Heterogeneous Catalysis

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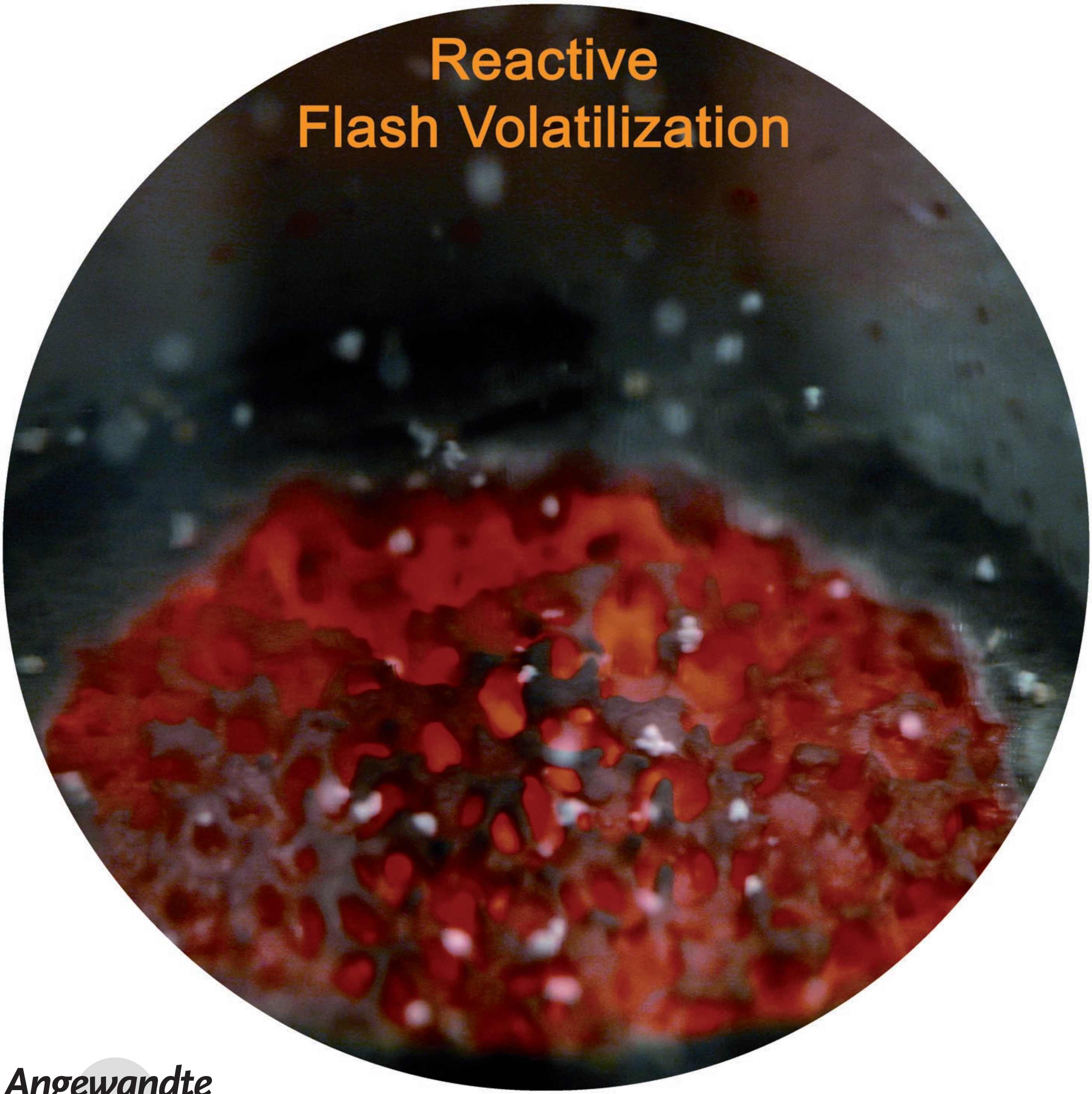
Millisecond Reforming of Solid Biomass for Sustainable Fuels**

