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George W Huber, *University of Massachusetts - Amherst*
T. R Carlson
G. A Tompsett

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ORIGINAL PAPER

Aromatic Production from Catalytic Fast Pyrolysis of Biomass-Derived Feedstocks

Torren R. Carlson · Geoffrey A. Tompsett · William C. Conner · George W. Huber

Abstract The conversion of biomass compounds to aromatics by thermal decomposition in the presence of catalysts was investigated using a pyroprobe analytical pyrolyzer. The first step in this process is the thermal decomposition of the biomass to smaller oxygenates that then enter the catalysts pores where they are converted to CO, CO_2, water, coke and volatile aromatics. The desired reaction is the conversion of biomass into aromatics, CO_2 and water with the undesired products being coke and water. Both the reaction conditions and catalyst properties are critical in maximizing the desired product selectivity. High heating rates and high catalyst to feed ratio favor aromatic production over coke formation. Aromatics with carbon yields in excess of 30 molar carbon% were obtained from glucose, xylitol, cellobiose, and cellulose with ZSM-5 (Si/Al = 60) at the optimal reactor conditions. The aromatic yield for all the products was similar suggesting that all of these biomass-derived oxygenates go through a common intermediate. At lower catalyst to feed ratios volatile oxygenates are formed including furan type compounds, acetic acid and hydroxyacetaldehyde. The product selectivity is dependent on both the size of the catalyst pores and the nature of the active sites. Five catalysts were tested including ZSM-5, silicalite, beta, Y-zeolite and silica–alumina. ZSM-5 had the highest aromatic yields (30% carbon yield) and the least amount of coke.

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T. R. Carlson · G. A. Tompsett · W. C. Conner ·
G. W. Huber (✉)
Department of Chemical Engineering, University of Massachusetts, 159 Goessmann Lab, Amherst, MA 01003, USA
e-mail: huber@ecs.umass.edu

Keywords Catalytic pyrolysis · Aromatics · Zeolite catalysts

1 Introduction

Due to its low cost and large availability, lignocellulosic biomass is being studied worldwide as a feedstock for renewable liquid biofuels [1–4]. Lignocellulosic biomass is not currently used as a liquid fuel because economical processes for its conversion have not yet been developed [1]. Currently there are several routes being studied to convert solid biomass to a liquid fuel, which involve multiple steps thus greatly increasing the cost of biomass conversion [5]. For example, ethanol production from lignocellulosic biomass, involves multiple steps including: pretreatment, enzymatic or acid hydrolysis, fermentation, and distillation [2]. Dumesic and co-workers have demonstrated that diesel range alkanes can be produced by aqueous-phase processing (APP) of aqueous carbohydrate solutions at low temperatures (100–300 °C) [6]. APP first requires that solid lignocellulosic biomass be converted into aqueous carbohydrates which would require pretreatment and hydrolysis steps. At high temperatures (~800 °C), Dauenhauer et al. have shown that solid biomass can be reformed to produce synthesis gas through partial oxidation in an auto thermal packed bed reactor over Rh catalysts [7]. The ideal process for solid biomass conversion involves the production of liquid fuels directly from solid biomass in a single step at short residence times. The catalytic fast pyrolysis process discussed in this paper comes very close to this ideal process since solid biomass is converted directly into liquid fuels (aromatics) in a single reactor at short residence times (<4 min). Fast pyrolysis involves rapidly heating biomass (>500 °C s^{-1})

to intermediate temperatures (400–600 °C) followed by rapid cooling (vapor residence times 1–2 s) [8]. The importance of pyrolysis heating rate is well known [9, 10]. One of the chief advantages of fast pyrolysis is that liquid fuels, called bio-oils or pyrolysis oils, are directly produced from solid biomass. This technology is economical on the smaller scale where smaller distributed plants can be built close to the location of the biomass [11, 12]. However, the bio-oils are of poor quality. They are thermally unstable, degrade with time, acidic, have a low heating value, and are not compatible with existing petroleum-derived oils [13]. Bio-oils must be catalytically upgraded if they are to be used as a conventional liquid transportation fuel [14–16]. As we have previously shown introduction of zeolite catalysts into the pyrolysis process can convert oxygenated compounds generated from pyrolysis into aromatics [17]. The purpose of this paper is to discuss in more detail aromatic production by catalytic fast pyrolysis of biomass-derived feedstocks.

2 Experimental

Fast pyrolysis experiments were conducted using a model 2000 pyroprobe analytical pyrolizer (CDS Analytical Inc.). The probe is a computer controlled resistively heated element which holds an open ended quartz tube (pictured in Fig. 1). Powdered samples are held in the tube with loose quartz wool packing; during pyrolysis vapors flow from the open ends of the quartz tube into a larger cavity (the pyrolysis interface) with a helium carrier gas stream.

The carrier gas stream is routed to a model 5890 gas chromatograph (GC) interfaced with a Hewlett Packard model 5972A mass spectrometer (MS). The pyrolysis interface was held at 100 °C and the GC injector temperature used was 275 °C. Helium was used as the inert pyrolysis gas as well as the carrier gas for the GCMS system. A 0.5 mL min^{-1} constant flow program was used for the GC capillary column (Restek Rtx-5sil MS). The GC oven was programmed with the following temperature regime: hold at 50 °C for 1 min, ramp to 200 °C at 10 °C min^{-1}, hold at 200 °C for 15 min. Products were quantified by injecting calibration standards into the GC/MS system. All yields are reported in terms of molar carbon yield where the moles of carbon in the product are divided by the moles of carbon in the reactant. The aromatic selectivity reported is defined as the moles of carbon in an aromatic species divided by the total moles aromatic species carbon. Similarly, the oxygenate selectivity is defined as the moles of carbon in an oxygenated species divided by the total moles oxygenated species carbon. Carbon on the spent catalyst was quantified by elemental analysis (performed by Schwarzkopf Microanalytical Lab, INC). The missing carbon can be attributed to: non quantified thermally unstable oxygenated species (which cannot be detected in our experimental setup), and coking of the pyrolysis interface or transfer lines.

Powdered reactants were prepared by physically mixing the carbohydrate feed and the catalyst. For a typical run 8–15 mg of reactant–catalyst mixture was used. Both the feed and the catalyst were sifted to <140 mesh before mixing. The physical mixtures of glucose were prepared with a ZSM-5 (Si/Al = 60, WR Grace) to D-glucose (Fisher) ratio of 19, 9, 4, 2.3, and 1.5. Xyliol (Fisher)/ZSM-5. Cellobiose (Acros)/ZSM-5, and cellulose (Whatman)/ZSM-5 with a catalyst to feed ratio of 19 were also tested. ZSM-5 was calcined at 500 °C in air for 5 h prior to reaction. Samples with a catalyst:glucose ratio of 19 were also prepared with the following catalysts: Silicalite (Grace), β-zeolite, Y-zeolite (Si/Al = 50, Degussa), and mesoporous SiO_2-Al_2O_3 (Si/Al = 8, Davison).

