Angewandte Chemie

Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Millisecond Reforming of Solid Biomass for Sustainable Fuels

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

Supplemental Information: Control of Solid Particle Flow

Solid particles were delivered to the reactor from a hopper consisting of a 4" diameter acrylic tube. Particles were metered with a ¼" diameter auger running axially through the hopper to an exit tube attached to flexible tubing that connected to the top of the reactor. The entrance point of the auger to the hopper was sealed using a 3/8" fitting sealed with an o-ring, and the turning rate was maintained at 3-70 rpm using a variable speed mixer motor. Solid particles were agitated to sufficiently fill the auger by impact of a plastic tube fastened to the front of a 10" subwoofer operating at 30 Hz. The top of the reactor consisted of an annulus of 7 mm OD through which solid particles and air flowed down to the front face of the catalyst foam bed. Gases were metered using mass flow controllers for N_2, O_2, and CH_4 at startup.

Supplemental Information: Reactor Setup

The reactor tube consisted of an 18-mm-i.d., ca. 55-cm-long quartz tube. The metal catalysts were loaded on a ceramic foam or sphere fixed bed by the wet impregnation technique described previously.[16] In table 1, "Foam" consisted of 2.5 wt% (~0.05 g) Rh and 2.5 wt% Ce on 45 ppi α-Al_2O_3 foams for the first 10 mm. The support foam from 10 mm to 30 mm consisted of 2.5 wt% Rh and 2.5 wt% Ce on a 5 wt% γ-Al_2O_3 washcoat supported on 80 ppi α-Al_2O_3 foams.   "Spheres" consisted of a bed 30 mm in length of 1 mm diameter spheres with 5 wt% γ-Al_2O_3 washcoat and the same amount of Rh and Ce as used in the foam.

The catalyst was initially heated by methane partial oxidation to 800 °C after which a continuous flow of solid particles was immediately applied to the front catalyst surface. Methane was removed from the system and the flow rate of air was adjusted to satisfy 0.6 < C/O < 1.0. No external heating was required as solid particles and air entered the reactor at room temperature. The quartz reactor tube was wrapped in 1 in. of insulation to prevent radial heat

losses. Gas samples were collected with a gas syringe after a water-cooled condenser and injected into a gas chromatograph. Column response factors and retention times were determined by injecting quantities of known species relative to N_2. Mass balances on carbon and hydrogen typically closed within $\pm 5\%$.

Supplemental Information: Experimental Feedstock

Cellulose in experiment 1 of Table 1 was obtained from Sigma-Aldrich. Cellulose in experiments 2 and 3 of Table 1 was obtained from FMC biopolymer. Starch in experiment 4 of Table 1 was obtained from Bob's Red Mill Natural Foods, Inc. as pelletized starch prepared from the Cassava plant. Aspen chips obtained from trees growing in Rosemount, MN, were dried and ground over a size 20 mesh. Polyethylene in experiments 6 and 7 of Table 1 was obtained from Alfa Aesar. The mass average MW of polyethylene was ~50,000 determined by GPC. Mass average particle sizes were determined from particle size distributions measured by light scattering. Moisture and ash content were determined gravimetrically.

Supplemental Information: Ni catalyst

We have repeated experiments with cellulose substituting 5 wt% NiCe for 5 wt% RhCe on alumina spheres, and we have observed selectivity to H_2 and CO similar to RhCe for as long as 10 hours. However, Ni-based catalysts have been shown to accumulate carbon during the reforming of oxygenates, and further testing is required to show that Ni is a viable catalyst for long-term biomass processing.[17]

Supplemental Information: Particle Size

The size of solid particles did not significantly affect processing characteristics. This agrees with models of cellulose particles contacting a hot surface which show that temperature gradients within the particle should become insignificant for particle diameters 1 mm or less.[18] However, larger particles of 1-5 mm have been shown to exhibit high temperature only at the hot surface interface, preventing a large fraction of the particle from slowly heating to form char.[19]

This was observed occasionally in our experiments as aggregated particles of cellulose as large as 5 mm exhibited steady continuous processing without significant char formation.

