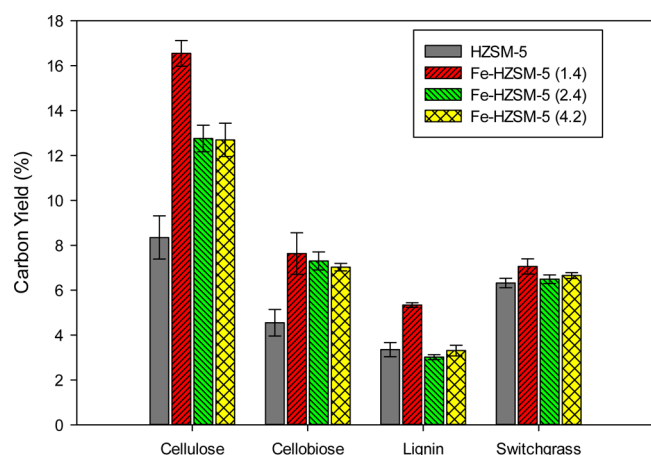
Figure 2. Aromatic hydrocarbon production from each biomass feedstock with different catalysts at (catalyst/feedstock = 5 w/w). Average of three replicates; error bars are one standard deviation.

tion to furans, which undergo a variety of reactions inside the pores of the catalyst to form aromatics, olefins, CO, CO_2, water and coke. The increase in aromatic hydrocarbons for the iron loaded catalysts is mostly due to an increase in the yield of naphthalenes, but at minimal to no cost to the production of total BTEX. For each of the Fe loaded catalysts, the selectivity to benzene increases (from about 11% to about 14%) while the selectivity for toluene remains steady, but the selectivity for *p*-xylene, ethylbenzene and trimethylbeznene decrease. This may indicate that Fe can affect the secondary reactions favoring those that increase the size of the molecules through further aromatization to naphthalenes over those that alkylate the benzenes initially formed (see below, Figure 3). This is the opposite of what is observed for Ga-exchanged HZSM-5 catalysts, where Ga is suggested to increase alkylation reactions.[14] Although accounting for only a small portion of the carbon yield, there is also variation in the production of phenols with the catalysts. Phenol and alkyl phenols (in this

case cresols, methyl cresols and ethylphenols) tend to account for only a small portion of the products in microscale catalytic pyrolysis experiments like these, but are often found in higher concentration in production scale biomass catalytic pyrolysis experiments.[6,8,11,12] From carbohydrates, phenols are thought to be intermediate products that are formed at higher levels when catalysts start to deactivate.[12,31] In this case, their production dropped with the addition of iron to the catalysts. CO production increased, indicating that Fe may promote decarbonylation reactions. Olefin (ethylene and propene) production also decreased for the iron containing catalysts compared with HZSM-5, with the most effective catalyst for aromatic production, the 1.4 wt % Fe loaded HZMS-5 producing the lowest amount of olefins.

To gain more insight into the effects of iron on these chemical pathways, the experiments were also conducted on cellobiose (Table 3). Cellobiose is a molecule consisting of only two glucose units, meaning in contrast to cellulose, depolymerization is not a major factor in its pyrolysis behavior. Therefore, its initial product distribution from pyrolysis is different than that of cellulose. For cellobiose, 5-hydroxymethylfurfural (HMF) is the major product of pyrolysis, along with a substantial amount of levoglucosan. Like the case of cellulose, the 1.4 wt % Fe loaded catalyst produced the largest increase in aromatics, but unlike cellulose, there was a dramatic increase in both naphthalenes and BTEX production. Similar trends in the selectivity were seen with increasing selectivity for benzene and decreasing selectivity toward *p*-xylene, ethylbezene and trimethylbenzene. Similar again to the case of cellulose was an increase in CO production; however, in this case, the production of olefins was the same as that with the HZMS-5 catalyst.

