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Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass Derived Compounds

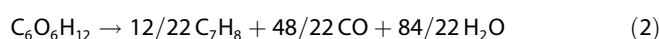
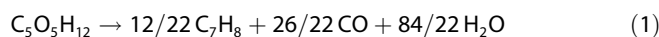
Torren R. Carlson, Tushar P. Vispute, and George W. Huber^{*[a]}

Owing 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 into 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 autothermal packed bed reactor over Rh catalysts.^[7] The ideal process for solid biomass conversion involves the production of liquid fuels from solid biomass in a single step at short residence times.

Herein, we report that gasoline-range aromatics can be produced from solid biomass feedstocks in a single reactor at short residence times (less than 2 min) and intermediate temperatures (400–600 °C) by a method we call catalytic fast pyrolysis. 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] Fast pyrolysis produces a thermally unstable liquid product called bio-oil, which is an acidic combustible liquid containing more than 300 compounds.^[9] Bio-oils are not compatible with existing liquid transportation fuels including gasoline and diesel. To use bio-oil as a conventional liquid transportation fuel, it must be catalytically upgraded.^[10–13] As we show here, introduction of zeolite catalysts into the pyrolysis process can convert oxygenated compounds generated by pyrolysis of the biomass into gasoline-range aromatics.

Catalytic fast pyrolysis first involves pyrolysis of solid biomass (e.g. cellulose) into volatile organics, gases, and solid coke. The organics then enter the zeolite catalyst where they

are converted into aromatics, carbon monoxide, carbon dioxide, water, and coke. Inside the zeolite catalyst, the biomass-derived species undergo a series of dehydration, decarbonylation, decarboxylation, isomerization, oligomerization, and dehydrogenation reactions that lead to aromatics, CO, CO₂, and water. The challenge with selectively producing aromatics is to minimize the undesired formation of coke, which can be from homogeneous gas-phase thermal decomposition reactions or from heterogeneous reactions on the catalyst. The overall stoichiometry for the conversion of xylitol and glucose into toluene, CO, and H₂O is shown in Equation (1) (76 and 24% carbon yields) and Equation (2) (63 and 36% carbon yields), respectively. Oxygen must be removed from the biomass-derived species as a combination of CO (or CO₂) and H₂O when aromatics are produced. The maximum theoretical yield of toluene from xylitol and glucose is 76 and 63%, respectively, when CO and H₂O are produced as by-products.



A handful of previous researchers have studied the conversion of biomass-derived species using zeolites.^[14–18] Chen et al. studied the conversion of aqueous carbohydrate solutions over ZSM5 catalysts in a fixed bed reactor.^[14] They obtained a yield of aromatics of 18% (carbon) for an aqueous glucose feed (with the other products being CO, CO₂, and coke), which is significantly lower than the aromatic yield (31%) we have observed in our fast pyrolysis reactor. ZSM5 has also been added to fluidized bed pyrolysis reactors. Olazar et al. studied the fast pyrolysis of pine saw dust with ZSM5 in a spouted bed reactor and observed a yield of aromatics of 12% (carbon).^[15] Other studies have also reported that an organic liquid phase can be produced by pyrolysis of biomass with zeolite-based catalysts, however, these studies did not quantify the composition of the organic phase.^[16–17] Olefins and aromatics can also be produced from thermally stable biomass-derived oxygenates (like glycerol) over zeolite-based catalysts.^[18] Chen et al. defined the effective hydrogen-to-carbon ratio (H/C_{eff}) as shown in Equation (3) (H, C, and O correspond to the number of atoms of hydrogen, carbon, and oxygen, respectively). The H/C_{eff} ratios of glucose, sorbitol, and glycerol (all biomass-derived compounds) are 0, 1/3, and 2/3, respectively. The H/C_{eff} ratio of petroleum-derived feeds ranges from slightly over 2 (for liquid alkanes) to 1 (for benzene).

$$H/C_{\text{eff}} = \frac{H - 2O}{C} \quad (3)$$

Our experimental results indicate that aromatics can be selectively produced from solid biomass-derived species by 1) se-

