Chemical Processing in High-Pressure Aqueous Environments. 7. Process Development for Catalytic Gasification of Wet Biomass Feedstocks

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Through the use of a metal catalyst, gasification of wet biomass can be accomplished with high levels of carbon conversion to gas at relatively low temperature (350 °C). In a pressurized-water environment (20 MPa), near-total conversion of the organic structure of biomass to gases has been achieved in the presence of a ruthenium metal catalyst. The process is essentially steam reforming, as there is no added oxidizer or reagent other than water. In addition, the gas produced is a medium heating value gas due to the synthesis of high levels of methane, as dictated by thermodynamic equilibrium. While good gas production was demonstrated, biomass trace components caused some processing difficulties in the fixed catalyst bed tubular reactor system used for the catalytic gasification process. Results are described for tests using both bench-scale and scaled-up reactor systems.

Introduction

Catalytic hydrothermal processing (250 °C to 360 °C, up to 22 MPa) can be used to treat wet biomass, organics-in-water process residues, and wastewaters by converting the organic contaminants to gases. The system is operated as a liquid-phase, heterogeneously catalyzed process at nominally 350 °C and 20 MPa to produce a methane/carbon dioxide product gas from the water solutions or slurries of organics.

Earlier papers in this series have addressed the processing environment,[1] catalyst systems for this environment,[2] continuous-flow reactor tests with fixed beds of catalyst in a tubular reactor,[3] and demonstration-scale tests with organic chemical manufacturing wastewaters.[4] Here we report the preliminary results of continuous-flow reactor studies with wet biomass feedstocks using new catalyst systems developed specifically for these processing conditions.

Background

The use of hydrothermal processing (high-pressure, high-temperature liquid water) has received relatively limited study.[5] Some recent biomass-related work has focused on the chemical mechanisms of the breakdown of biomass components under these conditions.[6] Although work was performed with actual biomass, containing mineral components, no discussion of the fate of these materials is given.[7] One application of this processing environment has been demonstrated in the catalytic gasification of organics.[3] In this application, heterogeneous metal catalysts accelerate the reaction of organics with water and produce methane and carbon dioxide as the product gases. It has been reported both as a means of recovering useful energy from organic-in-water streams and as a water treatment system for wet organic contaminants.

Developing catalysts for this processing environment has also been an important factor in making this processing technology viable.[2] Previous reports of continuous reactor tests with biomass feedstocks provide preliminary short-term processing results,[8,9] but also show the problems of long-term operation of the process with the contaminants inherent in biomass. Attempts to pretreat biomass by removing certain components, like alkaline earths, to allow extended use with catalysts, have also been documented.[10] More recently, we have demonstrated more stable catalyst formulations for wet gasification as described in patents claims.[11,12] This article provides additional results of catalytic gasification with these improved catalysts using wet biomass feedstocks (dairy manure and ethanol from grain fermentation residue, aka distillers' dried grain and solubles).

Experimental Section

The equipment and procedures described below were used for testing the catalytic hydrothermal gasification of wet biomass.

Equipment. Gasification tests were carried out in fixed-bed catalytic tubular reactors. A microscale reactor was used for long-term tests of liquid-only feedstocks and operated at 80 mL/h.[13] A bench-scale unit described earlier[3] was also used, as was a mobile scaled-up reactor system (MSRS), based on the bench-scale continuous-flow design. The MSRS was designed at a scale of 10 L/h of aqueous feed for obtaining engineering data for further scale-up, whereas the bench-scale unit operated at 2 L/h. The MSRS, shown schematically in Figure 1, includes the reactor system mounted in a fifth-wheel trailer unit and also a small operations control and analytical room. Design working conditions for the reactor systems were 350 °C at 24 MPa.