The near complete conversion of all oxygenated species in the above-described experiments suggests that these experiments were done at excess catalysts loading (catalyst/biomass = 10 w/w). To gain more insight into the possible chemical effects of added iron on the catalytic pyrolysis of these

**Table 4. Carbon Yields and Aromatic Selectivities for Pyrolysis of Cellulose (Catalyst/Cellulose =5 w/w)**

catalyst	none	HZSM-5	Fe-HZSM-5 (1.4)	Fe-HZSM-5 (2.8)	Fe-HZSM-5 (4.2)
carbon yield (%)					
BTEX[a]	0.04	6.30[C]	11.32[A]	8.88[B]	8.20[B]
naphthalenes[b]	0.01	1.82[D]	5.09[AB]	3.81[C]	4.45[BC]
phenols[b]	0.05	1.24[A]	0.34[B]	0.35[B]	0.30[B]
acetic acid	0.15	1.04[A]	0.08[B]	0.21[B]	0.26[B]
levoglucosan	28.78	0.17[B]	1.19[AB]	2.62[A]	2.42[A]
HMF[d]	1.69	0.00[B]	0.03[A]	0.00[B]	0.00[B]
other oxygenates[e]	1.41	0.31[A]	0.00[B]	0.29[A]	0.36[A]
CO	0.95	8.44[C]	10.67[AB]	9.32[BC]	8.64[C]
CO_2	1.18	3.90[D]	5.37[A]	4.63[BC]	4.14[D]
Olefins[f]	0.08	0.98[C]	1.56[B]	1.90[A]	1.47[B]
aromatic hydrocarbon selectivity (%)					
benzene		11.91[B]	13.71[A]	11.93[A]	11.84[A]
toluene		39.35[B]	38.42[A]	39.25[A]	36.36[A]
p-xylene		18.14[A]	13.35[C]	15.18[B]	14.03[BC]
o-xylene		0.72[A]	1.44[A]	1.09[A]	0.89[A]
ethylbenzene		5.39[A]	1.48[C]	2.19[B]	1.48[C]
1,2,4-trimethylbenzene	2.62[A]	0.82[B]	0.52[C]	0.38[C]	
naphthalenes[b]		21.86[C]	30.78[B]	29.85[B]	35.02[A]

[a–f]See Table 2 footnote for definitions. Values in a row that do not share a superscript capital letter are statistically different based on ANOVA of three replicates.

Table 5. Carbon Yields and Aromatic Selectivities for Pyrolysis of Cellobiose (Catalyst/Cellobiose = 5 w/w)

catalyst	none	HZSM-5	Fe-HZSM-5 (1.4)	Fe-HZSM-5 (2.8)	Fe-HZSM-5 (4.2)
carbon yield (%)					
BTEX[a]	0.03	3.05[A]	4.47[A]	4.72[A]	4.27[A]
naphthalenes[b]	0.02	1.43[A]	3.14[B]	2.55[B]	2.73[B]
phenols[c]	0.03	0.66[A]	0.17[B]	0.20[B]	0.18[B]
acetic acid	0.24	1.07[A]	0.35[B]	0.37[B]	0.43[B]
levoglucosan	10.32	2.63[A]	3.05[A]	1.91[A]	1.78[A]
HMF[d]	19.35	0.18[A]	0.11[A]	0.01[A]	0.18[A]
other oxygenates[e]	2.12	2.25[A]	0.44[B]	0.44[B]	0.56[B]
CO	1.60	8.24[B]	12.73[A]	9.10[B]	9.24[B]
CO_2	2.98	5.52[A]	8.20[A]	6.81[A]	7.03[A]
olefins[f]	0.10	1.60[A]	2.09[A]	1.88[A]	1.65[A]
aromatic hydrocarbon selectivity (%)					
benzene		13.07[A]	11.78[B]	11.77[B]	11.54[B]
toluene		36.01[A]	31.98[A]	36.01[A]	33.97[A]
p-xylene		13.23[A]	12.63[A]	14.58[A]	13.56[A]
o-xylene		0.98[A]	1.24[A]	0.88[A]	0.86[A]
ethylbenzene		3.80[A]	0.93[B]	1.45[B]	0.92[B]
1,2,4-trimethylbenzene	1.57[A]	0.35[B]	0.36[B]	0.33[B]	
naphthalenes[b]		31.34[C]	41.09[A]	34.94[BC]	38.82[AB]