Supplemental Information: Processing of polyethylene

The processing of low-density polyethylene exhibited higher selectivity to H_2 and CO than cellulose, starch, and Aspen. The absence of oxygen atoms in the polymer permits significantly higher equilibrium selectivity to H_2 and CO than the oxygen-containing polymers. Another key difference is that highly volatile oxygenated compounds exhibit very high conversion in millisecond reactors,[16] while polyethylene produces small hydrocarbons, including olefins, that do not react completely to synthesis gas even at low C/O ratios. Under high operating temperatures, these olefins are believed to be formed from the gas phase decomposition of the parent polymer to radicals and subsequent beta-scission or beta-hydrogen elimination.[20,21]

Supplemental Information: Equilibrium Calculations

Equilibrium was calculated using HSC software.[22] Carbon equilibrium lines of Figure 1 were calculated using the feed ratios of C, H, and O and permitting a solid phase of C along with a gas phase of N_2, O_2, CO, CO_2, CH_4, H_2O, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_{10}, C_4H_8, C_5H_{12}, C_5H_{10}, CH_3OH, C_2H_5OH, CH_2O, C_2H_4O. Equilibrium selectivity to CO, H_2, and CH_4 in Figure 1 were calculated permitting the same species at the temperature measured 30 mm down in the catalytic bed.

Supplemental Information: Figure 2 Experimental Technique

Figure 2 shows the temperature of the catalyst reactor system processing cellulose at 25 g/hr with air on a foam support at C/O=0.7 and C/O=0.9. This data was collected with 1 mm resolution using a capillary technique developed by Horn, et al. to insert a K-type thermocouple into the fixed catalytic bed during operation.[23] Data points were collected by averaging the observed temperature for 30 seconds at each fixed location. This was completed twice for each C/O ratio, and the two data sets were averaged.

Supplemental Information: Integrated Gasification and Fuel Production

The production of synthetic fuels from biomass gasification remains complicated to optimize and improve due to the number of available options for assembling a system capable of converting raw biomass all the way to a liquid fuel. Complete systems can include but are not limited to the following steps: feed preparation, feed gas compression, an oxygen plant if not using air, gasification, clean up, synthesis gas cooling, synthesis gas reforming, removal of CO_2 or other diluents, liquid fuels synthesis, power generation, and liquid fuels processing. Determination of an optimum system requires an examination and comparison of all parameters while considering sources of biomass and possible fuels such as that carried out for synthetic alkanes[24], mixed alcohols, methanol[25] or dimethyl ether, and hydrogen.[26]

Systems capable of converting biomass to synthetic fuels can be improved by either removing process steps, or reducing the requirements of any one step. The catalytic biomass process considered here has the possibility of improving the overall process by both of these methods. A typical fluidized bed gasifier produces a synthesis gas rich stream in seconds to minutes containing several impurities including particulates and tars.[25] The catalytic method described here could reduce the physical size of the gasifier due to a significantly shorter residence time. Additionally, the fixed bed approach prevents particulates and tars from exiting the reactor without being converted to gases possibly eliminating the requirement for a cyclone and/or particulate filter such as a candle or moving bed filter system. Thirdly, synthesis gas processing for synthetic fuels commonly requires a water-gas-shift stage to adjust the H_2/CO ratio as needed for each synthetic fuel: H_2/CO~2.0 for Fischer-Tropsch alkanes [27], H_2/CO~1.0 for dimethyl-ether[28], and H_2/CO>>1 (<10 ppm CO) for hydrogen[29]. This catalytic method has shown that a wide-variety of feedstocks can be converted to a synthesis gas rich stream with 1.0 < H_2/CO < 1.3 as shown in Table 1. However, the direct application of catalysts for oxidative conversion of oxygenates and alkanes has shown that co-feeding steam can result in synthesis gas effluent of 0.9 < H_2/CO < 4.0 at millisecond time scales using a Rh-based catalyst.[16,30]

Similar experiments considering steam addition to millisecond processing of biomass could potentially expand the H_2/CO ratio of the reactor effluent. Further study will be required to show that it is possible, but this technique has the capability to combine the gasification step, the tar and particulate removal step, and shift stage into a single step system considerably smaller than a conventional gasifier.