At the front end of the larger two reactor systems, the wet biomass feedstock was loaded into the feed tank equipped with an electrically driven paddle stirrer to agitate the contents. The feed stream was pumped with a high-pressure reciprocating plunger pump. In the bench-scale unit, a progressing cavity pump was used to maintain flow to the high-pressure pump. Preheating

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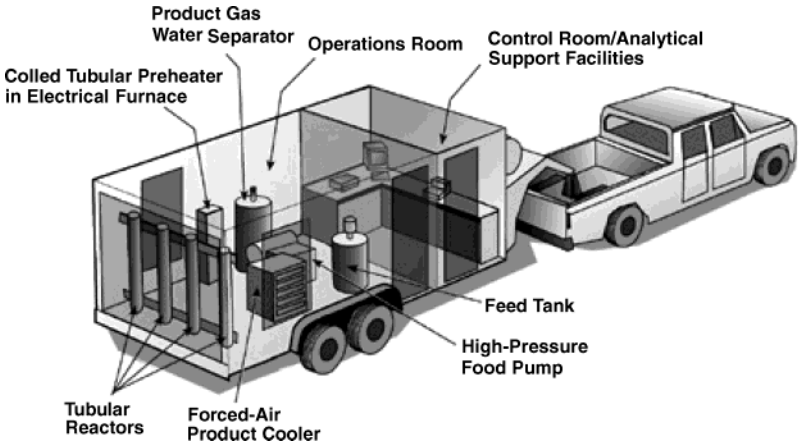

Figure 1. Schematic of mobile scaled-up reactor system.

the pressurized feedstock was different in the two systems. Originally, the bench-scale unit was designed for the initial portion of the tubular reactor to act as the preheater as well. The addition of a continuous-flow stirred-tank reactor (CSTR) was required to prevent the buildup of solids at the opening of the reactor as was found when using many biomass slurry feedstocks.[14] In the scaled-up system the feedstock was pumped directly from the feed tank through the tube side of the heat exchanger. The heat exchanger was a double-tube heat exchanger constructed of 316SS tubing. With a total length of 17 m, the heat exchanger could bring the feedstock to within 100 °C of the final operating temperature when using biomass feedstocks. The final heating of the feed occurred in the coiled tubular preheater. The catalytic gasification reactors were of a tubular fixed-bed design. After leaving the reactor(s), the product stream was routed through a heat exchanger, which provided heat for preliminary heating of the feed stream in the scaled-up version, but was simply a cooler in the bench-scale unit. Downstream of the exchanger, the process pressure was reduced to ambient over a back-pressure regulator. The product stream then entered a liquid/gas separator tank, where process water was reclaimed and combustible gases were sampled for analysis, measured, and then vented.

Procedures. Actual startup of the experiment usually required 2 to 4 h to bring operating conditions to the desired levels. Operating data were recorded, and data windows were defined on the basis of steady-state (or near steady-state) operating conditions.

(a) Gas Analysis. Gas samples could be withdrawn manually and analyzed every 30 to 60 min. The gaseous stream was mainly composed of CO_2, CH_4, H_2, and C_2+ hydrocarbons, as well as water vapor. Gas analysis was performed by gas chromatography (GC) as described earlier.[3] The gas samples were withdrawn after cooling and depressurizing the product effluent to near ambient conditions. In the process, the gas product is effectively scrubbed by the liquid aqueous byproduct. As a result, the liquid byproduct contains some dissolved product gases. Particularly in the case of carbon dioxide, it is retained in the water by participating in acid/base chemistry with alkali and ammonium cations derived from the biomass feedstocks.

(b) Calculation of Carbon Conversion to Gas. Once the gas samples from the experiments were analyzed, calculations were made to determine the conversion of the organic feedstock to gases. Carbon conversion to gas was then calculated on a mass basis for the carbon in the product gases as a percent of the carbon in the feedstock. The carbon balance is the key elemental balance for this process involving low concentration aqueous streams.