[a] T. R. Carlson, T. P. Vispute, Prof. G. W. Huber
Department of Chemical Engineering
University of Massachusetts
159 Goessmann Lab, 686 North Pleasant St.
Amherst MA 01003-9303 (USA)
Fax: (+1) 413-545-1647
E-mail: huber@ecs.umass.edu

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lecting a proper catalyst, 2) using high heating rates, and 3) using high catalyst-to-feed ratios. The high heating rates and high catalyst-to-feed ratios are necessary to ensure that volatile organic compounds, formed from pyrolysis of the solid feeds, enter the catalyst before they thermally decompose to coke. The catalytic chemistry is a function of both the pore structure and nature of the active site. Our catalytic fast pyrolysis experiments were conducted in a Pyroprobe 2000 batch pyrolysis reactor (CDS Analytical Inc.) with powdered catalyst and feeds (< 140 mesh size). The Pyroprobe reactor is described in detail elsewhere.^[19] Our preliminary results with the Pyroprobe indicate that a nominal temperature of 600 °C gives the highest yield of aromatics.

Figure 1 shows the carbon yields and aromatic selectivity for catalytic fast pyrolysis of xylitol, glucose, cellobiose, and cellulose.

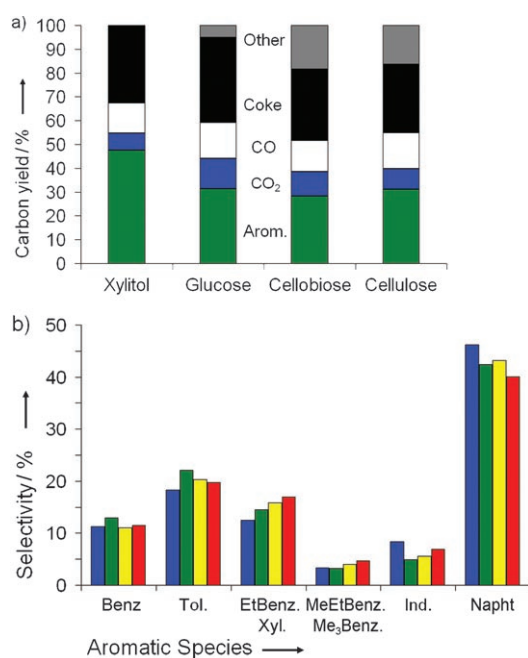


Figure 1. Catalytic fast pyrolysis of solid cellulose, cellobiose, glucose, and xylitol (reaction conditions: catalyst-to-feed weight ratio 19, catalyst ZSM5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$), nominal heating rate 1000 °C s^{-1} , reaction temperature 600 °C , reaction time 240 s). a) Carbon yields for various biomass-derived feedstocks: aromatics (green), CO_2 (blue), CO (white), coke (black), and unidentified (gray). b) Aromatic selectivity for different feeds: glucose feed (blue), cellulose feed (yellow), cellobiose feed (green), and xylitol feed (red). The aromatics quantified include benzene (Benz), toluene (Tol), xylenes (Xyl), ethylbenzene (EtBenz), methyl ethylbenzene (MeEtBenz), trimethylbenzene (Me_3Benz), indanes (Ind), and naphthalenes (Napht).

lose with ZSM5. As can be seen from Figure 1a, the major products include aromatics, CO, CO_2 , and coke. No olefins were detected during catalytic fast pyrolysis in our reactor system, which is different to what has been reported elsewhere.^[15,17] Xylitol gives a higher yield of aromatics than the other feeds. Xylitol also has a higher $\text{H}/\text{C}_{\text{eff}}$ ratio (2/5) than the other feeds (0 for cellulose, glucose, and cellobiose). The aromatic yields of these reactions are about half the theoretical yield given by Equations (2) and (3). The yield of coke is over 30% for all of

these feeds. 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 estimate that 12% of the carbon of the solid biomass-derived feedstock would need to be burned to provide the process heat for catalytic fast pyrolysis. Real biomass feedstocks (wood, grasses, etc.) would require more carbon to be combusted, which would depend on the water content of the feed and the composition of the biomass. Corma and co-workers demonstrated that zeolite catalysts (including ZSM5) can be completely regenerated by high-temperature treatment with oxygen after they have been exposed to aqueous biomass-derived oxygenates (including glycerol and sorbitol feedstocks).^[18]