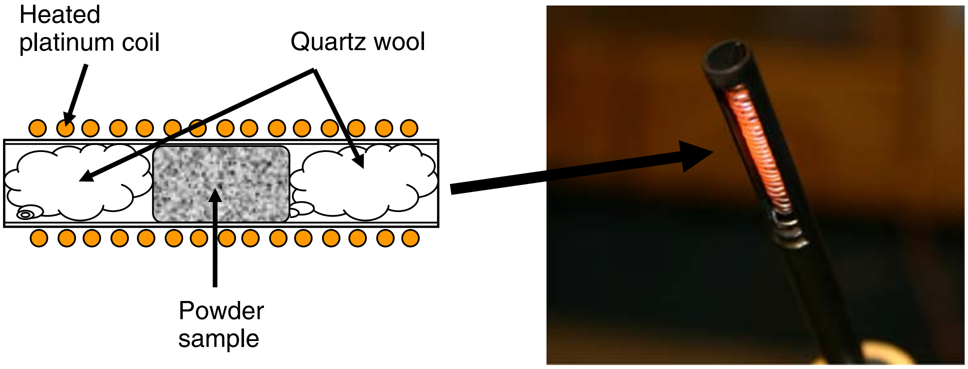

Fig. 1 Diagram of the pyroprobe reactor setup. On the left a schematic cross section of the prepared sample is pictured (not to scale). Powdered reactants and catalysts are held with loose quartz wool packing. Pictured on the right is the resistively heated element which holds the sample tube (2 mm × 25 mm). During reaction product vapors flow from the open ends of the sample tube into the GC/MS interface via a helium sweeper gas stream

3 Results

3.1 Chemistry of Catalytic Fast Pyrolysis

As shown in Fig. 2 catalytic fast pyrolysis first involves pyrolysis of solid biomass (e.g., cellulose) into volatile organics, gases, and solid coke. The volatile organics undergo dehydration reactions to produce water and the dehydrated species. These reactions can occur in either the heterogeneous catalyst or in the homogeneous gas phase. These dehydrated species then enter into the zeolite catalyst where they are converted into aromatics, carbon monoxide, carbon dioxide, water, and coke. Inside the zeolite catalyst, the volatile species undergo a series of dehydration, decarbonylation, decarboxylation, isomerization, oligomerization, and dehydrogenation reactions that lead to aromatics, CO, CO_2 and water. The challenge with selectively producing aromatics is minimizing undesired coke formation. The coke formation comes from homogeneous gas phase thermal decomposition reactions and from heterogeneous reactions on the catalyst. The coke can form from the biomass feedstock, the volatile oxygenates, the dehydrated species or the aromatics. As will be shown in this paper, high heating rates and high catalyst to feed ratio can minimize homogeneous coke formation.

Ligno-cellulosic biomass is composed of three components: cellulose, hemicellulose, and lignin [13]. For this study we used the compounds glucose, cellobiose (dimer of glucose), cellulose and xylitol. The overall stoichiometry for conversion of xylitol and glucose to toluene, CO and H_2O is shown in Eqs. 1 and 2, respectively. Oxygen must be removed from the biomass as a combination of CO (or CO_2), and H_2O when aromatics are produced. The maximum theoretical molar carbon yield of toluene from xylitol and glucose is 76% and 63%, respectively, when CO and H_2O are produced as by-products.

$$\begin{aligned} C_5O_5H_{12} \rightarrow {} & 12/22\ C_7H_8(76\%\ \text{carbon yield}) \\ & + 26/22\ CO(24\%\ \text{carbonyield}) + 84/22H_2O \end{aligned} \tag{1}$$

$$\begin{aligned} C_6O_6H_{12} \rightarrow {} & 12/22C_7H_8(63\%\ \text{carbon yield}) \\ & + 48/22CO(36\%\ \text{carbonyield}) + 84/22H_2O \end{aligned} \tag{2}$$

The hydrogen-to-carbon effective ratio (H/C_{eff}) as defined in Eq. 3 is a way of comparing the relative amounts of hydrogen in different feeds [18, 19]. This metric can be used to classify biomass feedstocks. Feedstocks with the same H/C_{eff} ratio will have similar theoretical yields of aromatics. For example, cellulose, glucose and cellobiose all have a H/C_{eff} ratio of 0. All feedstocks with a H/C_{eff} ratio of 0 will have a molar carbon toluene yield of 63% if CO and water are the byproducts. The H/C_{eff} ratio of biomass-derived feedstocks is significantly lower than petroleum feedstocks. For example, glucose, sorbitol and glycerol (all biomass-derived compounds) have H/C_{eff} ratios of 0, 1/3 and 2/3, respectively. The H/C_{eff} ratio of petroleum-derived feeds ranges from slightly larger than 2 (for liquid alkanes) to 1 (for benzene).

$$H/C_{eff} = \frac{H - 2O}{C} \tag{3}$$

Figure 3 shows the carbon yields for catalytic fast pyrolysis of xylitol, glucose, cellobiose and cellulose with ZSM-5. As can be seen from Fig. 3, the major products include aromatics, CO, CO_2 and coke. No olefins were detected during catalytic fast pyrolysis in our reactor system. Olefins have been observed when glycerol and sugars where passed over ZSM-5 catalysts in previous studies [20, 21]. Xylitol has a higher yield of aromatics than the other feeds. The aromatic yields of these reactions are about half the theoretical yield given by Eqs. 2 and 3. The yield of coke is

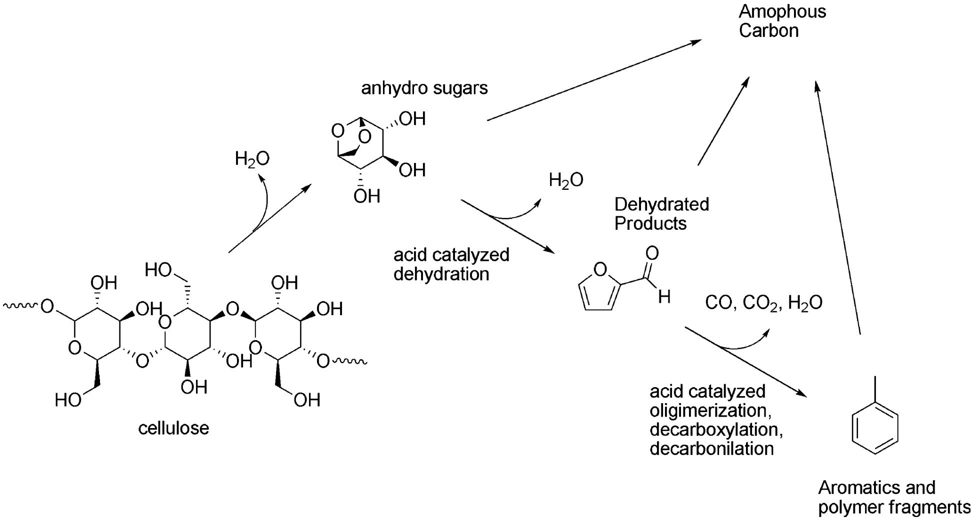

Fig. 2 Reaction chemistry for the catalytic fast pyrolysis of cellulose on solid acid catalyst

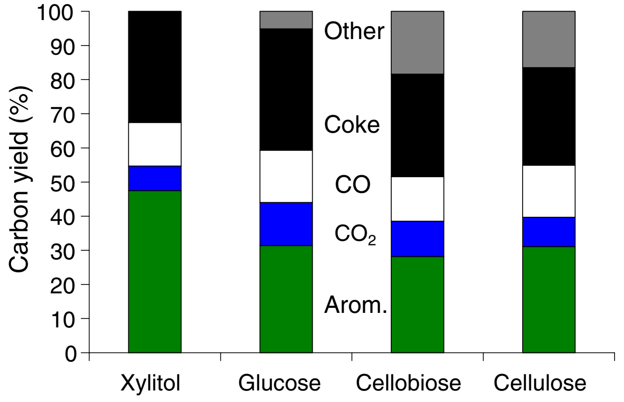

Fig. 3 Catalytic fast pyrolysis of solid cellulose, cellobiose, glucose and xylitol. Carbon yields for various biomass-derived feedstocks. *Reaction conditions*: catalyst to feed weight ratio 19, catalyst ZSM-5 (Si/Al = 60), nominal heating rate 1000 °C s^{-1}, reaction temperature 600 °C, reaction time 240 s. *Key*—Aromatics: green, CO_2: blue, CO: white, coke: black, and unidentified: gray

over 30% for all of these catalysts. The coke can be burned to provide process heat for the pyrolysis reactor.