(c) Analysis of Liquid Effluent. The liquid effluent was analyzed for chemical oxygen demand (COD) and pH, with spot checks for ammonia, inorganic anions (principally chloride and sulfate), and trace metals. Percent COD reduction from the feed to product was a major process indicator, which was monitored to determine catalyst effectiveness. Anions, including chloride, were measured by ion chromatography (IC) using a Dionex DX 500 IC consisting of a GP40 pump, EG40 eluent generator, and ED40 electrochemical detector, with an AS3500 autosampler. An ASRS-Ultra 4 mm suppressor was used (at 100 mW) to minimize baseline drift. The chromatography was performed using an AG-11 guard column and an AS-11HC column running at 30 °C, with a hydroxide gradient from 0.5 mM to 41 mM and a flow rate of 1.2 mL/min. Certified standards were used to calibrate the IC.

(d) Elemental Analysis of Solids. Elemental analysis of solid samples was performed by both inductively coupled plasma−optical emission spectrometry (ICP) and X-ray fluorescence (XRF). The ICP was a Perkin-Elmer 3000DV with an AS90 autosampler, which has an instrument detection limit of about 1 ppb (for most elements) with a linear calibration up to 100 ppm (for most elements). Solid samples were prepared via microwave digestion in concentrated nitric and hydrochloric acids, then diluted to volume. The ICP was calibrated and verified with two independent certified standard sets. Spikes and dilutions were down for each batch of samples to check for and/or mitigate any matrix effects. The ICP process ran a constant pump rate of 1.5 mL/min for all samples and standards during analysis. A 3 mL/min rinse and initial sample flush was used to switch between each sample and standard. The plasma was run at 1450 W with argon flow. Trace metal grade (sub-ppb) acids and two independently NIST-certified calibration standard sets were used for calibration and method verification. The XRF analysis was performed on the solids as loose ground powders.

(e) X-ray Photometric Spectrometry (XPS) Analysis. The XPS measurements were made using a Physical Electronics Quantum 2000 scanning ESCA microprobe. This system uses a focused monochromatic Al Kα X-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 16-element multichannel detection system. The X-ray beam used was a 37.4

Table 1. Bench-Scale Test Results

	WSU dairy manure			Midwest Grain DDG&S			Furst-McNess DDG&S		
on stream, h	6	9	14.5	5 (+14.5)	8.5 (+14.5)	14.5 (+14.5)	3	5.5	7.5
feed COD, ppm	47000	47000	47000	79500	79500	79500	65000	126000	126000
LHSV, L/L/h	1.65	2.09	2.60	1.54	1.73	1.40	1.37	1.59	1.37
temperature, °C	356	355	355	350	350	355	350	350	350
% COD conversion	99.89	99.78	98.30	99.72	99.52	95.48	99.78	99.94	99.91
% carbon recovery as gas	99.4	99.2	97.6	100.1	99.8	95.1	102.0	99.9	99.9
gas yield, L/g dry solids	0.81	0.76	0.67	0.72	0.67	0.57	0.86	0.74	0.74
higher heating value, MJ/m^3	21.9	24.9	28.6	24.8	24.3	24.6	24.4	23.3	23.6
gas composition, vol %									
methane	54	61	54	59	58	52	60	57	58
carbon dioxide	45	37	39	38	40	42	37	41	40
hydrogen	1.0	1.2	1.5	1.5	1.4	2.0	2.6	2.5	2.6
ethane	<0.1	<0.1	0.5	0.2	0.4	1.7	<0.1	<0.1	<0.1
hydrocarbons	0.4	0.5	6.0	0.8	0.9	2.4	0.3	0.3	0.4

W, 200 μm at full-width half-maximum (fwhm) beam spot. The X-ray beam is incident normal to the sample, and the X-ray detector is at 45° away from the normal. The high energy resolution data were collected using a pass energy of 46.95 eV. For the Ag $3d_{5/2}$ these conditions produce a fwhm of better than 1.05 eV. The collected data were referenced to an energy scale with binding energies for Cu $2p_{3/2}$ at 932.62 ± 0.05 eV and Au $4f_{7/2}$ at 83.96 ± 0.05 eV.