$^{a-f}$See Table 2 footnote for definitions. Values in a row that do not share a superscript capital letter are statistically different based on ANOVA of three replicates.
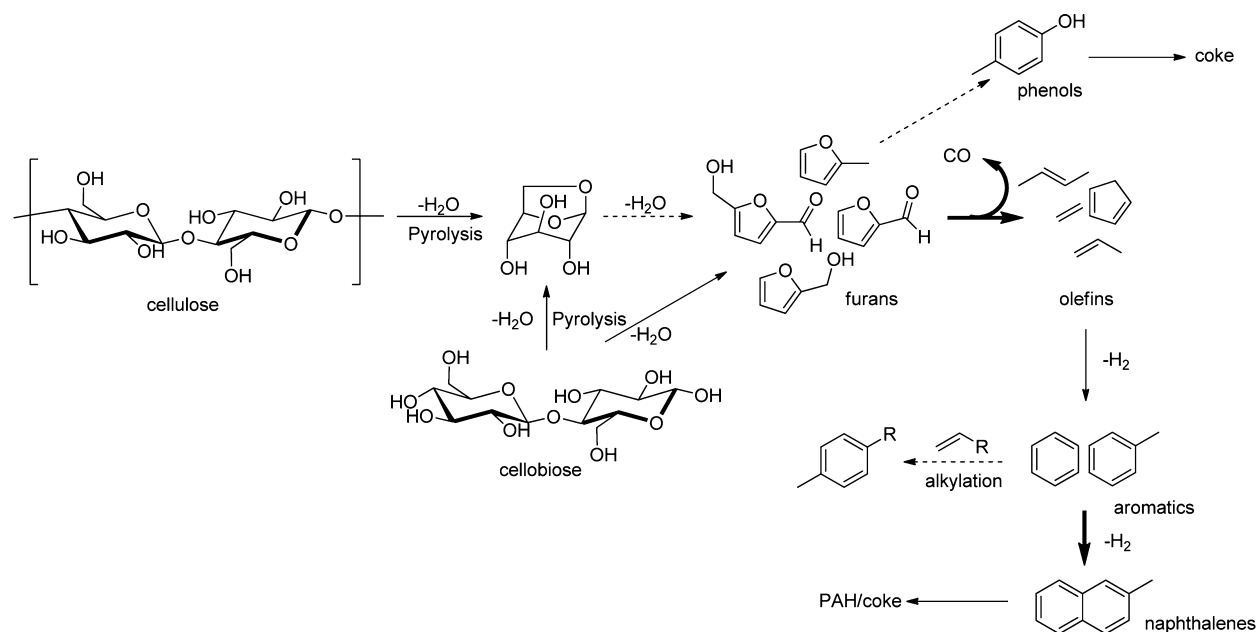
Figure 3. Scheme for production of aromatic hydrocarbons from biomass carbohydrates via catalytic pyrolysis over (Fe) H-ZSM-5. Bold arrows indicate pathways suggested to be enhanced by the presence of small amounts of Fe, and dashed arrows indicate pathways suggested to be suppressed by addition of Fe.

carbohydrates, the experiments were conducted at a lower catalyst loading where intermediate species can be observed. The comparisons of total aromatic hydrocarbon production for each of the feedstocks and each of the catalysts at a 5/1 catalyst to biomass ratio are shown in Figure 2, and detailed results for cellulose are presented in Table 4. For cellulose, at a 5/1 loading, all of the Fe-containing catalysts exhibit higher production of aromatic hydrocarbons than standard HZSM-5 with the catalyst loaded at 1.4 wt % again performing the best. The carbon yield of aromatic hydrocarbons using this catalyst at 5/1 ratio (16.4%) approached that achieved at 10/1 (18%), while the production of aromatic hydrocarbons with standard