The aromatic distribution from catalytic fast pyrolysis of biomass-derived oxygenates is shown in Figure 1b. The feedstocks had a similar aromatic product distribution when tested under the same reaction conditions. The motor octane number of the aromatics products is approximately 111 (based on summation of the individual aromatic components). This aromatic product can be used as a fuel directly or more likely as a high-octane fuel additive. In the US, aromatics are currently limited to 25% volume in gasoline.^[20] The aromatics can also be hydrogenated to cyclic alkanes in a secondary process. The hydrogen could come from steam reforming of coke deposits or from water gas shift reaction of product carbon monoxide.

The product yield for catalytic fast pyrolysis of glucose is a function of heating rate as shown in Figure 2. The maximum yield of aromatics and the lowest yield of coke are obtained at

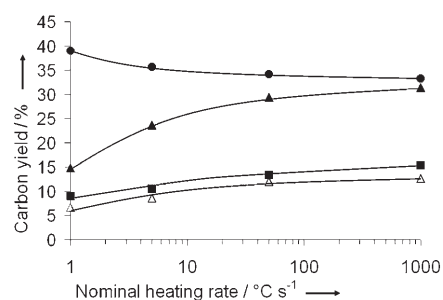


Figure 2. Carbon yield as a function of nominal heating rate for catalytic fast pyrolysis of glucose with ZSM5 (reaction conditions: catalyst-to-feed weight ratio 19; catalyst ZSM5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$), reaction temperature 600 °C , reaction time 240 s): CO (■), aromatics (▲), CO_2 (▼), coke (●).

a nominal heating rate of 1000 °C s^{-1} . The yield of aromatics decreases by half and that of coke increases from 35 to 40% when the heating rate is decreased from 1000 °C s^{-1} to 1 °C s^{-1} . The high heating rates probably reduce undesired thermal decomposition reactions. A solid residence time of 240 s at 600 °C is required to reach 100% conversion (see Supporting Information). At high heating rates, the biomass spends a maximum amount of time at the reaction temperature thus maximizing the yield of liquid.

In addition to high heating rates, the product yields are a strong function of the catalyst-to-biomass ratio. Figure 3 shows the product selectivity for catalytic fast pyrolysis of glucose

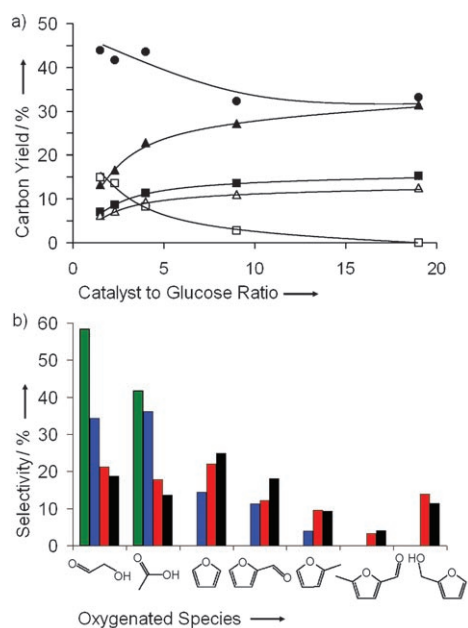


Figure 3. Effect of the catalyst-to-glucose ratio for catalytic fast pyrolysis (reaction conditions: nominal heating rate $1000^{\circ}\text{C s}^{-1}$, final reaction temperature 600°C , reaction time 240 s). a) Carbon yield as a function of catalyst-to-glucose ratio: carbon monoxide (■), aromatics (▲), CO₂ (△), partially deoxygenated species (□), and coke (●). b) Distribution of partially deoxygenated species: catalyst/glucose = 9 (green), catalyst/glucose = 4 (blue), catalyst/glucose = 2.3 (red), and catalyst/glucose = 1.5 (black). The species quantified include hydroxyacetaldehyde, acetic acid, furan, furfural, methylfuran, 4-methylfurfural, and furan-2-methanol.

