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# Improved utilization of biomass-derived carbon by co-processing with hydrogen-rich feedstocks in millisecond reactors†

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A reactor capable of improving the utilization of biomass-derived carbon during thermochemical conversion to synthesis gas is demonstrated experimentally. By co-processing hydrogen-deficient biomass (H/C~2) with hydrogen-rich feedstocks (H/C≥4) through catalytic partial oxidation, 100% of the fuel carbon atoms fed to the reactor can be converted to CO.

Liquid hydrocarbons are appealing for their high energy density and ease of storage. Collectively, these characteristics are unique to carbon-rich liquid fuels produced almost entirely from petroleum. Biomass, the only source of renewable carbon, represents the only sustainable feedstock for the production of carbon-rich fuels.<sup>1</sup> It will, therefore, become important to develop processes that effectively utilize all of the biomass-derived carbon. No commercial process capable of converting biomass into useful fuels and chemicals, without significant carbon losses to char or CO<sub>2</sub>, exists presently because of process or thermodynamic constraints.<sup>2,3</sup>

Thermochemical conversion of biomass to synthesis gas, a mixture of H<sub>2</sub> and CO, is a route for the production of synthetic, carbon-rich liquid fuels. The gasification of biomass by partial oxidation, used commercially to make synthesis gas, produces some combustion products in an overall exothermic, char-free reaction.



With existing technology, only ~50% of biomass carbon is converted to CO, and the remainder is emitted as CO<sub>2</sub>.<sup>4</sup> Ideally, gasification would convert 100% of the carbon in biomass to CO, eliminating the generation of CO<sub>2</sub>.

CO yields can be improved by co-feeding CO<sub>2</sub> with biomass and O<sub>2</sub>. The addition of CO<sub>2</sub> favors a reverse water-gas shift (RWGS), increasing CO production at the expense of molecular hydrogen.



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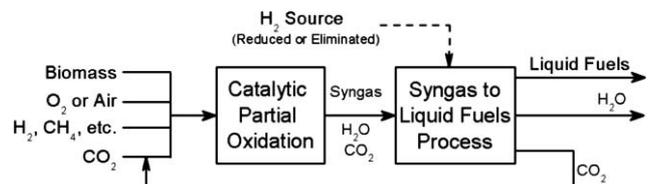
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However, CO<sub>2</sub> addition under typical biomass gasification conditions does not provide the thermodynamic driving force necessary to convert all of the biomass-derived carbon to CO. To overcome this thermodynamic limitation, H<sub>2</sub> must be co-fed into the reaction, supplying the energy needed to drive the RWGS reaction, as discussed in greater detail by Xiaoding *et al.*<sup>5</sup>

The addition of molecular hydrogen to traditional biomass processes has been considered for improving product quality and yield by improving carbon utilization and increasing product H<sub>2</sub>/CO ratios.<sup>6–8</sup> It has also been considered as a method for mitigating CO<sub>2</sub> emissions by chemical reduction, rather than sequestration.<sup>5,9</sup> With advancing technologies, H<sub>2</sub> may ultimately be obtained from alternative sources such as electrochemical or photochemical conversion of water.<sup>1,10</sup> However, until more efficient technologies are developed for producing H<sub>2</sub>, inexpensive hydrocarbons rich in hydrogen, such as natural gas or biogas, may be exploited as a cheap hydrogen source.

We hypothesize that biomass partial oxidation with CO<sub>2</sub> addition can be exploited to recover all fuel carbon atoms as CO by generating molecular hydrogen *in situ* from hydrogen-rich sources (Fig. 1). Previously, we have shown that through a process called reactive flash volatilization, cellulose can be rapidly converted to synthesis gas by catalytic partial oxidation (CPO) over Rh-based catalysts without the formation of char.<sup>11,12</sup> The results presented here suggest that biomass reforming, CH<sub>4</sub> reforming and water-gas shift reactions (WGS) can be integrated into one catalytic reactor stage. Our results show that a mixture of cellulose (a biomass surrogate), CO<sub>2</sub>, and CH<sub>4</sub> can be converted to synthesis gas with no char formation and >100% yield of CO, defined here to be the ratio of the moles of CO produced to the moles of carbon in the fuel feed.