HZSM-5 was much lower than that achieved at the higher loading (8.1% vs 14.6%). For all of the Fe-containing catalysts the carbon yield of naphthalenes remains high (∼5%) even at the lower catalyst loading. The conversion of oxygenates for HZSM-5 remains high, but for the iron added catalyst some levoglucosan (1.2−2.5%) remains unconverted. This difference is likely a reflection of the decreased acidity of the catalyst effecting the dehydration of levoglucosan to furans. At the lower catalyst loadings (5/1) the yield of phenols from cellulose pryolysis over HZSM-5 increases to greater than 1% of the input carbon. The yield of phenol is lower for each of the Fe-HZMS-5 catalysts, indicating that iron addition may

Table 6. Carbon Yields and Aromatic Selectivities for Pyrolysis of Lignin (Catalyst/Lignin = 10 w/w)

catalyst	none	HZSM-5	Fe-HZSM-5 (1.4)	Fe-HZSM-5 (2.8)	Fe-HZSM-5 (4.2)
carbon yield (%)					
BTEX[a]	0.10	3.20[BC]	3.68[AB]	2.18[CD]	2.72[D]
naphthalenes[b]	0.01	0.69[C]	1.47[A]	0.88[C]	1.13[B]
phenols[c]	0.40	0.09[B]	0.15[A]	0.09[B]	0.07[B]
methoxylated phenols[d]	8.36	3.69[A]	2.26[B]	3.14[A]	2.45[B]
CO	1.00	1.30[B]	1.47[B]	1.70[A]	1.77[A]
CO_2	1.73	1.73[B]	1.39[C]	2.30[A]	2.47[A]
olefins	0.33	2.25[A]	1.30[A]	1.43[A]	2.03[A]
aromatic hydrocarbon selectivity (%)					
benzene		5.24[C]	9.99[AB]	8.79[B]	11.37[A]
toluene		31.96[B]	36.97[A]	33.80[A]	34.46[A]
p-xylene		33.84[A]	19.12[B]	23.39[B]	19.76[B]
o-xylene		2.65[A]	2.45[A]	2.45[A]	2.59[A]
ethylbenzene	2.47[A]	0.80[B]	0.82[B]	0.51[B]	
1,2,4-trimethylbenzene		7.49[A]	2.91[B]	2.78[B]	2.69[B]
naphthalenes[b]		16.35[B]	27.76[A]	27.98[A]	28.62[A]

[a–c]See Table 2 footnote for definitions. [d]Methoxylated phenols = guaiacol, 4-methyl guaiacol, isoeugenol, vanillin, 1-(4-hydroxy-3-methoxyphenyl)acetone, syringol, syringaldehyde and 1-(4-hydroxy-3,5-dimethoxyphenyl)acetone. [e]Olefins = ethylene, propene. Values in a row that do not share a superscript capital letter are statistically different based on ANOVA of three replicates.

Table 7. Carbon Yields and Aromatic Selectivities for Pyrolysis of Lignin (Catalyst/Lignin = 5 w/w)

| catalyst	none	HZSM-5	Fe-HZSM-5 (1.4)	Fe-HZSM-5 (2.8)	Fe-HZSM-5 (4.2)
carbon yield (%)					
BTEX[a]	0.10	2.72[B]	3.95[A]	2.20[B]	2.37[B]
naphthalenes[b]	0.01	0.43[C]	1.26[A]	0.74[B]	0.85[B]
Phenols[c]	0.40	0.13[B]	0.23[A]	0.13[B]	0.13[B]
methoxylated phenols[d]	8.36	5.25[A]	3.38[B]	4.40[B]	4.03[B]
CO	1.00	1.28[B]	1.37[B]	1.34[B]	1.53[A]
CO_2	1.73	1.58[BC]	1.19[C]	1.72[AB]	1.89[A]
olefins[e]	0.33	2.07[A]	1.20[A]	1.55[A]	1.82[A]
aromatic hydrocarbon selectivity (%)					
benzene		5.51[C]	9.09[AB]	7.28[BC]	8.58[AB]
toluene		32.78[C]	39.04[A]	33.84[B]	31.24[B]
p-xylene		37.29[A]	23.10[B]	29.02[B]	28.63[B]
o-xylene		1.64[A]	1.61[A]	1.67[A]	2.05[A]
ethylbenzene	3.79[A]	1.13[B]	1.21[B]	1.03[B]	
1,2,4-trimethylbenzene	6.26[A]	2.38[B]	2.47[B]	2.68[B]	
naphthalenes[b]	12.72[B]	23.66[A]	24.51[A]	25.77[A]	

