

# Aromatic Production from Biomass by Catalytic Fast Pyrolysis

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## Introduction

Due to its low cost and abundance lignocellulosic biomass is being studied worldwide as a feedstock for renewable liquid biofuels.<sup>[1-4]</sup> Lignocellulosic biomass is not currently used as a liquid fuel because economical processes for its conversion have not yet been developed.<sup>[1]</sup> 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.<sup>[5]</sup> The ideal process for solid biomass conversion involves the production of liquid fuels from solid biomass in a single step at short residence times. As we will show in this presentation, gasoline range aromatics can be produced directly from solid biomass feedstocks in a single reactor at short residence times (less than 2 min) and intermediate temperatures (400-600°C) by catalytic fast pyrolysis.

## Materials and Methods

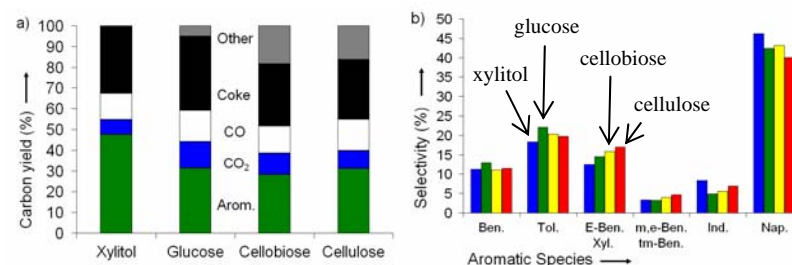
Fast pyrolysis experiments were conducted using a model 2000 pyroprobe analytical pyrolyzer (CDS Analytical Inc.). The probe is a computer controlled resistively heated element which holds an open ended quartz tube. Powdered samples are held in the tube with loose quartz wool packing; during pyrolysis vapors flow from the open ends of the quartz tube into a GC/MS system where products are quantitatively analyzed. Powdered reactants were prepared by physically mixing the carbohydrate feed and the catalyst.

## Results and Discussion

Catalytic fast pyrolysis involves several steps. First, the solid biomass feedstocks thermally decompose into volatile oxygenates. The oxygenates then enter the catalyst pores where they are converted into aromatics, CO, CO<sub>2</sub> and H<sub>2</sub>O. Rapid heating in this process reduces the amount of undesired reactions and coke that is formed. Figure 1 shows the carbon yields and aromatic selectivity for catalytic fast pyrolysis of xylitol, glucose, cellobiose and cellulose with a ZSM5 catalyst. As can be seen from Figure 1a the major products include aromatics, CO, CO<sub>2</sub> and coke. 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).<sup>[6]</sup>

The aromatic distribution from catalytic fast pyrolysis of biomass-derived oxygenates is shown in Figure 1b. The aromatic product distribution is independent of the feedstock used. The motor octane number of the aromatics products is approximately 111 (based on summation of the individual aromatic components).

We have elucidated some of the reaction chemistry by performing catalytic fast pyrolysis with mixtures of <sup>13</sup>C and <sup>12</sup>C labeled glucose. The oxygenates (such as furan) produced from pyrolysis are monoisotopic whereas single ring aromatics contain a random mixture of carbon isotopes. Single ring aromatics can react further with oxygenates to form polycyclic aromatics (e.g. naphthalene). One pathway for naphthalene formation includes the reaction of benzene with oxygenates as has been determined from our isotopic studies.



**Figure 1** Catalytic fast pyrolysis of solid cellulose, cellobiose, glucose and xylitol. Reaction conditions: catalyst to feed weight ratio 19, catalyst ZSM5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 30), nominal heating rate 1000 °C s<sup>-1</sup>, reaction temperature 600 °C, reaction time 240 s. a) Carbon yields for various biomass-derived feedstocks. b) Aromatic selectivity for different feeds. 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

## Significance

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 process represents a new method for conversion of solid biomass to fuels and chemicals. Unlike other biomass conversion routes the aromatics produced by catalytic fast pyrolysis are compatible with the current petroleum infrastructure. Understanding of the chemistry and catalysis of this process undoubtedly motivates the design of new catalysts and reactors that can be used to selectively produce aromatics from solid biomass.

## References

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