

# MILLISECOND AUTOTHERMAL REFORMING OF LIGNOCELLULOSIC MODEL COMPOUNDS OVER Rh-BASED CATALYSTS

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## Summary

Millisecond reforming over Rh-based catalysts may provide a means to efficiently and autothermally convert lignocellulosic biomass to syngas and liquid products. However, the complexity of lignocellulosic biomass requires the study of model compounds to simplify experiments and gain a better understanding of the fundamental chemistry. Monoaromatics serve as a model for lignin, a major component of biomass, and reforming demonstrates a high stability of aromatics in the reactor system and conversion mainly to syngas and combustion products. Cellulose is another major component and preliminary autothermal oxidative pyrolysis experiments demonstrate production of liquid hydrocarbons, with nearly 40 % selectivity to C<sub>3+</sub>.

## Keywords

Biomass processing technologies, Chemical feedstocks from biomass, Alternate energy, Sustainability

## Introduction

Recent interest in alternative fuel sources has been motivated by increased environmental and fossil fuel concerns. Biomass provides the only source of renewable carbon to create fuels and chemicals. Well-developed gasification and pyrolysis technologies can utilize biomass, but also have intrinsic disadvantages. Gasification requires extensive downstream cleanup stages to purify the synthesis gas (syngas) product and pyrolysis is generally unselective and requires high energy inputs.

Autothermal, Rh-based catalytic reforming has demonstrated that a wide variety of feedstocks, and most recently solid cellulose particles, can be converted to a tar and char-free syngas stream.<sup>1</sup> High-speed photography has also revealed that solid cellulose reacts on the catalyst surface through a liquid intermediate to volatile species, which are then convected into the catalyst bed and react further.<sup>2</sup>

This work examines autothermal reforming over Rh-based catalysts of monoaromatics and solid cellulose, as model compounds for two major components of lignocellulosic biomass, lignin and cellulose, respectively. Five different monoaromatics were studied over several Rh-based catalysts at varying feed compositions to examine conversion and product selectivities.<sup>3</sup> Preliminary results

of cellulose oxidative pyrolysis over Rh and selectivities to higher hydrocarbon products are also presented.

## Experimental

Benzene, toluene, ethylbenzene, cumene, and styrene were studied using a liquid feed system and reactor. A single-stage, high throughput, autothermal reactor was used to study these feeds over 1 cm, Rh-based, monolithic, 45 ppi catalysts. Metals were applied to an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> foam monolith using the incipient wetness technique to create three catalysts: 2.5 wt% Rh; 2.5 wt% Rh and 2.5 wt% Ce; 2.5 wt% Rh and 2.5 wt% Ce on 5 wt%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> washcoat. A syringe pump fed liquids to a nebulizer where they were nebulized with oxygen. The effect of varying the ratio of inlet carbon moles to the moles of oxygen, C/O ratio, was also investigated. Preheated nitrogen was fed slightly upstream of the nebulizer and the mixture was then passed through a heated bed of glass beads to ensure complete vaporization and mixing of the reactants before contacting the catalyst. Temperatures throughout the system and in the catalyst bed were measured using type K thermocouples. A micro-capillary sampling technique, fed directly to an HP6890 Gas Chromatograph, was used to sample gases directly after the reactor bed to measure relative quantities of product species.

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Solid cellulose was studied using an auger/hopper feed system with a 1 cm, 65 ppi Rh-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalytic bed. O<sub>2</sub> and N<sub>2</sub> were fed by mass flow controller. Again, C/O ratio was studied. Reactor effluent was immediately quenched with nebulized water and large hydrocarbons were condensed. Temperatures at the back face of the catalyst were measured using type K thermocouples. Permanent gases were injected to an HP6890 GC and analyzed for relative quantities of product species.