The aromatic distribution from catalytic fast pyrolysis of biomass-derived oxygenates with ZSM-5 is shown in Fig. 4. The feedstocks had a similar aromatic product distribution when tested under the same reaction conditions. The similarity of the aromatic distributions for the various feeds suggests that a common intermediate forms from all of these products. The aromatic selectivity decreases as naphthalene >> toluene > xylenes > benzene > substituted benzene ~ indane.

Naphthalene is the aromatic that is made in the highest yield. It is known that this larger poly-aromatic has very slow diffusion in ZSM-5 [22] and therefore, it might be speculated that naphthalene is not formed within the pores. However, naphthalene has a sufficiently small kinetic diameter (~6.2 Å) to fit within the ZSM-5 pore (~6.2 Å with Norman radii adjustment [23]), and furthermore at the elevated reaction temperature (600 °C), the energetic barrier to diffusion will be decreased. Hence, naphthalene is believed to be formed within the pores rather than on the surface.

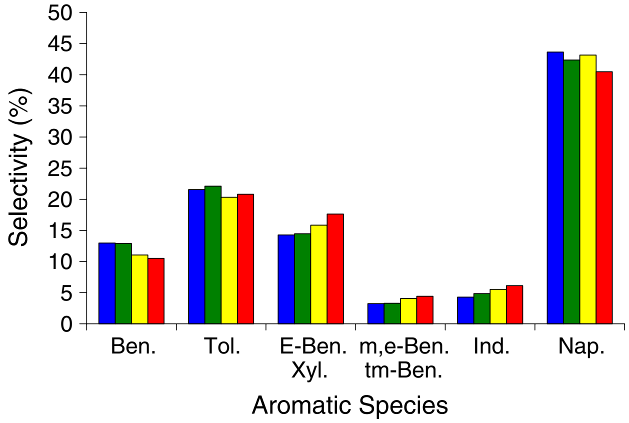

Fig. 4 Aromatic selectivity for different feeds for catalytic fast pyrolysis of solid cellulose, cellobiose, glucose and xylitol. *Reaction conditions*: catalyst to feed weight ratio 19, catalyst ZSM5 (Si/Al = 60), nominal heating rate 1000 °C s^{-1}, reaction temperature 600 °C, reaction time 240 s. *Key*—glucose feed: blue, cellulose feed: yellow, cellobiose feed: green, and xylitol feed: red. Aromatics quantified include: *Ben.* benzene, *Tol.* toluene, *E-Ben., Xyl.* xylenes, ethyl-benzene, *m,e-Ben., tm-Ben.* methyl-ethyl-benzene, trimethyl-benzene, *Ind.* indanes, *Nap.* naphthalenes

3.2 Heating Rate and Reaction Time

We used glucose to determine how the reaction parameters affect the product selectivity. As shown in Fig. 4 the aromatic distribution is similar for the all feeds suggesting that the other feeds will be similar to glucose. High heating rates are needed to avoid coke formation by homogeneous thermal decomposition reactions as shown in Fig. 5. This figure shows product yields as a function of nominal heating rate with ZSM-5 as the catalyst and glucose as the feed. As can be observed from Fig. 5, the maximum aromatic yield and the lowest coke yield are obtained at the highest heating rate (1000 °C s^{-1}). The aromatic yield decreases by half and the coke yield increases from 35% to 40% when the heating rate decreases from 1000 °C s^{-1} to 1 °C s^{-1}. The aromatic selectivity is not a function of heating rate, for heating rates greater than 50 °C/s as shown in Fig. 6. However, for lower heating rates the aromatic selectivity is a function of heating rate. The naphthalene selectivity decreases from 57% to 44% when the heating rate increases from 1 °C s^{-1} to 50 °C s^{-1}. At high heating rates the biomass spends a maximum amount of time at the reaction temperature thus maximizing the liquid yield. These results show the importance of the heating rate in obtaining high yields of aromatics. The heating rate in

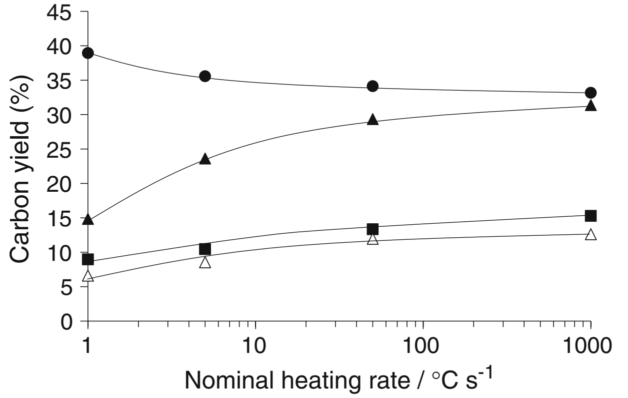

Fig. 5 Carbon yield as a function of nominal heating rate for catalytic fast pyrolysis of glucose with ZSM-5. *Reaction conditions*: catalyst-to-feed weight ratio = 19; catalyst ZSM-5 (Si/Al = 60), reaction temperature 600 °C, reaction time 240 s. *Key*—■: carbon monoxide; ▲: aromatics; Δ: carbon dioxide; ●: coke

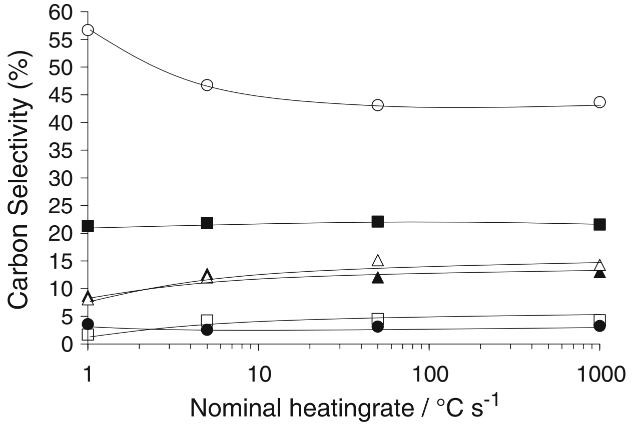

Fig. 6 Aromatic selectivity as a function of nominal heating rate for catalytic fast pyrolysis of glucose with ZSM-5. *Reaction conditions*: catalyst-to-feed weight ratio = 19; catalyst ZSM-5 (Si/Al = 60), reaction temperature 600 °C, reaction time 240 s. *Key*—■: toluene; ▲: benzene; Δ: xylenes, ethyl-benzene; ●: methyl-ethyl-benzene trimethyl-benzene; □: indanes; ○: naphthalenes