While the described system provides several possibilities for reducing the complexity of biomass conversion to synthesis gas, several other factors must be considered. The described system provided oxygen to the system as air, $N_2/O_2 = 3.76$. At these conditions, N_2 comprises nearly half of the moles of gaseous reactor effluent. The presence of a significant diluent has led to descriptions of once-through systems, but these processes are limited by large downstream equipment with low overall conversion to synthetic fuels.[31] The presence of CO_2 could have a similar effect on the size of downstream synthesis equipment. The catalytic biomass conversion method has the benefit that the presence of N_2 and other diluents presents a "worst-case-scenario." Diluents such as N_2 significantly increase convection in the reactor increasing heat flow away from the front face in competition with heat conduction backwards in the reactor. By reducing or eliminating N_2 and any other diluent, the front face of the catalyst bed should increase in temperature and permit faster processing in an overall smaller catalytic bed.

Another important consideration for combination of the catalytic biomass process with a downstream synthesis is the system pressure. The described process was examined at atmospheric conditions, while conversion of synthesis gas to synthetic fuels or H_2 is favored thermodynamically at higher pressures of 20-80 bar depending on the specific process. Combination with secondary processing could occur by compressing either the gasification step effluent or compressing the feed gases to the gasifier step and operating at pressures greater than atmospheric. Compressing the effluent synthesis gas is much less favorable than compressing the gasification feed gases due to the significant change in gaseous moles on conversion of

biomass to synthesis gas. For this reason, catalytic conversion of biomass with this method at pressure greater than 1 atm will be a future research focus.

While the catalytic method could reduce the size of the gasification step and potentially eliminate other steps such as cyclone separator, bag filter, or shift-stage, there remain gas-cleaning steps that cannot be removed from the system. Biomass sources such as Aspen will always contain volatile impurities such as S, N, P, Cl, Na and K which must be significantly reduced in the synthesis gas stream. Significant research has focused on techniques for hot gas cleanup methods to remove tars and alkali that can foul or deposit downstream equipment.[32,33] Adsorption materials or other processes that remove these species will be necessary before combining the gasification step with the fuel synthesis step.

Technology to reduce the capital and operating costs of processing to clean conditioned synthesis gas can significantly affect the full biomass-to-fuels system. Full processing of biomass to clean conditioned synthesis gas has been shown to account for over half[25] and even as high as 75%[27] of the total capital cost of biomass-to-methanol processes. The full economic benefit of a catalytic technique to convert biomass to synthesis gas will require a complete technical and economic analysis considering all of the possible technical options and combinations.

Complete References

[1] A.J. Ragauskas, C.K. Williams, B.H. Davison, G. Britovsek, J. Cairney, C.A. Eckert, W.J. Frederick Jr., J.P. Hallett, D.J. Leak, C.L. Liotta, J.R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **2006,** 311, 484-489.

[2] A.V. Bridgwater, *Chem. Eng. J.* **2003,** 91, 87-102.

[3] J.P. Ciferno, J. Marano, *Benchmarking Biomass Gasification Technologies for Fuels,* National Energy Technology Laboratory, US Department of Energy, Pittsburgh, PA, USA, **2002**.

[4] T. Miyazawa, T. Kimura, J. Nishikawa, K. Kunimori, K. Tomishige, *Sci. Technol. Adv. Mater.* **2005**, 6, 604-614.

[5] J.R. Rostrup-Nielsen, *Science* **2005**, 308, 1421-1422.