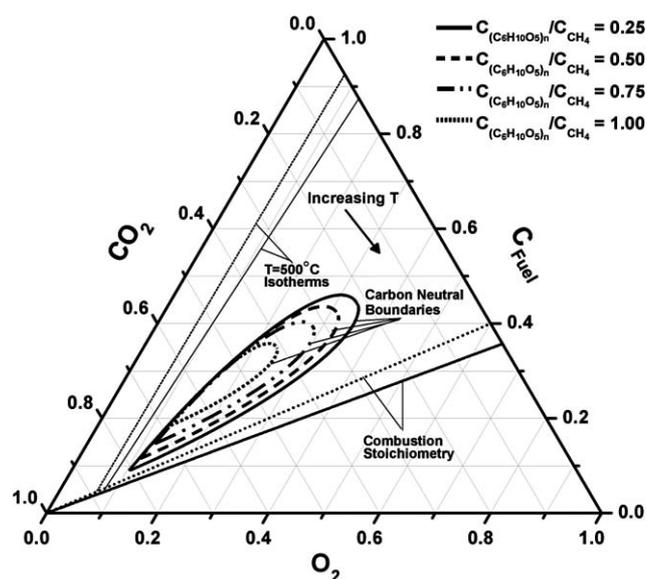
**Fig. 1** A possible schematic of the proposed process. An optimum process design would require, among other things, a coupled economic and process analysis, and detailed product specifications. Furthermore, depending on the CO<sub>2</sub> source, recycling may not be preferred.

The relevant feed ratios for experimental consideration were predicted by calculating the adiabatic equilibrium of all possible feed combinations of carbohydrates (cellulose), CH<sub>4</sub>, air and

CO<sub>2</sub> (the calculation algorithm is presented in Section 2 of the ESI†). Under the considered carbon fuel feed ratios of  $0.25 < C_{(C_6H_{10}O_5)_n}/C_{CH_4} < 1.00$ , there exists a distinct division (Fig. S1 of the ESI†) between the operating conditions that generate CO<sub>2</sub> and a region for which there is no net generation of CO<sub>2</sub> from the fuel.

This complex chemistry can only occur rapidly with heterogeneous catalysts, at high temperatures, near adiabatic reactor conditions, where there is no steady build-up of surface coke. There also exists a distinct set of reactor feed ratios for which no solid graphitic or amorphous carbon is predicted at equilibrium (Fig. S2 of the ESI†).

Under feed conditions where the fuel carbon is not converted to CO<sub>2</sub> or solid carbon, the carbon is converted to CO. Therefore, the overlap of these two regions on the ternary diagram in Fig. 2 depicts a narrow region of feed conditions that will permit CO yields >100% through catalytic biomass and CH<sub>4</sub> co-processing. These inlet concentrations minimize complete fuel combustion and result in temperatures higher than those at which methanation and carbon formation occurs (~500 °C). Details of the calculations that were used to construct Fig. 2 can be found in the ESI.†