*Paul J. Dauenhauer, Bradon J. Dreyer, Nick J. Degenstein, and Lanny D. Schmidt**



Dependence on petroleum and continued carbon emissions have led to a focus on methods of utilizing a large supply of biomass in the form of grasses, trees, and agricultural residue.[1] However, biomass presents a significant processing challenge because it is a complex mixture of biopolymers dispersed across the countryside. Current techniques to produce synthesis gas for liquid fuels such as fast pyrolysis or gasification are complicated and require long residence times and significant transportation to the processing location.[2–4] Here we demonstrate a unique catalytic method to convert nonvolatile biomass polymers into synthesis gas without an external heat source, at least an order of magnitude faster than existing systems. Small particles directly contacting a hot catalytic surface maintained by heat generated from partial oxidation undergo rapid decomposition without detectable char production to form a tar-free synthesis gas stream at millisecond reaction times. Considered solid fuels include cellulose, starch, wood chips from Aspen (*Populus tremuloides*), and polyethylene, an example of common municipal waste. Conversion by this technology has the potential to permit production of synthesis gas from solid biomass in small, simple processes.

Direct thermochemical conversion of biomass to a stream of synthesis gas (H_2 and CO) is an attractive route to transportation fuels without extensive preprocessing of biomass. Clean, conditioned synthesis gas can be converted into diesel fuel or mixed alcohols through the Fischer–Tropsch process or to methanol or dimethyl ether allowing high-efficiency end use in modern diesel engines without significant changes in the current transportation infrastructure.[5] While the thermochemical route to synthesis gas can convert a solid mixture of biopolymers, this process lacks an effective catalytic method that is easily scalable and sufficiently simple.

A major challenge with direct catalytic conversion of solid biomass is to avoid the formation of solid char that can cover catalyst surface sites and block surface reactions. Slow heating of biomass such as cellulose, $(C_6H_{10}O_5)_n$, at low temperatures can result in a significant fraction converting to solid char similar to charcoal production from wood [Eq. (1)]. Global homogeneous models such as the Shafizadeh model which describe this conversion predict significantly less production of char above 400 °C with most of the biomass being converted into volatile organic compounds (VOCs) at 500 °C in about a second [Eq. (2)].[6,7] At even higher temperatures, conversion occurs much faster with higher selectivity to gases and little selectivity to char [Eq. (3)].[8]

$$(C_6H_{10}O_5)_n \xrightarrow{\Delta} \text{char} + H_2O \qquad (1)$$

$$(C_6H_{10}O_5)_n \xrightarrow{\Delta} \text{VOCs} \quad \text{(i.e. hydroxyacetaldehyde)} \qquad (2)$$

$$(C_6H_{10}O_5)_n \xrightarrow{\Delta} \text{gases} \quad \text{(i.e. CO} + H_2) \qquad (3)$$

In a recent paper, we showed that nonvolatile liquids such as soy oil and sugar-water droplets could be converted into synthesis gas without any carbon formation by reactive flash volatilization, in which cold drops impinge on a hot catalyst surface.[9] Here we demonstrate that particles of starch, cellulose, Aspen, and polyethylene ranging in size from 10 μm to 1 mm can be converted into synthesis gas on a hot Rh surface of a 30 mm catalytic bed without detectable deactivation from carbon formation. This process occurs at a total gas residence time of less than 70 ms, which is more than ten times faster (and thus ten times smaller) than reported biomass gasification processes.[3]

Biomass can currently be converted into synthesis gas in several different types of gasifiers that oxidize and pyrolyze biomass particles in large systems. At shorter residence times, a technique called fast pyrolysis heats biomass particles for about one second to produce a predominately liquid product, bio-oil, that can be catalytically reformed to synthesis gas using Rh or Ni catalysts.[4,10] This concept has been demonstrated as a complex integrated fast pyrolysis and catalytic reforming system at moderate temperatures, but it still requires external heating and residence times of about one second to operate.[11,12]