[6] A.G.W. Bradbury, Y. Sakai, F. Shafizadeh, *J. Appl. Polym. Sci.* **1979**, 23, 3271-3280.

[7] A.L. Brown, D.C. Dayton, J.W. Daily, *Energy & Fuels* **2001**, 15, 1286-1294.

[8] D.S. Scott, J. Piskorz, M.A. Bergougnou, R. Graham, R.P. Overend, *Ind. Eng. Chem. Res.* **1988**, 27, 8-15.

[9] J.R. Salge, B.J Dreyer, P.J. Dauenhauer, L.D. Schmidt, *Science* **2006,** 314, 801-804.

[10] D. Wang, S. Czernik, D. Montane, M. Mann, E. Chornet, *Ind. Eng. Chem. Res.* **1997**, 36, 1507-1518.

[11] M. Inaba, K. Murata, M. Saito, I. Takahara, *Energy Fuels* **2006,** 20, 432-438.

[12] M. Asadullah, K. Tomishige, K. Fujimoto, *Cat. Comm.* **2001**, 2, 63-68.

[13] Further information in the online supplemental information section.

[14] M. Heitz, E. Capek-Menard, P.G. Koeberle, J. Gagne, E. Chornet, R.P. Overend, J.D. Taylor, E. Yu, *Bioresour. Technol.*, **1991**, 35, 23.

[15] M.K. Misra, K.W. Ragland, A.J. Baker. *Biomass Bioenergy* **1993,** 4, 103-116.

[16] P.J. Dauenhauer, J.R. Salge, L.D. Schmidt, *J. Cat.* **2006**, 244, 238-247.

[17] D.K. Liguras, K. Goundani, X.E. Verykios, *Journal of Power Sources* **2004**, 130, 30-37.

[18] C. Di Blasi, *Polymer International* **2000**, 49, 1133-1146.

[19] C. Di Blasi, *Chemical Engineering Science* **1996**, 51(10), 2211-2200.

[20] H. Sinn, W. Kaminsky, J. Janning, *Angew. Chem.* **1976**, 88, 737.

[21] W. Kaminsky, M. Predel, A. Sadiki, *Polymer Degradation and Stability* **2004**, 85, 1045-1050.

[22] Outokumpu Research Oy, HSC Chemistry, version 4.1, http://www.outokumpu.com/hsc

[23] R. Horn, K.A. Williams, N.J. Degenstein, L.D. Schmidt, *J. Cat.* **2006**, 242, 92-102.

[24] M.J.A. Tijmensen, A.P.C. Faaij, C.N. Hamelinck, M.R.M van Hardeveld, *Biomass & Bioenergy* **2002**, 23, 129-152.

[25] C.N. Hamelinck, A.P.C. Faaij, *Journal of Power Sources* **2002**, 111, 1-22.

[26] P.L. Spath, M.K. Mann, W.A. Amos. (December 2003). Update of Hydrogen from Biomass – Determination of the Delivered Cost of Hydrogen. NREL Milestone Report. http://www.nrel.gov/docs/fy04osti/33112.pdf

[27] P.L. Spath, D.C. Dayton, (December 2003). Preliminary Screening – Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas. http://www.nrel.gov/docs/fy04osti/34929.pdf

[28] X.D. Peng, B.A. Toseland, P.J.A. Tijm, *Chemical Engineering Science*, **1999**, 54, 2787-2792.

[29] C. Song, *Catalysis Today*. **2002**, 77, 17-49.

[30] B.J. Dreyer, I.C. Lee, J.J. Krummenacher, L.D. Schmidt, *Applied Catalysis A: General*, **2006**, 307, 184-194.

[31] J.R. Rostrup-Nielsen, *Catal. Today* **2000**, 63, 159-164.

[32] K.R. Cummer, R.C. Brown, *Biomass and Bioenergy*, **2002**, 23, 113-128.

[33] J. Oakey, N. Simms, P. Kilgallon, *Materials Research*, **2004**, 7(1), 17-25.