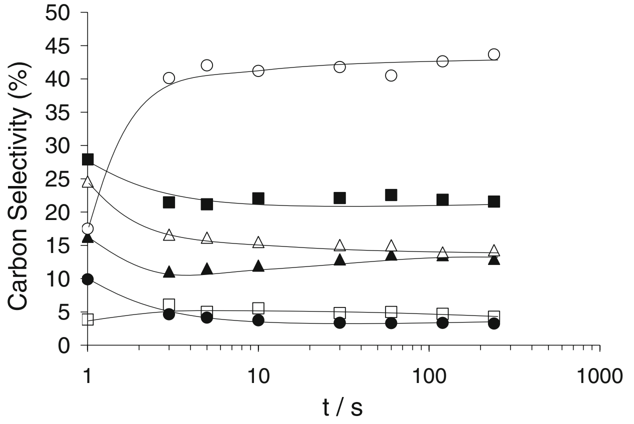

Fig. 8 Aromatic selectivity as a function of reaction time for catalytic fast pyrolysis of glucose with ZSM-5. *Reaction conditions*: catalyst-to-feed weight ratio = 19; catalyst ZSM-5 (Si/Al = 60), nominal heating rate 1000 °C s^{-1}, reaction temperature 600 °C. *Key*—■: toluene; ▲: benzene; Δ: xylenes, ethyl-benzene; ●: methyl-ethyl-benzene trimethyl-benzene; □: indanes; ○: naphthalenes

continuous catalytic fast pyrolysis reactors can be controlled by proper reaction engineering.

Figures 7 and 8 show the yields and aromatic selectivities as a function of reaction time with glucose and ZSM-5 at 600 °C and the highest heating rate (1000 °C/s). The time on both of these figures is shown on a logarithmic scale, and varies from 1 s to 240 s. As can be observed from Fig. 7 the rates of product formation are a function of time. The rate of aromatic production changes significantly as the reaction time increases from 1 to 240 s. In comparison the rate of CO and CO_2 production does not change as much over this same time period as the rate of aromatic production. Thus, the gases leave the reactor faster than the aromatics. This is probably due to transport restrictions of the aromatics versus the CO and CO_2 since the aromatics absorb more strongly onto the zeolites than the CO and CO_2.

After 3 s of time on stream the aromatic selectivity does not change with time as shown in Fig. 8. However in the initial stages of reaction (1 s of reaction time) the lighter aromatics (toluene, xylenes) are higher in selectivity than after 3 s. Again this could be to a combination of both transport and kinetic reasons.

3.3 Catalyst-to-Feed Ratio

In addition to high heating rates, the product yields are also a function of the catalyst to biomass ratio. Figure 9 shows the product selectivity for catalytic fast pyrolysis of glucose with ZSM5 as a function of the catalyst-to-glucose

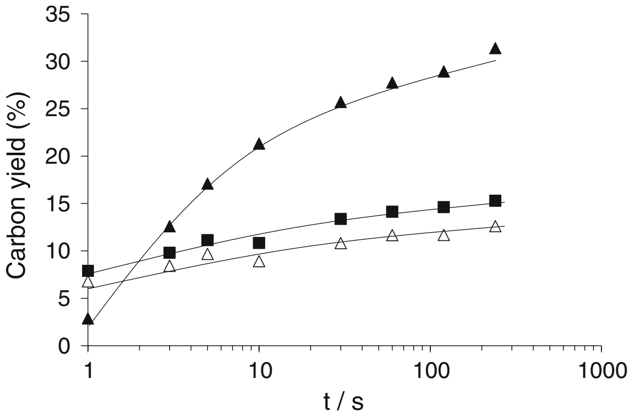

Fig. 7 Carbon yield as a function of reaction time for catalytic fast pyrolysis of glucose with ZSM-5. *Reaction conditions*: catalyst-to-feed weight ratio = 19; catalyst ZSM-5 (Si/Al = 60), nominal heating rate 1000 °C s^{-1}, reaction temperature 600 °C. *Key*—■: carbon monoxide; ▲: aromatics; Δ: carbon dioxide

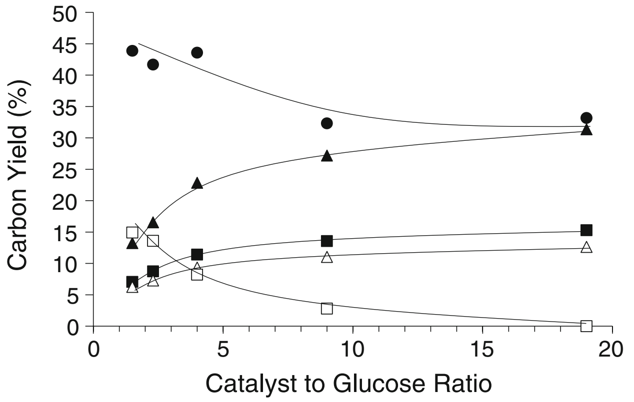

Fig. 9 Effect of catalyst-to-glucose ratio for catalytic fast pyrolysis. *Reaction conditions*: nominal heating rate 1000 °C s^{-1}, final reaction temperature 600 °C, reaction time 240 s. **a** Carbon yield as a function of catalyst-to-glucose ratio. *Key*—■: carbon monoxide; ▲: aromatics; Δ: carbon dioxide; □: partially deoxygenated species; ●: coke

weight ratio. The coke yield increases and the aromatic yield decreases as the catalyst-to-glucose ratio decreases. Thermally stable oxygenates form as the catalyst-to-glucose ratio decreases. The oxygenates include: furan, 2-methyl furan, furfural, 4-methyl-furfural, furan-2-methanol, hydroxyacetylaldehyde, and acetic acid, as shown in Fig. 10. These thermally stable oxygenates are intermediates in the production of aromatics. The furan compounds are formed from acid catalyzed dehydration of carbohydrates [24]. The acid catalyst can be both the heterogeneous solid acid and the homogenous organic acid products. It has previously been shown that hydroxyacetaldehyde is formed from pyrolysis of carbohydrates [25]. Trace amounts of anhydrosugars were also observed.

Our experimental setup does not allow us to detect thermally unstable compounds which are also formed in the pyrolysis process. At high catalyst-to-glucose ratios the major oxygenated products are hydroxyacetaldehyde and acetic acid. The furan selectivity increases as the catalyst-to-glucose ratio decreases. These results indicate that in addition to aromatics, catalytic fast pyrolysis can be tuned to form oxygenates, which could be used as chemicals or fuel precursors.

The aromatic selectivity is not a strong function of the catalyst-to-glucose ratio as shown in Fig. 11. Increasing the catalyst to feed ratio slightly increases the selectivity for toluene, xylenes, and ethyl-benzene while slightly decreasing the selectivity for benzene, methyl-ethyl-benzene, trimethyl-benzene, indanes and naphthalenes decreases.