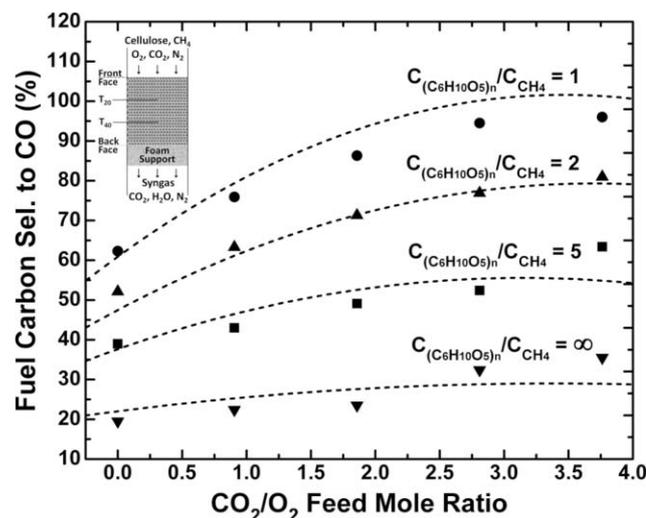


**Fig. 2** An operating diagram derived from adiabatic equilibrium calculations for the CPO of cellulose and CH<sub>4</sub> at four constant feed ratios in air with no pre-heat, and varying air/fuel and air/CO<sub>2</sub> ratios over all possible concentrations. The results (re-normalized without N<sub>2</sub>) describe a regime of operation where solid carbon is not a thermodynamic product and there is zero net generation of CO<sub>2</sub>, corresponding to CO yields of >100%. Details of the calculations and the assembly of this figure can be found in the ESI.†

The results predicted by these equilibrium calculations were tested in experiments conducted with 300 μm cellulose particles with CH<sub>4</sub>, O<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub> in a 20 mm ID quartz reactor tube over a Rh–Ce/γ–Al<sub>2</sub>O<sub>3</sub> catalyst supported on a 6 cm bed of 1.3 mm diameter α–Al<sub>2</sub>O<sub>3</sub> spheres (inset, Fig. 3; described in detail elsewhere<sup>13†</sup>). The Rh–Ce/γ–Al<sub>2</sub>O<sub>3</sub> catalyst was selected for its high WGS and reforming activity, and stability.<sup>14</sup> Temperatures measured at 20 and 40 mm below the front of

the catalyst surface ranged from 850–1125 °C, depending on the operating conditions and the position in the catalyst bed. Complete conversion to synthesis gas and combustion products with no observable char or tar formation was observed at a <30 ms gas residence time under continuous operation for all of the experiments reported.

The selectivity to CO in the reactor effluent showed that increasing the concentration of CO<sub>2</sub> in the absence of CH<sub>4</sub> co-feed had a weak effect on CO yield, consistent with the thermodynamic calculations represented by the dashed lines in Fig. 3. Alternatively, increasing the concentration of CH<sub>4</sub> in the absence of CO<sub>2</sub> co-feed significantly improved the CO yield, increasing the selectivity to CO from 19 to 62% for C<sub>(C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>/C<sub>CH<sub>4</sub></sub> feed ratios of ∞ and 1, respectively. Furthermore, increasing the concentration of CO<sub>2</sub> with high concentrations of CH<sub>4</sub> increased the CO yield by as much as 34% at the ratio C<sub>(C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub>/C<sub>CH<sub>4</sub></sub> = 1. At CO<sub>2</sub>/O<sub>2</sub> = 3.76 and CH<sub>4</sub>/O<sub>2</sub> = 0.6, the system approached a CO yield of 100%, indicating a zero net generation of CO<sub>2</sub> in the reactor.</sub></sub>



**Fig. 3** Fuel carbon selectivity to CO rapidly approaches equilibrium-predicted concentrations (dashed lines) in the reforming of cellulose at a constant flow rate of 50 g h<sup>-1</sup> and a fuel carbon to oxygen from O<sub>2</sub> ratio (C/O) of 0.6, while varying the ratio of the two fuels (cellulose and CH<sub>4</sub>), N<sub>2</sub>/O<sub>2</sub> and CO<sub>2</sub>/O<sub>2</sub>. At CO<sub>2</sub>/O<sub>2</sub> = 3.76 and CH<sub>4</sub>/O<sub>2</sub> = 0.6, the system approached CO yields of 100%.