(f) Scanning Electron Microscope (SEM). The catalyst specimen was ground and polished for the analysis. The images obtained included backscattered electron images (black and white images) and energy-dispersive X-ray microanalysis dot maps (colored images).

(g) X-ray Diffraction (XRD) Analysis. X-ray powder diffraction patterns were collected on fresh catalyst specimens and solid samples collected from the reactors. The diffractometer was a Philips PW3040/00 X'Pert MPD system with a vertical $\theta-\theta$ goniometer (220 mm radius). The X-ray source was a sealed ceramic tube with a long-fine-focus Cu anode ($\lambda = 1.5406$ Å). Operating power was 1.8 kW (45 kV, 40 mA). The optical train consisted of incident- and diffracted-beam Soller slits (0.04 rad), programmable divergence, anti-scatter, and receiving slits, plus a 10 mm brass axial beam mask, curved graphite monochromator, and Xe-filled proportional counter detector. The study specimens were front-loaded into a cavity-type holder (18 mm diameter × 0.5 mm deep) cut in an off-axis single-crystal quartz plate. The data were analyzed using the program JADE (Materials Data Inc., Livermore, CA) and reference data from the Powder Diffraction File database (International Centre for Diffraction Data, Newtown Square, PA).

Results and Discussion

The testing discussed here produced initial results for continuous-flow processing of wet biomass feedstocks in the bench-scale reactor, in a scaled-up reactor system, and in a microscale reactor (longer term tests).

Bench-Scale Testing. The bench-scale reactor system was used to generate process information for the catalytic gasification of several wet biomass feedstocks. The process was operated at nominally 21 MPa and 350 °C. The slurry feedstocks were ground in a stirred ball mill to pass a 60-mesh screen before being pumped by a progressive-cavity, low-pressure pump that fed the high-pressure reciprocating plunger pump. The feed slurry passed through the CSTR which served as a preheater in order to liquefy the biosolids. The 1 L tubular reactor was filled with a fixed bed of catalyst particles. The results presented in Table 1 are for three different days of operation. The same catalyst bed was used for the first 2 days of operation with the manure and Midwest Grain Products, distillers' dried grains and solubles (DDG&S); a different catalyst bed was used for the Furst-McNess DDG&S test.

The test with manure provided very positive results. The feed slurry was pumped smoothly, without interruption or plugging. The reaction proceeded well with good gas production and nearly complete manure gasification. An important result of this test was that the manure-derived inorganic material passed through the reactor and into the downstream product collection system, where it was simply settled from the product water as a powder. The effect of process rate on the extent of gasification is evident by comparing the three data sets, as they represent a progression to faster throughput over the period of the experiment.

The test with the Midwest Grain DDG&S feed was also relatively problem-free. However, it is noticeable that there is a tendency toward catalyst deactivation over the time of this experiment. The destruction of the organics causing the COD is reduced, as is the gas yield. Also, there is a shift in gas composition away from methane and toward hydrogen, and higher hydrocarbon gas production, indicating less effective reforming and gas synthesis reactions. The active catalyst drives the gas composition toward the thermodynamic equilibrium, which highly favors methane synthesis to the detriment of hydrogen and carbon monoxide, as described in our earlier publication.[15]

The test with the Furst-McNess DDG&S was similarly successful. There was no sign of loss of catalyst activity over the short period of the run. The same high level of conversion was seen with good gas quality. There were some indications of pumping difficulties, such as loss of pump prime and some pressure drop buildup over the catalyst bed.

A second test with higher concentration DDG&S from Furst-McNess was plagued by plugging problems following initial time on stream of about 5 h. Analysis of these solids showed that they were primarily mineral matter precipitates (magnesium phosphate was a major component), as opposed to fibrous biomass material.