## Results

Results from the monoaromatic experiments demonstrated the stability of the aromatic ring in the described reactor system as well as the high activity of the Rh-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Figure 1 illustrates feed conversion as a function of inlet C/O ratio. Benzene and toluene were the least reactive in the system, and produced syngas and combustion products, most likely a result of heterogeneous catalytic conversion. Ethylbenzene and cumene were converted at much higher rates, reaching 100 % at low C/O ratios. At least one third of the feed survived as aromatic products, especially styrene, and small hydrocarbons, likely as a result of increased gas phase reactions. Finally, styrene was found to have conversions similar to benzene and toluene, due to the higher bond energy of its ethenyl group, lowering the rate of gas phase chemistry.

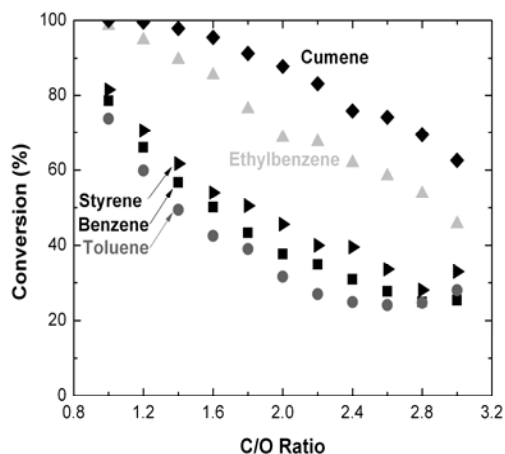


Figure 1. Plot of C/O ratio against fuel conversion for cumene (■), ethylbenzene (◆), benzene (●), toluene (▲), styrene (▶).<sup>1</sup>

From these results, it may be expected that the aromatics found in lignin would survive autothermal reforming. A high selectivity to syngas or to hydrocarbons could be achieved by adjusting the C/O ratio. These results may also provide insight into the behavior of other aromatic-containing polymers and plastics over Rh-based catalysts.

Preliminary oxidative pyrolysis experiments with cellulose particles were run between C/O ratio of 0.9 to 1.3 with

100 % conversion (Fig. 2). As the C/O ratio increases, carbon selectivity shifts from syngas and combustion products to C<sub>3+</sub> hydrocarbons, reaching nearly 40 % at a C/O of 1.3. Above this range, cellulose began accumulating on the catalyst front face as there was not enough oxygen and catalyst surface area to generate the heat necessary for reactive boiling of cellulose at the front face.<sup>2</sup> Further studies will investigate the effect of catalyst ppi, bed length, as well as compare cellulose behavior to that of other polymers, including polyethylene.

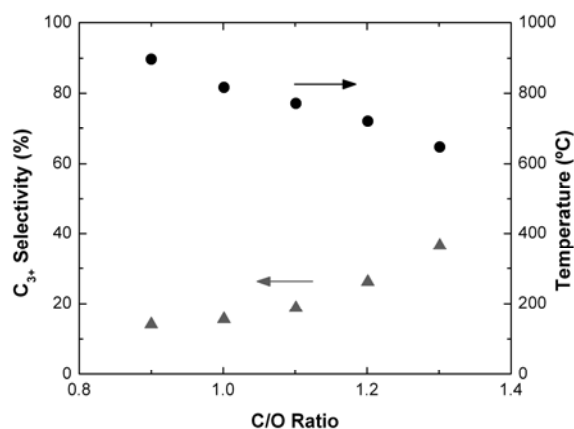


Figure 2. Plot of C<sub>3+</sub> selectivity (▲) and catalyst back face temperature (●) for cellulose reforming over a 1 cm, 65 ppi Rh-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalytic monolith.

## Significance

Autothermal oxidative pyrolysis of lignocellulosic biomass could provide a means to produce liquid hydrocarbons, with potentially high retention of stable aromatics from lignin, without external energy requirements. Aromatics were found to have a high survival rate within the reactor system, and those that did react produced mostly syngas and combustion products. Solid cellulose was converted over a Rh-Ce/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst to C<sub>3+</sub> with a selectivity nearing 40 % in preliminary studies.

## References

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