Figure 1 shows the results of the catalytic processing of cellulose particles approximately 230 μm in diameter at residence times of less than 70 ms in a fixed foam bed with a Rh catalyst (inset) described elsewhere.[13] In this experiment, we varied the ratio of cellulose to air feed rate defined as C/O (carbon atoms from fuel/oxygen atoms from air). The temperatures, measured with thermocouples at 10 mm and 30 mm from the top of the catalytic bed, never decreased below 600 °C into the region at which surface carbon becomes a thermodynamic product (dashed line; Figure 1). For these high temperatures, only H_2, H_2O, and single-carbon-atom products are thermodynamically predicted, and the observed products followed this behavior well with selectivity to H_2 and CO of about 50 % near equilibrium.

In this experiment (in Figure 2), solid particles directly contact a glowing hot surface at 700–800 °C to rapidly heat and avoid significant char formation. We postulate that VOCs produced by solid decomposition from rapid heating mix with air and undergo surface oxidation reactions within millimeters of the reactor front surface. These surface oxidation reactions are highly exothermic and produce a rapid increase in temperature as shown. The accompanying photo in Figure 2 shows that the front catalyst face remains bright orange when operating with a continuous flow of cellulose (white particles) in air. The gases produced should then undergo surface chemistry such as water gas shift reactions or

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[*] P. J. Dauenhauer, B. J. Dreyer, N. J. Degenstein, Prof. L. D. Schmidt
Department of Chemical Engineering and Materials Science
University of Minnesota—Twin Cities
421 Washington Ave. SE, Minneapolis, MN 55455 (USA)
Fax: (+1) 612-626-7246
E-mail: schmi001@umn.edu
Homepage: http://www.cems.umn.edu/research/schmidt/

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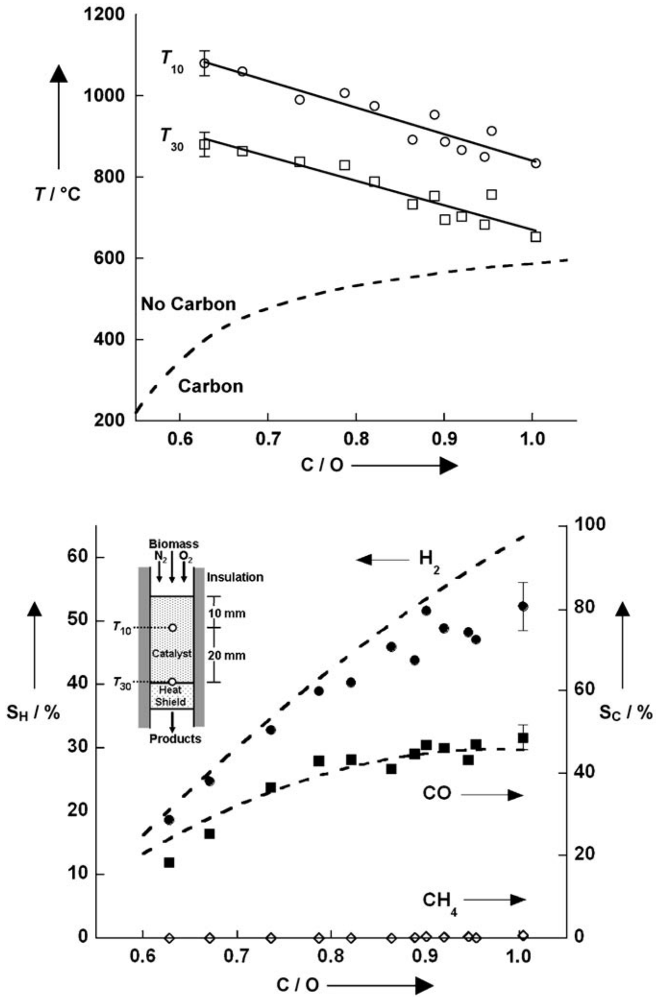