Scaled-Up Reactor Operation. A limited amount of scaled-up testing has been completed in the MSRS engineering demonstration unit (Table 2). Engineering issues related to feeding the slurry to the high-pressure reactor were the focus of much of the work. As in the

Table 2. Scaled-Up Engineering Demonstration Results

	w/CSTR	bypass CSTR	bypass CSTR	bypass CSTR
on stream, h	3	7.5	7 (+7.5)	2 (+14.5)
feed COD, ppm	72600	33000	67000	12975
LHSV, L/L/h	2.46	2.14	2.35	2.66
temperature, °C	340	345	350	345
COD conversion, %	99.96	99.83	50.1	22.93
carbon recovery as gas, %	100.0	99.8	25.9	8.1
gas yield, L/g dry solids	0.75	0.68	0.15	0.22
higher heating value of gas, MJ/m^3	23.5	24.0	17.6	13.8
gas composition, vol %				
methane	56	57	31	2.9
carbon dioxide	40	39	57	12
hydrogen	3.6	3.0	6.6	81[a]
ethane	<0.1	<0.1	2.5	1.3
hydrocarbons	0.6	0.5	2.9	3.4

[a] Due to low gas yield, not all of the hydrogen added for catalyst reactivation had been purged from the system.

bench-scale unit, a CSTR was installed between the pump and the catalytic reactor beds. Solids buildup at the entrance to the catalyst bed and resulting flow stoppage were to be avoided by the liquefaction caused in the preheating by the CSTR. The progressing cavity pump was not used in the scaled-up system, since adequate flow could be achieved by gravity feed. The feed slurry was processed by wet grinding in a Union Process Attritor stirred ball mill to achieve a pumpable slurry of the Midwest Grain DDG&S feedstock.

In the first day of operation pumping problems again occurred. The pump stopped numerous times, mainly because of clogged check valves. Plugging at the entrance to the reactor was also a problem, and was not relieved by using the CSTR, i.e., it occurred whether or not the CSTR was on line. However, the process operated quite well, chemically, giving high levels of conversion and good gas quality.

For the second day of operation, the reactor entrance was reconfigured to allow better flow into the reactor bed. The system was run only without the CSTR. The tube-in-tube heat exchanger provided all the required liquefaction of the biosolids and also provided heat recovery, preheating the feed from 25 °C to 250 °C while effectively cooling the product from 355 °C to 30 °C. Following the test, an examination of the inside of the tube-in-tube heat exchanger showed only a light powder coating on the tube wall and no significant fouling of the surface. Consistent pumping was less of a problem in this test. By the time 8 h of testing had been completed, there was an indication of plugging at the front end of the reactor, as evidenced by a 2 MPa pressure drop.

The catalyst showed evidence of being deactivated at the early stages of the test (low COD conversion and low recovery of carbon gases). The carbon recovery as gases is less definitive (and less repetitive) than the COD conversion and is also normalized to carbon balance for the operating time window. One possible explanation for the deactivation was that the opening of R-1 (the first reactor tube) to rebuild the front end may have been sufficient to allow oxygen into the beds to react with the ruthenium metal. However, as shown in the final column of data in Table 2, it was found that an on-line exposure to warm hydrogen was not sufficient to reverse the effect and regenerate the catalyst activity.