Selected experimental (experiments 1–5) and theoretical (calculations 6–10) results are presented in Table 1. The results from experiment 5 show a condition with >100% CO yield in the laboratory reactor, indicating complete conversion of carbon in cellulose and CH<sub>4</sub>, and partial conversion of CO<sub>2</sub> carbon to CO.

The theoretical data presented in calculation 9 of Table 1 shows a condition with ~100% CO yield and a H<sub>2</sub>/CO ratio of 1.46, compared to a H<sub>2</sub>/CO ratio of 1 for traditional biomass gasification. The theoretical data presented in calculation 10 shows >130% CO yield, compared to ~50% for traditional biomass gasification, which can be achieved at a cost to the product H<sub>2</sub>/CO ratio.

This process works by co-reforming carbohydrate pyrolysis vapors with CH<sub>4</sub> and CO<sub>2</sub> in one heat-integrated catalyst bed.

**Table 1** Selected experimental and theoretical (italics) data for the millisecond CPO of cellulose and CH<sub>4</sub> with CO<sub>2</sub> addition<sup>a</sup>

Experiment/calculation	1	2	3	4	5	6	7	8	9	10
<b>Parameters</b>										
Catalyst bed length/mm	60	60	60	60	60	—	—	—	—	—
C/O ratio	0.6	0.6	0.6	0.6	0.6	0.82	0.79	1.00	0.91	0.70
C <sub>(C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>)<sub>n</sub></sub> /C <sub>CH<sub>4</sub></sub>	∞	5	2	1	0.5	0.50	0.25	0.75	0.25	0.5
CH <sub>4</sub> /O <sub>2</sub> ratio	0	0.2	0.4	0.6	0.8	1.09	1.27	1.14	1.45	0.93
CO <sub>2</sub> /O <sub>2</sub> ratio	0	0.91	1.86	2.81	3.76	1.81	1.59	0.57	0.31	2.6
N <sub>2</sub> /O <sub>2</sub> ratio	3.76	2.86	1.91	0.95	0	3.76	3.76	0	0	0
Cellulose flow/g h <sup>-1</sup>	50	50	50	50	50	—	—	—	—	—
<b>Results</b>										
<i>T</i> /°C										
20 mm	1061	1108	1040	1056	1139	—	—	—	—	—
40 mm	1018	965	897	916	985	—	—	—	—	—
Adiabatic	—	—	—	—	—	652	643	895	892	953
H selectivity (%)										
H <sub>2</sub>	14.9	27.4	26.3	23.7	29.6	63.9	66.4	74.9	83.6	36.6
H <sub>2</sub> O	85.1	72.6	72.9	74.1	68.8	33.7	29.3	25.0	16.2	63.3
C selectivity (%)										
CO yield <sup>b</sup>	19.5	43.0	71.3	94.5	107.6	100.9	101.6	101.6	101.4	131.4
CO <sub>2</sub>	80.5	57.0	28.2	3.9	-8.7	-2.8	-5.4	-1.7	-1.5	-31.4
CH <sub>4</sub>	0	0	0.5	1.6	1.1	1.8	3.7	0.0	0.1	0.0
Residence time/ms										
28.1	23.4	19.1	13.7	9.3	—	—	—	—	—	—
Mass velocity/h <sup>-1</sup>										
43.0	51.6	64.5	86.1	129.1	—	—	—	—	—	—
H <sub>2</sub> /CO ratio										
0.74	0.55	0.46	0.40	0.41	1.02	1.15	1.11	1.46	0.45	—
Synthesis gas yield (%)										
6.5	16.1	27.5	40.0	51.1	41.6	42.8	85.1	89.6	65.1	—

<sup>a</sup> Details of the calculations and assumptions that went into the assembly of this table can be found in the ESI. <sup>b</sup> The results for CO selectivity are identical to CO yield because there is always 100% conversion of the cellulose to C<sub>1</sub> products in the reactor.