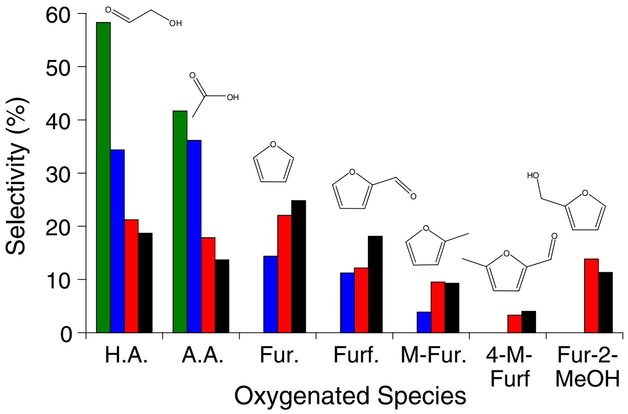

Fig. 10 Distribution of partially deoxygenated species as a function of catalyst-to-glucose ratio for catalytic fast pyrolysis. *Reaction conditions*: nominal heating rate 1000 °C s^{-1}, final reaction temperature 600 °C, reaction time 240 s. *Key*—catalyst:glucose ratio = 9 (green), catalyst:glucose ratio = 4 (blue), catalyst:glucose ratio = 2.3 (red), catalyst:glucose ratio = 1.5 (black). The species quantified include: *H.A.* hydroxyacetylaldehyde, *A.A.* acetic acid, *Fur.* furan, *Furf* furfural, *M-Fur* methyl furan, *4-M-Furf* 4-methyl furfural, *Fur-2-MeOH* furan-2-methanol

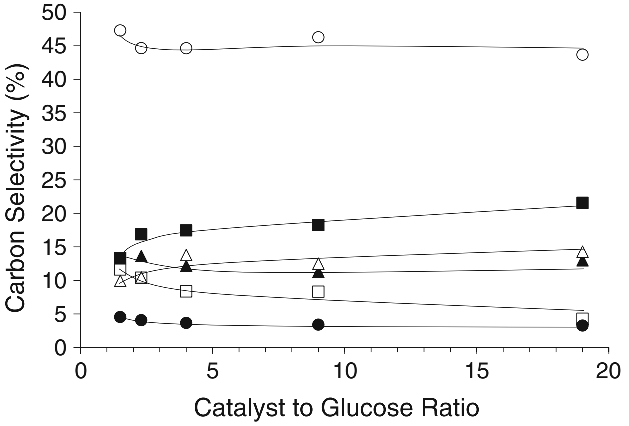

Fig. 11 Distribution of aromatic species as a function of catalyst-to-glucose ratio for catalytic fast pyrolysis. *Reaction conditions*: nominal heating rate 1000 °C s^{-1}, final reaction temperature 600 °C, reaction time 240 s. *Key*—■: toluene; ▲: benzene; Δ: xylenes, ethyl-benzene; ●: methyl-ethyl-benzene trimethyl-benzene; □: indanes; ○: naphthalene

3.4 Catalyst Selection

Proper catalyst selection is crucial for high aromatic selectivity. Figure 12 shows catalytic fast pyrolysis of glucose with different catalysts. The catalyst that had the highest aromatic yield was ZSM-5. When no catalyst is used the primary product is coke. The catalytic parameters that have an effect on the product distribution are pore structure and the type of acid sites. We tested ZSM-5, silicalite and mesoporous silica–alumina to test the relationship between catalytic parameters and catalytic activity. Silicalite and ZSM-5 have the same pore structure, but different number of acid sites. ZSM-5 contains Brønsted acid sites while silicalite does not. Silica–alumina contains Brønsted acid sites, but is an amorphous material. Silicalite produces primarily coke indicating that Brønsted acid sites are needed for aromatic production. Silica–alumina also produces mainly coke indicating that the pore structure of the zeolite is also needed to produce aromatics selectively. Figure 12 also includes catalytic fast pyrolysis with β-zeolite and Y-zeolite catalysts which both produce large amounts of coke. The pore structures of the catalysts tested are quite different in nature. The ZSM-5 catalyst is a system of two perpendicularly intersecting channels. The larger of the two channels has a near circular pore structure with dimensions of 0.54 × 0.56 nm^2. The smaller channels have a geometry of 0.51 × 0.54 nm^2. The intersection of these channels which contains the proposed active site is approximately a 0.9 nm cavity. Y-zeolite has a three dimensional faujasite structure. The supercages have a 1.2–1.3 nm diameter while the channels connecting the supercages have a diameter of 0.8–0.9 nm [26]. β-zeolite has intersecting channels similar to ZSM-5, however, this zeolite is a mixture of three polymorphs which have pore diameters of ~0.7 nm [27].

As seen in Fig. 13, the aromatic selectivity can be modified with proper catalyst selection. If smaller aromatics are desired, such as benzene and toluene, then the best catalysts are Y-zeolite, *β*-zeolite and SiO_2-Al_2O_3 are the best catalysts. If the larger aromatics are desired, including naphthalene and indane, then ZSM-5 and silicalite are the optimal catalysts. Y-zeolite, *β*-zeolite and SiO_2-Al_2O_3, therefore a significant challenge with these catalysts is to try and figure out how to minimize coke formation. Our results suggest that aromatic production is a shape selective reaction where the selectivity is a function of the structure of the zeolite catalyst. The type of active site is also important, and therefore the product selectivity is a function of both the structure and active site of the catalyst.

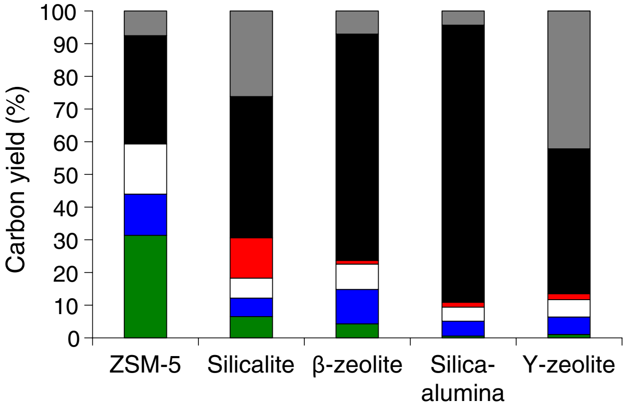

Fig. 12 Catalytic fast pyrolysis of glucose with various catalysts. *Reaction conditions*: catalyst-to-feed weight ratio = 19; nominal heating rate 1000 °C s^{-1}, reaction temperature 600 °C, reaction time 240 s. *Key*—aromatics: green, CO_2: blue, CO: white, partially deoxygenated species: red, coke: black, and unidentified species: gray. Partially deoxygenated species quantified include: hydroxyacetylaldehyde, acetic acid, furan, 2-methyl furan, 2,5-dimethyl furan, furfural, 4-methyl-furfural, furan-2-methanol

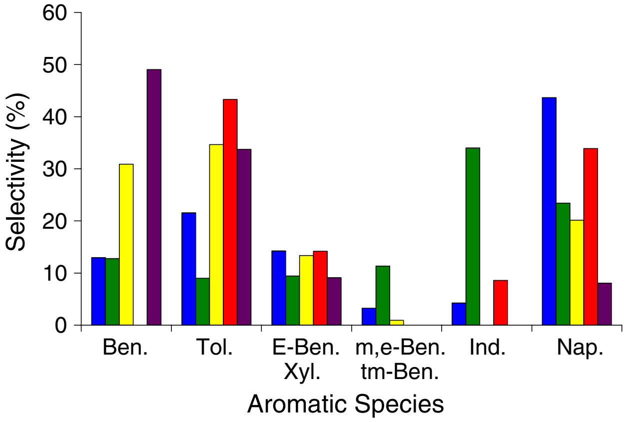

Fig. 13 Aromatic selectivity for catalytic fast pyrolysis of glucose with various catalysts. *Reaction conditions*: catalyst-to-feed weight ratio = 19; nominal heating rate 1000 °C s^{-1}, reaction temperature 600 °C, reaction time 240 s. *Key*—ZSM-5: blue, silicalite: green, *β*-zeolite: yellow, SiO_2-Al_2O_3: red, Y-zeolite: purple. Aromatics quantified include: *Ben.* benzene, *Tol.* toluene, *E-Ben., Xyl.* xylenes, ethyl-benzene, *m,e-Ben., tm-Ben.* methyl-ethyl-benzene, trimethylbenzene, *Ind.* indanes, *Nap.* naphthalenes