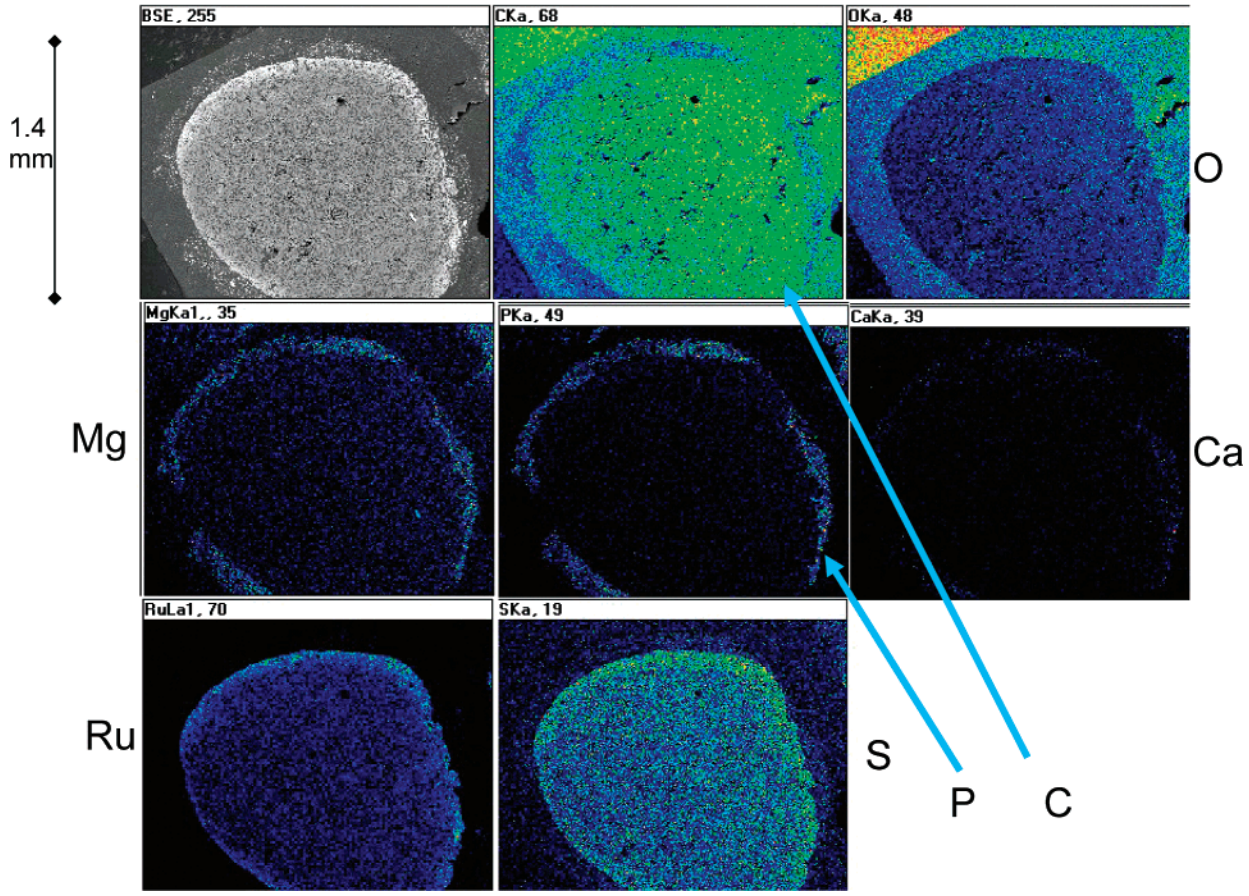

Figure 2. SEM analysis of a cleaved used catalyst pellet.