[a–c]See Table 2 footnote for definitions. [d,e]See Table 6 footnote for definitions. Values in a row that do not share a superscript capital letter are statistically different based on ANOVA of three replicates.

suppress the formation of these intermediates, which are likely converted to coke at the higher catalyst loading.[32] Similar to the results at the higher loading, the aromatic selectivity to alkyl benzenes (p-xylene, ethylbenzene and trimethylbezne) is decreased with the addition of iron to the catalyst.

Cellobiose shows similar trends to cellulose when the catalyst loadings are decreased; although in this case the lower carbon yield of BTEX (3–5%) is observed for all catalysts (Table 5). However, the carbon yield of naphthalenes remains at levels near that produced at the higher loading for all the Fe-containing catalysts (2.5–3%). Both BTEX and naphthalenes production is increased for Fe-containing catalysts as compared to the standard HZSM-5. Like in the case of cellulose, some levoglucosan remains unconverted for all of the catalysts at this lower catalyst loading, and the aromatic selectivity trends are also similar. Taken together the effects of Fe-doping on the chemistry of aromatics production from biomass carbohydrates can be summarized, as shown in Figure 3; the decreased acidity

of the catalyst slows the dehydration of levoglucosan to furans, and decarboxylation of furans to olefins may be increased. After initial aromatic formation, ring growth to naphthalenes is favored over alkylation, and formation of phenols is suppressed. The possibility that ring growth only to naphthalenes without further ring growth to larger polyaromatic hydrocarbons and coke is supported by the observation of increased overall yields of naphthalenes at the higher catalyst loading (10/1).

To understand how the loading of Fe onto HZSM-5 catalyst may influence the breakdown of the noncarbohydrate portion of biomass, these experiments were also performed on isolated lignin (Tables 6 and 7). Lignin is known to produce poor yields of aromatic hydrocarbons via catalytic pyrolysis over HZSM-5 based catalysts, due to large amounts of char and coke formation.[10,28,29] In these experiments total aromatic hydrocarbon yield from lignin was 3.5–5% carbon. Despite the aromatic structure of the lignin, the hydrocarbons that do form are thought to be derived from the aliphatic linkers of the
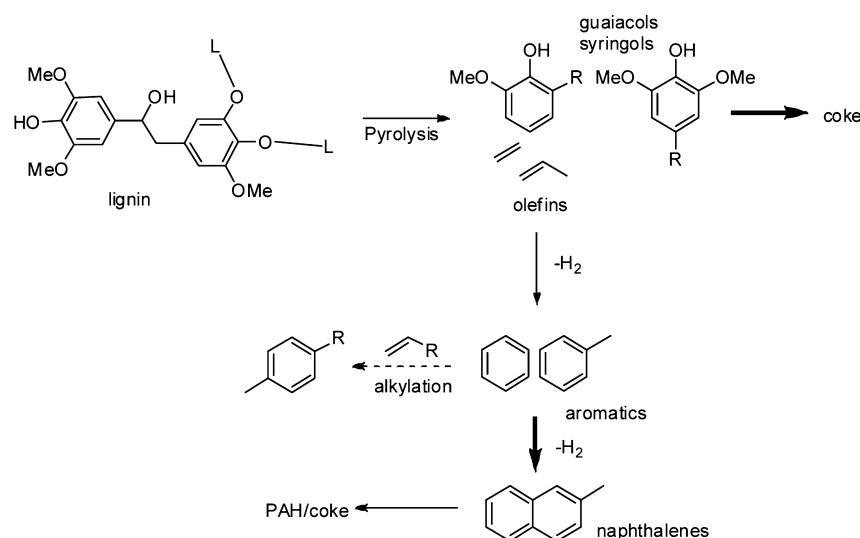
Figure 4. Scheme for production of aromatic hydrocarbons from lignin via catalytic pyrolysis over (Fe) H-ZSM-5. Bold arrows indicate pathways suggested to be enhanced by the presence of small amounts of Fe, and dashed arrows indicate pathways suggested to be suppressed by addition of Fe.