4 Discussion

4.1 Comparison of this Study to Previous Studies of Biomass-Derived Feedstock Conversion with Zeolite Catalysts

Zeolite catalysts have been tested for conversion of biomass-derived feedstocks to aromatics in both fluidized bed reactors and fixed bed reactors. Table 1 shows previous groups who have added catalysts to fluidized bed reactors. The yields from the previous studies are all reported in wt% without characterizing the bio-oil effluent. When aromatics are produced (instead of oxygenated bio-oils) the wt% yield of the bio-oils decreases because oxygen is being removed as water, CO and CO_2. The aromatics have a higher heating value than the typical bio-oil because of there reduced oxygen content. A number of these previous studies report that catalyst addition to fast pyrolysis reactor is detrimental because it decreases the wt% yield of the resultant bio-oil. While the wt% yield does decrease, the advantage of catalyst addition is that a higher quality bio-oil is produced. Olazar et al. [20] used a spouted bed reactor with saw dust, showed that a high percentage of aromatics (12% carbon yield) in the product oils could be obtained with high catalyst-to-feed ratios. The aromatic yield they obtained is about half the aromatic yield we obtained in this study, however, pine sawdust was used as a feed instead of pure cellulose. Horne et al. [28] reported low organic liquid yields using a low catalyst-to-feed ratio. The result of low organic yield with low catalyst-to-feed ratio is in agreement with our study although it is difficult to make a direct comparison since no specific aromatic yields were reported in this study. Furthermore, the reactor used was a two stage type where the outlet of a fluidized bed was passed over a packed bed of ZSM-5. Lappas et al. [21] did not observe increasing organic liquid yield with increasing catalyst-to-feed ratio, however, they observed a decrease in coke on the spent catalyst at the high catalyst to feed ratios. We also observed a decrease in coke with increasing catalyst-to-feed ratio, however, the aromatic yield also increased.

The first work on conversion of biomass feedstocks over zeolite catalysts was done by researchers at Mobil [29] who showed that ZSM-5 could be used to convert biomass feedstocks such as latex and seed oils to hydrocarbons. A high degree of conversion (>74%) of these biomass

Table 1 Effect of catalyst-to-feed ratio for several catalytic fast pyrolysis studies

Study	Catalyst-to-feed ratio (WHSV)	Feed	Catalyst type (Si/Al ratio)	Reactor type	Temperature (°C)	Yield
Olazar et al.	12.0–36.0	Pine wood	ZSM-5 (24)	Cononical spouted bed	450	30.8 wt% total organic liquid yield, 6.3 wt% yield aromatics (12% carbon yield aromatics)[a]
Horne et al.	1.16	Mixed wood	ZSM-5 (50)	Fluidized bed coupled to a fixed catalyst bed	550	5.7 wt% organic liquid yield
Lappas et al.	2.9–18	Lignocell HBS	ZSM-5 based FCC additive (10 wt% ZSM-5)	Circulating fluidized bed	405	30.6, 44.4, 36.4 wt% total organic liquid yield for 18, 4.9 and 2.3 cat/feed ratio, respectively
This study	9.9	Cellulose	ZSM-5 (60)	Fixed bed pyroprobe	600	31.1% carbon yield aromatics (13.5 wt% aromatic yield)
This study	9.9	Glucose	ZSM-5 (60)	Fixed bed pyroprobe	600	31.4% carbon yield aromatics (13.6 wt% aromatic yield)

[a] The WHSV for this run was not directly reported. The range of 12–36 WHSV was reported in the experimental

feedstocks over ZSM-5 to form hydrocarbons (including aromatics) was achieved in hydrogen flow. They also showed that aqueous glucose feedstocks can also be converted to aromatics. Since this early report, there have been an increasing number of publications using zeolites catalysts, predominately ZSM-5, to upgrade biomass feestocks. These studies have indicated that ZSM-5 is the preferred zeolite catalyst for biomass conversion. For example, Olazar et al. [20] reported 30.8 wt% total organic yield (12% carbon aromatics) for the pyrolysis of pine wood at 450 °C using ZSM-5. Further, Lappas et al. [21] report in excess of 30 wt% total organic yield depending on the catalyst-to-feed ratio.

The literature on the catalytic pyrolysis of lignocellulosic model compounds and biomass feedstocks is summarized in the Supplementary Material. Dao and coworkers [30–34] carried out several studies on aqueous fructose and glucose feeds with ZSM-5 catalysts and metal-doped ZSM-5 catalysts (ZnZSM-5 and MnZSM-5) in a fixed bed reactor at 350–500 °C. They found that increased yields of aromatics were realized using ZnZSM-5 and MnZSM-5 compared to undoped ZSM-5 catalysts with fructose and glucose feeds. Samolada et al. [35] used HZSM-5, fluid catalytic cracking (FCC) catalysts, transition metal catalysts (Fe/Cr), and aluminas in a fixed bed catalytic reactor using a mixture of model compounds (2-furaldehyde: 2.86; acetic acid: 17.14; cyclohexanone: 11.4; guaiacol: 17.1; vanillin: 8.6, and H_2O: 42.8 wt% ratio) to simulate biomass flash pyrolysis vapors. HZSM-5 lead to the production of aromatics, while transition metal catalysts (Fe/Cr) lead to the production of phenol and light phenolics.

The catalytic pyrolysis of cellulose was reported by Fabbri et al. [36] using zeolites and nanopowder metal oxides. Zeolite catalysts were found to reduce the overall yields of anhydrosugars with respect to pure cellulose while all nanopowder oxides but silicon oxide provided higher yields. Fabbri et al. [36] carried out catalytic pyrolysis experiments using a similar pyroprobe system employed in this work. To date, few other workers have utilized the pyroprobe system in order to screen potential catalyst materials for the pyrolysis of biomass. Nokkosmaki et al. [16] used a pyroprobe reactor to investigate zinc oxide as a potential catalyst for the conversion of sawdust pyrolysis vapors. They pyrolysed pine sawdust with ZnO catalyst at 600 °C with 30 ms residence time and found that ZnO was a mild catalyst for producing bio-oils showing only a small reduction in the liquid yield with only a 2% gas increase. More recently, Bridgwater and coworkers [37] reported the use of a pyroprobe reactor to screen several microporous (HZSM-5), and mesoporous (Al-MCM-41, Al-MSU-F, alumina-stabilized ceria MI-575) catalysts for the fast pyrolysis of cassava rhizome to gasoline. They heated the biomass/catalyst mixtures to 600 °C at a rate of 3000 °C/s and held at the reaction temperature for 30 s. All catalysts produced aromatic hydrocarbons and reduced oxygenated lignin derivatives. Bridgwater and coworkers [37] report ZSM-5 (Si/Al = 50) was the most effective catalyst for producing hydrocarbons from biomass (cassava rhizome). This activity was linked to the high quantity and strength of acids sites, together with the shape and size selectivity of the pores. These findings corroborate our results above. Furthermore, the larger pore mesoporous materials Al-MCM-41 and Al-MSU-F (31 and 150 Å, respectively) could facilitate larger molecules such as lignin and derivatives. Al-MSU-F produced higher yields of xylenes than ZSM-5, whereas alumina stabilized ceria favored the formation of benzene and toluene [37].