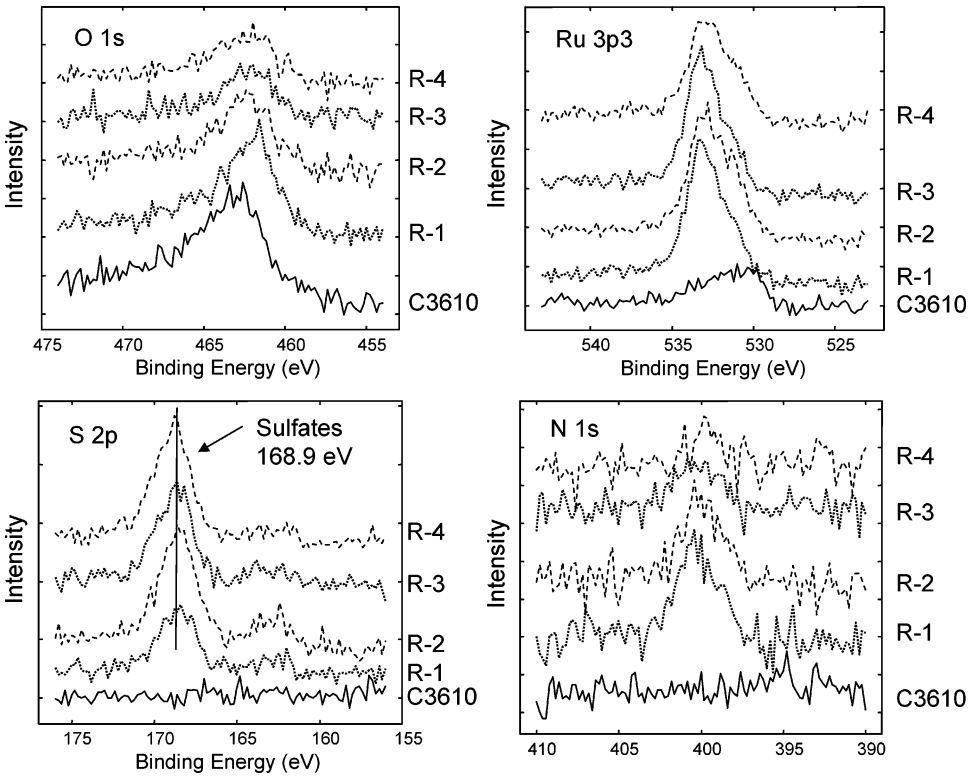

Figure 3. XPS photoemission spectra of cleaved catalyst pellets.

Table 3. Microscale Reactor Processing Test Results

	manure 1		manure 2		peptone	
on stream, h	34	57	52.5	56.5	14.5	70
feed COD, ppm	37000	37000	35500	35500	72500	72500
LHSV, L/L/h	1.90	1.93	2.50	2.47	1.38	1.38
temperature, °C	335	320	345	335	319	322
COD conversion, %	99.53	45.31	99.57	46.97	99.29	57.12
carbon recovery as gas, %	94.0	NA	98.1	42.2	101.9	22.2
gas yield, L/g DS	0.68	0.18	0.68	0.36	0.42	0.14
higher heating value of gas, MJ/m^3	23.6	13.1	21.9	15.1	30.0	21.3
gas composition, vol %						
methane	59	24	54.5	36.2	70.4	14.1
carbon dioxide	40	56	44.6	60.7	20.9	32.8
hydrogen	0.7	18.5	0.9	2.6	5.6	36.2
ethane	0.01	1.7	0.01	0.5	0.06	5.8

Samples from the plugging materials and the catalysts were analyzed by SEM, XPS, and XRD methods to determine changes in the catalyst in addition to ICP and XRF elemental analysis. These analyses clearly showed that certain biomass trace components precipitated and plugged the catalyst bed entrance, that a crust of trace components from the biomass was deposited onto the catalyst pellets, and that some of the biomass components passed through the catalyst bed reacting with and poisoning it as it went.

A combination of ICP and XRF elemental analysis and XRD showed that the plugging precipitate at the entrance to the catalytic bed in the reactor was composed primarily of hydroxyapatite ($Ca_5(PO_4)_3(OH)$) and iron-chrome stainless steel from the wet grinding media. As seen in Figure 2, the SEM analysis of the used ruthenium on carbon catalysts shows an outside crust in which magnesium is associated with phosphorus and lesser amounts of calcium are found. Sulfur contamination only was found within the catalyst pellet and was highly associated with the ruthenium (note particularly the higher concentrations toward the surface of the pellet). In Figure 3, XPS analysis of the internals of cleaved catalyst pellets (composed of ruthenium on carbon) showed that the contamination of the bulk of the material was limited to sulfur, which was found throughout all four of the reactor beds. In the figure, C-3610 indicates the analysis of the fresh catalyst, while R-1 through R-4 indicate samples from the four tubular reactors. Some evidence of nitrogen contamination was also found, but it appeared to be limited to the first reactor beds.