Table 8. Carbon Yields and Aromatic Selectivities for Pyrolysis of Switchgrass (Catalyst/Switchgrass = 10 w/w)

catalyst	none	HZSM-5	Fe-HZSM-5 (1.4)	Fe-HZSM-5 (2.8)	Fe-HZSM-5 (4.2)
carbon yield (%)					
BTEX[a]	0.07	15.97[A]	14.30[AB]	10.84[C]	11.68[BC]
naphthalenes[b]	0.01	2.24[C]	3.99[A]	2.54[BC]	2.89[B]
phenols[c]	0.14	0.34[A]	0.05[B]	0.03[B]	0.05[B]
methoxylated phenols[d]	1.06	0.08[A]	0.01[A]	0.01[A]	0.01[A]
acetic acid	2.12	0.18[A]	0.00[A]	0.00[A]	0.00[A]
levoglucosan	2.75	0.03[A]	0.00[A]	0.00[A]	0.03[A]
HMF[e]	0.58	0.00[A]	0.00[A]	0.00[A]	0.00[A]
other oxygenates[f]	1.98	0.16[A]	0.05[A]	0.06[A]	0.05[A]
CO	1.69	5.88[A]	5.71[A]	6.7[A]	6.57[A]
CO_2	3.94	5.26[A]	3.65[B]	6.27[A]	5.87[A]
olefins[g]	0.25	2.59[A]	1.72[A]	2.81[A]	2.47[a]
aromatic hydrocarbon selectivity (%)					
benzene		8.89[B]	11.12[A]	11.45[A]	11.72[A]
toluene		41.95[B]	39.43[B]	43.64[A]	42.64[A]
p-xylene		26.32[A]	20.53[B]	20.58[B]	20.03[B]
o-xylene		2.22[B]	4.38[A]	2.87[B]	3.25[B]
ethylbenzene		5.33[A]	1.38[B]	1.70[B]	1.61[B]
1,2,4-trimethylbenzene		3.42[A]	1.73[B]	0.97[C]	1.14[C]
naphthalenes[b]		11.88[D]	21.42[AB]	18.79[C]	19.61[BC]

[a−c,e−g]See Table 2 footnotes for definitions. [d]See Table 6 footnote for definitions. Values in a row that do not share a superscript capital letter are statistically different based on ANOVA of three replicates.

phenolic units.[29] The addition of Fe to the HZSM-5 catalysts did not greatly influence the overall yield of aromatics, but at both loadings studied the 1.4 wt % loaded Fe-ZSM5 was again best performing catalyst (Figures 1 and 2). The major volatile products of the initial pyrolysis, guaiacols and syringols (grouped as methoxylated phenols here) undergo higher conversion in the Fe-doped catalysts than the HZSM-5 based catalyst, but their ultimate product is unclear, coke perhaps. The trends in aromatic selectivity with Fe addition to the HZSM-5 are similar to those observed for the carbohydrates: selectivity for benzene and naphthalenes increases and selectivity for p-xylene, ethylbenzene and trimethylbenzene decreases. This indicates that once aromatics are formed, the effect of Fe on secondary reactions is the same as observed for the carbohydrate species, as would be expected. The effects of

added Fe on the chemical pathways of lignin pyrolysis are summarized in Figure 4.