with ZSM5, as a function of the catalyst-to-glucose weight ratio. The coke yield increases and the aromatic yield decreases as the catalyst-to-glucose ratio is decreased. Thermally stable oxygenates form as the catalyst-to-glucose ratio decreases. The oxygenates include furan, 2-methylfuran, furfural, 4-methylfurfural, furan-2-methanol, hydroxyacetaldehyde, and acetic acid (Figure 3b). Our experimental setup does not allow us to detect thermally unstable compounds that are also formed in the pyrolysis process. At high catalyst-to-glucose ratios, the major 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.

Proper catalyst selection is crucial for high aromatic selectivity. Figure 4 shows the results of catalytic fast pyrolysis of glucose with different catalysts. The catalyst that gave the highest yield of aromatics was ZSM5. In the absence of any catalyst, 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 used ZSM5, silicalite, and SiO₂-Al₂O₃ to test the relationship between catalytic parameters and catalytic activity. Silicalite and ZSM5 have the same pore structure but different types of acid sites. ZSM5 contains Brønsted acid sites whereas silicalite does not. Silica-alumina contains Brønsted acid sites but is an amorphous material. Silicalite produces primarily coke, indicating that Brønsted acid sites are

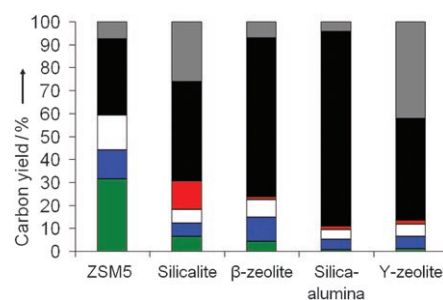


Figure 4. Catalytic fast pyrolysis of glucose with various catalysts (reaction conditions: catalyst-to-feed weight ratio 19; nominal heating rate $1000^{\circ}\text{C s}^{-1}$, reaction temperature 600°C , reaction time 240 s): aromatics (green), CO₂ (blue), CO (white), partially deoxygenated species (red), coke (black), and unidentified species (gray). Partially deoxygenated species quantified include hydroxyacetaldehyde, acetic acid, furan, 2-methylfuran, 2,5-dimethylfuran, furfural, 4-methylfurfural, and furan-2-methanol.

needed for the production of aromatics. Silica-alumina also produces mainly coke, indicating that the pore structure of the zeolite is also needed to produce aromatics selectively.

Figure 4 also includes the results of catalytic fast pyrolysis with β-zeolite and Y-zeolite catalysts, which both produce large amounts of coke. These results indicate that catalytic fast pyrolysis is shape-selective and the proper catalyst can be found by changing the type of active site and the pore shape.

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. There are three important parameters to maximize aromatic yields: 1) fast heating rates, 2) high catalyst-to-feed ratios, and 3) proper catalyst selection (both active site and pore structure). 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.

Experimental Section

Fast pyrolysis experiments were conducted using a model 2000 Pyroprobe analytical pyrolyzer (CDS Analytical Inc.). The probe is a computer-controlled resistively heated element, which holds an open-ended quartz tube. 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 interfaced with a Hewlett Packard model 5972A mass-selective detector. 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 GC-MS system. A constant flow program of 0.5 mL min^{-1} 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 $10^{\circ}\text{C min}^{-1}$, 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. 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. Both the feed and the catalyst were sifted to less than 140 mesh before mixing. The physical mixtures of glucose were prepared with a ZSM5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$, WR Grace) to D-glucose (Fisher) ratio of 19, 9, 4, 2.3, and 1.5. Xylitol (Fisher)/ZSM5, cellobiose (Acros)/ZSM5, and cellulose (Whatnam)/ZSM5 with catalyst-to-feed ratios of 19 were also tested. ZSM5 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, γ -zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$, Degussa), and mesoporous $\text{SiO}_2/\text{Al}_2\text{O}_3$ ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 4$, Davison).

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Keywords: biofuels · cellulose · flash pyrolysis · heterogeneous catalysis

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