Aho et al. [38] studied the influence of catalyst (Beta zeolite) acidity on the pyrolysis of wood chips to aromatics. These workers found that increasing the catalyst acidity (Si/Al = 25–300) increased the gas yield of compounds such as aldehydes, but also increased the coking. While the formation of polyaromatic hydrocarbons was only observed with using the catalyst. We observe lower aromatic yields using Beta zeolite compared to ZSM-5 (Si/Al = 60). Further, Iliopoulou et al. [39] also found for increasing the acidity of Al-MCM-41 catalysts, increased the conversion of biomass at 500 °C. Increasing the catalyst acidity while avoiding the formation of coke is an important step in optimizing hydrocarbon yield.

Several workers have utilized mesoporous acidic catalysts for the conversion of biomass using pyrolysis [14, 37, 39] due to the high surface areas, large pore size (>2 nm) and moderate acidity. In general, these mesoporous catalysts showed less activity compared to ZSM-5 under the same conditions. However, careful tuning of the pore size and acidity could improve product selectivity [39].

Metal exchanged zeolites used in the catalytic pyrolysis of biomass have been reported [40–42]. Park et al. [40] used Ga-ZSM-5 in the catalytic pyrolysis of sawdust at 500 °C in a fluidized bed reactor. GaZSM-5 produced a greater amount of aromatic hydrocarbons compared to ZSM-5 under the same conditions. Sulman and coworkers [41, 42] studied the catalytic pyrolysis of peat at 410 °C, using zeolites (Beta, Mordinite, HY, ZSM-5) catalysts and their iron impregnated counterparts. Iron impregnation was found to decrease the acidity by decreasing the number of Brønsted and Lewis sites. In general, all catalysts increased the light hydrocarbon yields of the gas released compared to no catalyst. Catalyst modification with iron increased the hydrocarbon yields by 2- to 3-fold compared to catalyst without iron impregnation, under the same conditions.

Predominately, solid acid catalysts (e.g., ZSM-5) have been used for the conversion of biomass to oils using pyrolysis. Only, Nokkosmaki et al. [16] and Fabbri et al. [36] applied basic oxides in catalytic pyrolysis, ZnO and MgO, respectively. Base catalytic activity has been shown to lead to much higher conversions compared to acid catalysts in other biofuel reactions, such as aldol condensation and transesterification [5]. Recently, strongly basic zeolites have been synthesized from reaction of zeolites with ammonia at elevated temperatures [43]. These basic zeolites provide unique activity and selectivity for base catalyzed reactions. The application of basic zeolites, for example amine-substituted ZSM-5, to biomass pyrolysis could be a promising candidate for conversion to hydrocarbons.

In summary, we can infer from the aromatic product ratios, that the conversion of biomass model compounds and cellulose undergo the same mechanism during catalytic pyrolysis. Hence, modification of the catalyst will effect the overall conversion. Specific catalysts could in theory be used to produce selective compounds from a range of feedstocks. Further studies are required to optimize the catalyst to maximize the yield of gasoline range hydrocarbons, these studies include:

(a) the effect of acid strength
(b) incorporation of metals in the zeolites,
(c) use of varying pore size catalysts in order to utilize a larger fraction of the biomass composition e.g., lignin, and
(d) the use of microporous basic catalysts.

4.2 Potential of Catalytic Fast Pyrolysis

As we have shown aromatics can be directly produced from lignocellulosic biomass in a single step reactor at short residence times without the co-feeding of hydrogen. The motor octane number, based on summation of the individual aromatic components, of the aromatic products is approximately 111. The octane number and vapor pressure of the aromatic products and gasoline is shown in Table 2. The ideal gasoline fuel will have the proper combination of octane and vapor pressure, and will also have low toxicity. The vapor pressure of gasoline range is around 222 mmHg. All the aromatics we produce have a high octane number. However, the aromatics larger than xylene have low volatility which limits the amount that can be blended with gasoline. Also in the U.S. aromatics are currently limited to 25 vol.% in gasoline [44]. Benzene is further limited to 0.8 vol.% in gasoline because of its carcinogenic properties. Benzene can be converted to toluene by an alkylation process. Naphthalene and the larger alkanes could be hydrogenated to cyclic alkanes in a secondary process. These cyclic alkanes could be used as a diesel fuel. The hydrogen could potentially come from steam reforming of coke deposits or from water–gas shift of product carbon monoxide.

The aromatics also have wide spread uses across the chemical industry. Figure 4 shows the primary product from the pyrolysis of biomass-derived compounds with ZSM-5 is naphthalene. The primary use of naphthalene (62% of the total U.S. consumption) is in the production of Phthalic anhydride. The second major use for naphthalene (20% of the total) is in the production of surfactants and plasticizers such as naphthalene sulfonate and naphthalene sulfonate–formaldehyde condensate [45]. Xylenes, toluene, and benzene produced during catalytic fast pyrolysis are also of chemical importance. Toluene and mixed xylenes are primarily used as an octane enhancer in motor gasoline. However, the pure para and ortho isomers of xylene are

Table 2 Properties of the quantified aromatic species

Compound	Boiling point (°C)[a]	Research octane number (RON)[b]	Motor octane number (MON)[b]	(R + M)/2	Vapor pressure (mmHg @ 25 °C)[a]
Benzene	84.35	98	90	94	100.84
Toluene	112.29	124	112	118	28.47
Ethyl-benzene	135.17	124	107	115.5	9.51
o-Xylene	140.15	120	102	111	6.62
m-Xylene	140.15	145	124	134.5	8.29
p-Xylene	140.15	146	126	136	8.75
Ethyl-methyl benzene	163.03	126–155	112–138	119–147	2.89
Tri-methyl benzene	168.01	118–170	104–136	111–153	1.87
Indan	174.44	161	140	150.5	1.48
Naphthalene	199.91	Not reported	90	–	0.23
Methyl-naphthalene	227.77	123–127	114–116	119–122	0.053
Gasoline	35–200	–	–	87–91	222[c]

[a] Yaws [47]

[b] ASTM [48]

[c] Refer to website [49]

also important chemical precursors of terephthalic acid and phthalic anhydride, respectively. Almost all of the para and ortho xylenes produced in the U.S. go into these chemicals for the production of platicizers and polymers [45]. Benzene was primarily used as an octane enhancing fuel additive until recent EPA regulations limited benzene to 0.8 vol% in gasoline [44]. Now almost all of the benzene produced in the U.S. is used for the manufacture of polymers such as polystyrene [46].