Microscale Reactor Operation. Extended time tests in the microreactor system demonstrated the marked catalyst deactivation caused by the biomass feedstocks. A test with liquefied and filtered manure was undertaken first. The manure solids were processed at 300 °C in a batch autoclave and then filtered on a Whatman #40 paper to produce a manure-derived feedstock that could be fed with the micrometering pump. This feedstock was processed over the ruthenium

Table 4. Trace Analysis in Feed and Products from Microscale Reactor Tests

feedstock	Ca, ppm	P, ppm	S, ppm	Mg, ppm	K, ppm	Na, ppm	Fe, ppm	N, wt %
manure feed	363	34	89	197	574	155	14	na
manure 1 products	0.2 → 20	0.1	3 → 0.5	0.03 → 5	130 → 55	38 → 15	0.1 → 0.05	na
manure 2 products	0.1 → 9	0.03	0.6 → 0.3	0.03 → 2.5	105 → 55	27 → 15	0.02 → 0.06	na
catalyst	4.6	0.01	0.4	30.7	0.07	0.01	7.4	0.20
peptone feed	3.8	38	712	38	79	745	1.1	0.67
peptone products	1.0 → 2.8	0.4	87 → 120	4.5 → 23	86 → 83	845 → 830	0 0.2	0.44 → 0.65
catalyst	0.02	0.02	0.5	0.3	<0.02	0.1	2.1	0.60

on carbon catalyst at 20.3 MPa, with results as shown in Table 3. The trace element analyses of the feedstock and the products from the test, shown in Table 4, gave important indications of elemental deposition in the reactor. As shown in Table 3, there was an initial period of high activity, which lasted for about 2 days. After about 55 h (as shown in the two different tests), the catalyst activity had dropped dramatically, producing a high COD effluent and low gas recovery. The liquid product during the period of high activity contained much reduced levels of alkaline earths and phosphorus compared to the feed. After the catalyst was deactivated and the COD increased, the levels of the alkaline earths increased to slightly nearer that of the feedstock, while sulfur and iron and the more soluble potassium and sodium actually dropped to lower levels.

SEM analysis of the used catalyst from the second test with manure showed results very similar to those from the scaled-up reactor test with DDG&S feedstock. The catalyst pellets were coated with a magnesium−phosphorus (with associated silicon) structure with some separate calcium-containing crystallites. The ruthenium was still well-dispersed throughout the carbon support, but sulfur was highly associated with it.

A test with hydrolyzed protein (peptone) was also undertaken, with results also given in Table 3. Again, the catalyst was strongly deactivated over a period of days. The deactivation was not so abrupt as with the manure, and the product COD increased steadily over 2 days rather than a few hours as with the manure. As seen in Table 4, similar to the manure test, the alkaline earths and phosphorus were much lower in the products compared to the feed. However, after the catalyst deactivation, the alkaline earths returned to nearly the level of the feed. Throughout the test, the amount of alkali metals in the product effluent was at or slightly above the level initially measured in the feed, suggesting essentially complete passage through the catalyst bed. As in the manure test, sulfur was lost from the aqueous phase throughout the test and found deposited onto the catalyst. Some nitrogen was also found to be deposited on the catalyst from the feed solution.

Conclusions

The wet gasification of biomass has now been demonstrated in continuous-feed, fixed-bed catalytic reactor systems at bench-scale and in a scaled-up engineering development system. The systems have been operated at conditions of 330−360 °C and 21 MPa at processing rates from 80 mL/h to 10 L/h despite complications related to the slurry nature of the feed and the inorganic components in the feedstocks. Aqueous effluents with low residual COD (as low as 100 ppm) and a product gas of medium-Btu quality have been produced from dairy manure and distillers' dried grains and solubles. These results have shown that careful monitoring and control of feedstock trace components (e.g., calcium, magnesium, sulfur, and phosphorus) are critical for maintaining long-term operability and catalyst activity. Clearly, more development work is needed to fully understand the nuances of the operation of this promising processing system.

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