Figure 1. Top: Temperature measured at 10 mm (T_{10}; ○) and 30 mm (T_{30}; □) from the top of the catalytic bed during the processing of approximately 230-μm particles of cellulose. Bottom: Selectivity to H_2 (●), CO (■), and CH_4 (◇) from cellulose. All solids enter the reactor in air at room temperature, converting within 70 ms of gas residence time, and no process heat is added (see inset). S_C and S_H are defined as the ratio of C or H atoms in the product to the number of C or H atoms in the converted fuel. Dashed lines represent thermodynamic equilibrium calculations based on T_{30}. Error bars represent 95 % confidence intervals.

steam reforming in the last 20 mm of the catalytic bed before exiting as predominately synthesis gas.

Other results, shown in Table 1, demonstrate that millisecond processing can be extended to other sources such as starch or the saturated hydrocarbon polymer, low-density polyethylene,[13] which produces high selectivity to H_2 ($S_H \approx 69\,\%$) and CO ($S_C \approx 71\,\%$). Additionally, a source of wood chips considered for millisecond conversion was Aspen (*Populus tremuloides*), a fast-growing hardwood tree in North America comprised of about 2/3 cellulose and hemicellulose and about 1/4 lignin, with the remaining fraction consisting of uronic acids and extracts as well as ash ($\approx 0.5\,\%$).[14] Table 1 shows that the processing of Aspen particles about 1 mm in diameter exhibited selectivity to H_2 of 51 % for 8 h using a bed of approximately 1-mm spheres impregnated with Rh and Ce catalyst. This corresponds to 0.2 g of Rh processing 0.5 kg of biomass, of which 2.5 g is ash.

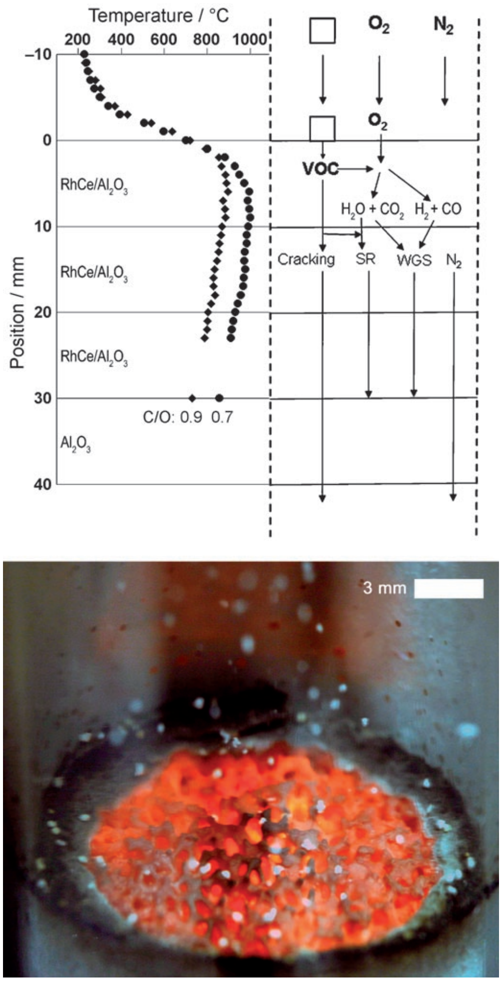

Figure 2. Top: Gas temperature for processing cellulose (□) at C/O ratios of 0.7 (●) and 0.9 (◆), and the reaction diagram for VOCs undergoing oxidation, steam reforming (SR: VOC + $H_2O \rightarrow H_2$ + CO), water gas shift (WGS: H_2O + CO$\rightarrow H_2$ + CO_2), and cracking reactions. The photograph shows the front face (0 mm) of the catalyst during millisecond reforming of approximately 230-μm particles of cellulose in air.

