

# Millisecond Catalytic Reforming of Biomass for Synthetic Fuels

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## Introduction

Carbon-based liquid transportation fuels are appealing for their extremely high energy density and ease of storage. However, extensive consumption of finite petroleum resources has led to dangerously volatile fuel prices and increased concentrations of CO<sub>2</sub> in the atmosphere. As a result, significant research has been conducted to develop alternative fuel sources for the transportation sector.

Biomass is the only source of renewable carbon. It is therefore the only source for sustainable carbon-based liquid fuel production. In order to maximize fuel yields from biomass it is important to develop routes capable of efficiently processing lignocellulosic biomass, an abundant and non-food based domestic resource. One process being heavily developed is the thermochemical conversion of biomass to CO and H<sub>2</sub> (synthesis gas) and subsequent conversion to synthetic fuels, a route generally referred to as biomass-to-liquids (BTL). This process is appealing because it is robust to variable feedstock compositions and requires minimal energy input.

This work describes a novel reactor capable of efficiently converting biomass to synthesis gas at millisecond time scales over a Rh based catalyst at ~1000°C. The system runs autothermally producing a clean synthesis gas stream free of undesired tars, necessary for secondary processing without the addition of costly cleanup stages [1]. By co-feeding H<sub>2</sub>O or CO<sub>2</sub> and CH<sub>4</sub> the relative yields of H<sub>2</sub> and CO can be adjusted to meet the interest of the application [2].

## Materials and Methods

Experiments were carried out in a 20 mm I.D. quartz tube packed with 1.3 mm diameter  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> spheres coated with 2 wt% Rh/Ce on a 5 wt%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> washcoat. Cellulose was used as the biomass feedstock, delivered to the reactor by a laboratory hopper/auger system. N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> were metered by mass flow controllers, and steam from a steam generator fed by a syringe pump. Reactor effluent was injected into an HP 5890 GC for quantification. Three data points were collected for each set of operating parameters with C, H, and O atomic errors closing within 5%. Temperature was monitored by type-K thermocouples placed 1/3 and 2/3 of the bed length from the front face.

## Results and Discussion

The catalytic reforming of cellulose proceeds in three primary zones: 1) the cellulose contacts the hot catalyst surface and is rapidly pyrolyzed to small organic molecules, 2) the small organics are convected into the catalyst bed and partially oxidized, and 3) the resulting products undergo reforming reactions and equilibrate via the water-gas-shift reaction.

Heat generated in the oxidation zone of the catalyst is rapidly conducted through the rest of the catalyst, powering the endothermic pyrolysis and reforming reactions.

Selected results for reactions under continuous autothermal operation achieving 100% conversion of cellulose to single carbon products (excluding char and surface carbon) are presented in Table 1. By co-feeding steam it was determined that the ratio of H<sub>2</sub>/CO could be significantly increased through the water-gas-shift and reforming reactions, increasing the yield of hydrogen. Conversely, by co-feeding CO<sub>2</sub> the ratio of H<sub>2</sub>/CO could be slightly decreased by the reverse water-gas-shift and reforming reactions, decreasing the yield of CO<sub>2</sub>. Finally, CH<sub>4</sub> could be supplemented to the CO<sub>2</sub> co-feed for its high hydrogen content to further decrease the yield of CO<sub>2</sub> through the reverse water-gas-shift reaction while mitigating loss in H<sub>2</sub>/CO.

**Table 1. Selected experimental data for cellulose reforming**

Experiment: Cellulose + O <sub>2</sub> + <sup>a</sup>	N <sub>2</sub> [2]	H <sub>2</sub> O [2]	CO <sub>2</sub>	CO <sub>2</sub> + CH <sub>4</sub>
Catalyst Bed Length/mm	30	60	60	60
(C in Fuel) / (O in O <sub>2</sub> )	0.9	0.9	0.6	0.6
Mass Flow/g hr <sup>-1</sup>	30	60	50	50
Residence Time/ms	33	29	29	14
H Selectivity, H <sub>2</sub> /%	48	79	64	1.2
C Selectivity, CO/%	38	27	11	25
Temperature Mid-catalyst/°C	600	825	988	980

<sup>a</sup> Cellulose was reacted with: 1) N<sub>2</sub> and O<sub>2</sub> fed at air stoichiometry, 2) substitution of N<sub>2</sub> with H<sub>2</sub>O, 3) substitution of N<sub>2</sub> with CO<sub>2</sub>, and 4) substitution of N<sub>2</sub> with CO<sub>2</sub>, supplemented with methane (CH<sub>4</sub>/O<sub>2</sub>=0.6).

<sup>\*\*</sup>Hydrogen and carbon selectivities were calculated excluding atomic contributions from the feed H<sub>2</sub>O and CO<sub>2</sub>.

Numerical minimization of Gibbs free energy reveals that the experiments proceeded completely to equilibrium for all data presented. Assuming the system proceeds to equilibrium at other feed concentrations, adiabatic equilibrium calculations describe regimes of operation where H<sub>2</sub>O addition can drive the H selectivity to H<sub>2</sub> from biomass >100%, or CO<sub>2</sub> and CH<sub>4</sub> addition can drive the C selectivity to CO<sub>2</sub> from biomass and CH<sub>4</sub> <0% (corresponding to CO selectivity >100%).

## Significance

This work describes a process capable of millisecond conversion of biomass to a clean syngas stream. Addition of steam can allow for tuning of H<sub>2</sub>/CO between 1 and 3, important for the production of synthetic fuels (Fischer-Tropsch fuels require H<sub>2</sub>/CO=2, mixed alcohols require H<sub>2</sub>/CO=1.2, etc.). Furthermore, addition of CO<sub>2</sub> and CH<sub>4</sub> can drive CO<sub>2</sub> generation in the system to zero, providing a carbon neutral processing route for the conversion of biomass to liquids.

## References

1. P.J. Dauenhauer, B.J. Dreyer, N.J. Degenstein, L.D. Schmidt, *Angewandte Chemie* 46, 5864-5867 (2007).
2. J.L. Colby, P.J. Dauenhauer, L.D. Schmidt, *Green Chemistry* 10, 773-783 (2008).