The high temperatures generated in the oxidation zone allow rapid heat conduction through the catalyst support, powering endothermic pyrolysis at the front of the catalyst and reforming within the catalyst bed, eliminating char generation.<sup>13,15</sup> The CPO of CH<sub>4</sub> in similar reactors has been shown to readily form CO and H<sub>2</sub>, a crucial step that provides the H<sub>2</sub> necessary to drive the RWGS reaction (eqn 1).<sup>16</sup>

Experiments show a rapid approach to equilibrium with minimal heat loss, validating the use of adiabatic equilibrium calculations to model reactor operation, as noted by the experiments and calculations presented in Fig. 3. The calculations indicate at least 20% lower CO selectivities are achieved for certain feeds with independent carbohydrate and CH<sub>4</sub> reforming, showing the importance of co-reforming CH<sub>4</sub> and biomass in one integrated reaction system (Table S2 of the ESI†). Similar results could be achieved with three reactors individually undergoing CH<sub>4</sub> CPO, carbohydrate reforming and product gas equilibration by water-gas shift. However, this arrangement is considerably more complex and increases the overall process cost.

Our research demonstrates for the first time that equilibrated, adiabatic, char-free biomass processing by co-feeding CH<sub>4</sub> at specific concentrations produces 100% carbon recovery as CO. Future research will focus on the mechanisms of the RWGS reaction in the presence of biomass-derived oxygenate CPO, as well as hydrogen-coupling by CH<sub>4</sub> decomposition, both of which are currently unknown. Utilizing the benefit of this reactor scheme requires considerable process design in conjunction with full biomass life-cycle and economic analysis. Finally, although lignocellulosic biomass has been experimentally shown to yield similar results to a pure cellulose feedstock,<sup>11</sup> in-depth experiments assessing the long-term effect of ash on catalyst site deactivation must be performed.

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## Notes and references

- G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044–4098.
- C. Schubert, *Nat. Biotechnol.*, 2006, **24**, 777–784.
- A. V. Bridgwater, *Chem. Eng. J.*, 2003, **91**, 87–102.
- R. D. Perlack, L. L. Wright, A. F. Turhollow, R. L. Graham, B. J. Stokes, D. C. Erblich, *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply*, Oak Ridge National Laboratory, Oak Ridge, TN, USA, DOE/GO-102005-2135, 2005.
- X. Xu and J. A. Moulijn, *Energy Fuels*, 1996, **10**, 305–325.
- R. Shinnar and F. Citro, *Science*, 2006, **313**, 1243–1244.
- R. Agrawal, N. R. Singh, F. H. Ribeiro and W. N. Delgass, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 4828–4833.
- D. Hildebrandt, D. Glasser, B. Hausberger, B. Patel and B. J. Glasser, *Science*, 2009, **323**, 1680–1681.
- B. C. Gates, G. W. Huber, C. L. Marshall, P. N. Ross, J. Siirola and Y. Wang, *MRS Bull.*, 2008, **33**, 429–435.
- R. Agrawal and N. R. Singh, *AIChE J.*, 2009, **55**, 1898–1905.
- P. J. Dauenhauer, B. J. Dreyer, N. J. Degenstein and L. D. Schmidt, *Angew. Chem., Int. Ed.*, 2007, **46**, 5864–5867.
- J. R. Salge, B. J. Dreyer, P. J. Dauenhauer and L. D. Schmidt, *Science*, 2006, **314**, 801–804.
- J. L. Colby, P. J. Dauenhauer and L. D. Schmidt, *Green Chem.*, 2008, **10**, 773–783.
- A. Donazzi, B. C. Michael and L. D. Schmidt, *J. Catal.*, 2008, **260**, 270–275.
- P. J. Dauenhauer, J. L. Colby, C. M. Balonek and L. D. Schmidt, *Green Chem.*, 2009, **11**, 1555–1561.
- D. A. Hickman and L. D. Schmidt, *Science*, 1993, **259**, 343–346.