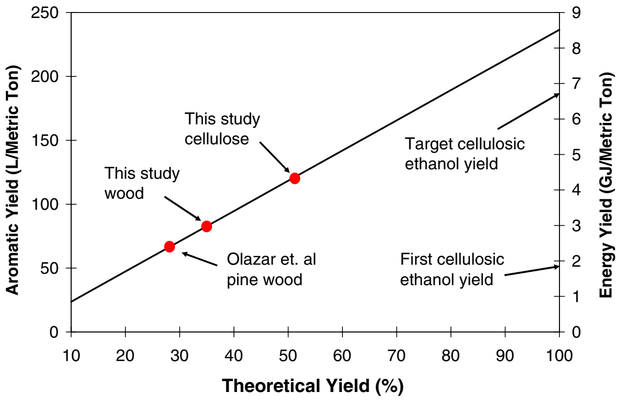

Fig. 14 Aromatic yield as a function of theoretical yield. Included in the figure are the results from Olazar et al. [20], the results from this study and our preliminary results using mixed wood as a feed (same reaction conditions as reported in Fig. 3)

The yield of aromatics that can be produced from biomass is a function of the composition of the biomass and the type of catalysts used. If the biomass contains 75 wt% carbohydrates then 240 L of aromatics per metric ton of biomass can be produced assuming that the remaining fraction of the biomass (which will be lignin and ash) is not converted. This also assumes that the oxygen is rejected as a combination of CO and H_2O as shown in Eq. 2 (Sect. 3.1). Theoretically 63% of the carbon in the carbohydrate can be converted to aromatics. Figure 14 shows the yield of aromatics as a function of the theoretical yield. Our current data show we can obtain a 50% of the theoretical yield with model compounds which corresponds to an output of 120 L of aromatics per metric ton of biomass. The yield of cellulosic ethanol in the first cellulosic ethanol plant (built in 1910) was 83 $L_{ethanol}$/metric ton of biomass, which is significantly lower than the yield of our process. Current targets for cellulosic ethanol production are over 300 $L_{ethanol}$ per metric ton of biomass [5]. However, ethanol has an energy density two-thirds that of toluene. Therefore, 120 $L_{aromatics}$/metric ton of biomass corresponds to an ethanol yield of 180 $L_{ethanol}$/metric ton of biomass. Furthermore, catalytic fast pyrolysis occurs in a single step, whereas cellulosic ethanol production requires multiple steps (including: pretreatment of the biomass, enzymatic hydrolysis, fermentation of both glucose and xylose, and distillation). The multiple steps of cellulosic ethanol production result in a plant capital cost that is 10 times larger than fast pyrolysis [12]. It is likely that future advances in design of new catalysts, combined with proper reaction engineering will lead to even further improvements in the production of aromatics from cellulosic biomass.

4.3 Challenges with Catalytic Fast Pyrolysis

Our results indicate the two important reactor parameters to maximize aromatic yields are fast heating rates and high catalyst-to-feed ratios. Therefore, the optimal reactor for catalytic fast pyrolysis will be designed to allow for fast heating of the biomass while maintaining a high feed-to-catalyst ratio. As described in the literature [9, 10], the heating rate is known to be an important parameter to control the product distribution in pyrolysis. Fast (>500 °C s^{-1}) heating rates produce high grade bio-oil and gasoline range compounds, particularly in the presence of a catalyst. Theoretically, microwaves could heat biomass materials at very high rates due to the volumetric heating and this process is likely to offer significant efficiencies over conventional resistively heated reactors. There have been few reports on microwave catalytic pyrolysis in the literature [50, 51], however non-catalytic microwave pyrolysis of biomass materials such as cellulose [52–54] and lignin/wood [51, 55, 56] have been reported. Early work by Baysar et al. [50] described a microwave heated fluidized bed reactor used to convert biomass feedstocks to bio-fuel. Heating rates of 17 K min^{-1} were achieved. Further, Kriegler-Brockett [51] investigated the microwave pyrolysis of lignin, with catalyst additives of NaOMe, NaOH, $NaHCO_3$, SiO_2 and $Ca(OH)_2$. Yu et al. [57] report the microwave pyrolysis of corn stover and the bio-oils properties were determined. Stover was heated for 40 min at 600 W but no heating rate was recorded. Te addition of NaOH as a homogeneous catalyst dramatically increased the syngas yield. Further, Ruan [58] and coworkers at the University of Minnesota have constructed a microwave waveguide pyrolysis reactor for converting biomass feedstocks to bio-oils.

Conventionally heated fluidized beds may also be suitable for catalytic fast pyrolysis. These reactors have been successfully used with non-catalytic and catalytic fast pyrolysis since this reactor type provides easy control of heating rates and product collection [9]. Furthermore, as shown in Table 1 high catalyst to feed ratios are obtainable with fluidized bed reactors.

One of the biggest challenges in catalytic fast pyrolysis is suppressing the formation of undesired coke. As seen in Figs. 3 and 12 all of the runs yield more than 30% coke. However, the coke can be burned to provide process heat for the catalytic fast pyrolysis reaction. Using dry glucose reacted at 600 °C as a basis, we calculate that 12% of the carbon of the biomass feedstock would need to be burned to provide the process heat for catalytic fast pyrolysis. Real biomass feedstocks (e.g., wood and grasses.) would require more carbon to be combusted, which would depend on the water content of the feed and the composition of the biomass. Zeolite catalysts can also be completely regenerated by burning the coke if the proper zeolite with proper preconditioning is chosen. Corma and co-workers demonstrated that zeolite catalysts (including ZSM-5) can be completely regenerated by high temperature oxygen treatments after they have been exposed to aqueous biomass-derived oxygenates (including glycerol and sorbitol) feedstocks [59].

Due to the moderate amounts of coke produced the aromatic yields obtained are currently about half of the theoretical yield. Future work in this area will focus on elucidating the reaction kinetics of catalytic fast pyrolysis. As eluded to earlier the similarity of product distribution for similar feedstocks suggests there are common dehydrated intermediate products that form aromatics. By determining the way in which aromatics are formed from these common intermediates the role of the structure and nature of the active sites of the catalyst can be further understood. Once these parameters are understood new catalysts specifically tailored for biomass conversion can be synthesized.

5 Conclusions

The general conclusion from this study is that high quality aromatic fuel additives can be produced directly from solid biomass feedstocks by catalytic fast pyrolysis in a single catalytic reactor at short residence times. This reaction involves homogeneous thermal decomposition of the biomass to smaller oxygenates. These oxygenates are then dehydrated. The dehydrated oxygenates then diffuse into the zeolite catalysts where they undergo a series of oligomerization, decarbonylation, and dehydration reactions to produce aromatics, CO, CO_2, and water. The major challenge with catalytic fast pyrolysis is avoiding undesired coke formation, which can be produced from both homogeneous or heterogeneous reactions.

Coke formation can be minimized and aromatic formation can be maximized by three important parameters:

(1) fast heating rates
(2) high catalyst to feed ratios, and
(3) proper catalyst selection (both active site and pore structure).

The fast heating rates and high catalyst feed ratios are necessary to avoid undesired thermal decomposition reactions in the homogeneous phase. The pore structure and active sites of the catalyst can be tuned to control the product selectivity. The aromatics produced include benzene, toluene, xylenes, substituted benzenes, indanes, and naphthalene. The pyroprobe reactor used in this study offers a convenient method to study the fundamental science of catalytic fast pyrolysis and for screening catalysts in order to scale up to real systems. It is likely that advances in understanding the chemistry of catalytic fast pyrolysis combined with the development of improved catalytic materials, which are specifically designed for biomass conversion, will lead to further process improvements.

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