Next, the set of catalysts were applied to switchgrass to determine if the effects seen on the model components translated to an actual biomass sample. As can be seen in Figures 1 and 2, unlike the model components, overall production of aromatic hydrocarbons was not significantly affected by the addition of Fe at 1.4 wt % to the HZSM-5 for switchgrass, and decreased the yield at higher loadings. This can perhaps be attributed to factors not present when working with the pure components such as the influence of mineral components including additional iron that is present within the biomass samples.[27,33] Although the overall yield of aromatics was not improved with the Fe-containing catalysts, the other trends that were observed in the components held

Table 9. Carbon Yields and Aromatic Selectivities for Pyrolysis of Switchgrass (Catalyst/Switchgrass = 5 w/w)

catalyst	none	HZSM-5	Fe-HZSM-5 (1.4)	Fe-HZSM-5 (2.8)	Fe-HZSM-5 (4.2)
carbon yield (%)					
BTEX[a]	0.07	5.06[A]	4.88[A]	4.89[A]	4.79[A]
naphthalenes[b]	0.01	0.99[D]	2.08[A]	1.53[CD]	1.80[BC]
phenols[c]	0.14	0.60[A]	0.18[B]	0.18[B]	0.18[B]
methoxylated phenols[d]	1.06	0.57[A]	0.22[B]	0.25[B]	0.28[B]
acetic acid	2.12	1.13[A]	0.22[B]	0.18[B]	0.19[B]
levoglucosan	2.75	0.17[A]	0.16[A]	0.18[A]	0.29[A]
HMF[e]	0.58	0.00	0.00	0.00	0.00
other oxygenates[f]	1.98	0.42[A]	0.15[B]	0.12[B]	0.14[B]
CO	1.69	5.88[A]	5.71[A]	6.76[A]	6.57[A]
CO_2	3.94	5.26[A]	3.65[B]	6.27[A]	5.87[A]
olefins[g]	0.25	2.59[A]	1.72[A]	2.81[A]	2.47[A]
aromatic hydrocarbon selectivity (%)					
benzene		9.19[A]	9.53[A]	9.58[A]	9.58[A]
toluene		37.66[A]	34.69[A]	37.81[A]	36.15[A]
p-xylene		25.55[A]	21.28[B]	24.13[AB]	22.79[B]
o-xylene		1.32[A]	1.75[A]	1.17[A]	1.41[A]
ethylbenzene	6.44[A]	1.93[C]	2.72[B]	2.10[C]	
1,2,4-trimethylbenzene	4.12[A]	1.34[B]	1.03[B]	0.97[B]	
naphthalenes[b]	15.71[D]	29.48[A]	23.56[C]	27.00[B]	

[a−c,e−g]See Table 2 footnotes for definitions. [d]See Table 6 footnote for definitions. Values in a row that do not share a superscript capital letter are statistically different based on ANOVA of three replicates.

when switchgrass was tested. The selectivities for benzene and naphthalenes were increased compared to the standard HZSM-5 catalyst and those for p-xylene, ethylbenzene and trimethylbenzene were decreased (Tables 8 and 9). At the lower catalyst loading (5/1), most of the remaining oxygenates were converted at higher rates using the Fe-containing catalysts, although this did not directly translate to a higher yield of total aromatics. These results indicate that Fe-HZSM-5 catalysts, particularly at low loadings of Fe, may be effective for use in applications where higher concentrations of benzene or naphthalenes in the product stream are desired. Studies on the effects of partial Fe-exchange on the long-term stability and effectiveness of HZSM-5 catalysts are currently underway.

CONCLUSIONS

Iron modification of HZSM-5 at low levels was effective for increasing the yield of aromatic hydrocarbons from carbohydrates via catalytic fast pyrolysis. Of the Fe-loadings studied, the smallest loading of 1.4 wt % proved to be the most effective. Iron modification of the zeolite changes the chemical pathways to favor formation of benzene and naphthalenes over p-xylene and other alkyl benzenes. Phenol formation was also inhibited by the addition of Fe, which may result in lower coke production. Although the yield increases were not shown to translate from the model carbohydrates to actual biomass (switchgrass), the selectivity changes did. Therefore, Fe-modified HZSM-5 catalysts may be effective for applications in which the product mixture rich in those components is desired.

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Notes
The authors declare no competing financial interest.
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