A significant problem in implementing catalytic gasification of biomass involves managing and removing the solid ash which would otherwise accumulate in the reactor. Biomass sources commonly contain the impurities N, S, Cl, K, Na, P, Si, Mg, and Ca, many of which are volatile as elements or compounds at these high temperatures. However, Aspen contains the minerals Ca, K, and Mg which make up over 90 % of the produced ash in the form of oxides and carbonates such as CaO, MgO, and $CaCO_3$ which have very low vapor pressure.[15] Short-term accumulation of these nonvolatile components does not shut down the process because the ash conducts heat from the catalytic oxidation region to the upper surface where biomass decomposition occurs. However, long-term operation will probably require a process such as a moving (non-fluidized) catalytic sphere bed that continuously removes catalyst from the reactor, separates the spheres and nonvolatile ash, and returns the catalyst to the front of the

Table 1: Selected experimental data for the millisecond reforming of solid particles.[a]

Experiment	1	Cellulose 2	3	Starch 4	Aspen 5	Polyethylene 6
Fuel Properties						
Av. particle size [μm]	20	230	230	690	780	370
Ash [wt %]	0.002	0.025	0.025	0.06	0.5	<0.01
Water [wt %]	6	5.2	5.2	9.1	5.4	<0.01
Experimental Conditions						
Support	foam	foam	spheres	foam	spheres	foam
C/O ratio	0.90	1.00	1.00	1.00	0.85	0.65
Mass flow [$\mathrm{g\,h^{-1}}$]	30	30	30	30	20	30
Residence time [ms]	62	60	66	69	89	22
T at 10 mm (T_{10}) [°C]	759	833	615	867	676	867
T at 30 mm (T_{30}) [°C]	593	652	537	716	488	695
H Selectivity [%]						
H_2	58	52	56	55	51	69
H_2O	39	46	39	41	34	28
C Selectivity [%]						
CO	36	49	39	37	29	71
CO_2	63	50	59	62	65	26
CH_4	1.3	0.6	2.2	1.5	4.2	1
$C_2H_4 + C_3H_6$	<0.1	<0.1	<0.1	<0.1	2	2
H_2/CO ratio	1.31	0.99	1.31	1.21	1.27	1.04

[a] Selectivity was defined as the ratio of C or H atoms in the product to C or H atoms in the converted fuel. Conversion was over 99%. All experiments were conducted at 1 atm with air stoichiometry ($N_2/O_2 = 3.76$).

bed. Volatile impurities passing through the catalyst can be removed by adsorption techniques downstream.

This method has the potential for smaller, simpler production of clean synthesis gas. Reactor systems operating with millisecond residence times are at least an order of magnitude smaller than conventional systems and exhibit high power densities of about 5 $\mathrm{kW\,L^{-1}}$ of catalytic reactor volume (calculated for cellulose at $C/O \approx 1.0$ producing synthesis gas for a fuel cell operating with 50% efficiency). At these conditions, approximately two-thirds of the fuel value of the biopolymer is retained as synthesis gas. This process appears to be robust with respect to particle size and type of biomass, and the reactor effluent does not contain tars and organics observed from fluidized bed gasifiers. Additionally, operation can occur in air with rapid startup times of less than 5 min on Rh catalysts that have been operated for 20 h without significant evidence of deactivation.

However, catalytic oxidation with air does not provide the optimum feed for this process or secondary processing to synthetic fuels. Dilution with N_2 cools the catalyst owing to increased convection and increases the size of equipment downstream of the reactor. Solid processing with pure O_2, as well as other considerations such as steam addition or preheat, could permit operation at higher C/O ratios resulting in an effluent stream with higher selectivity to synthesis gas that is more adaptable to secondary processing. See the Supporting Information for a full discussion regarding the combination of this process with secondary processing to synthetic fuels. Further research into key parameters as well as a more-detailed understanding of the process mechanism should have the potential to improve direct millisecond processing of biomass.

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