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CHEMICAL PROCESSING IN HIGH-PRESSURE AQUEOUS ENVIRONMENTS:

Low-Temperature Catalytic Gasification

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A gasification system is under development that can be used with most types of wet organic wastes. The system operates at 350°C and 21 MPa using a liquid water phase as the processing medium. Since a pressurized system is used, the wet waste can be fed as a solution or slurry to the reactor without drying. Through the development of catalysts, a useful processing system has been produced. The system has utility both for direct conversion of high-moisture biomass to fuel gas or as a wastewater cleanup system for wet organic wastes including unconverted biomass from bioconversion processes. By the use of this system >99% conversions of organic waste to medium-heating value fuel gas can be achieved.

Keywords: catalysis; gasification; waste organics; aqueous processing; methanation; bench-scale tests; high pressure; low temperature; liquid phase

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INTRODUCTION

A pressurized catalytic gasification process, operated at low-temperature, is effective for treating wet waste streams for both environmental cleanup and energy recovery. Through a liquid-phase, heterogeneously catalyzed process operated at nominally 350°C and 21 MPa, it produces a methane/carbon dioxide product gas from water solutions or slurries of organics. This gasification process was specifically developed for processing high-moisture biomasses (high-growth grasses, marine and aquatic biomass, and food processing residues), which are not efficiently gasified in conventional, low-pressure thermal systems[1]. Later studies applied the technology to the destruction of hazardous organic chemical wastes and organic chemical manufacturing wastewaters[2], as well as biomass feedstocks.

Several issues related to the innovative processing environment have been identified for research. Development was required of catalysts which can survive at processing conditions for economically attractive active lifetimes. Specifically, both the catalytic metal and the support material must be appropriate. Another issue of importance is reactor material identification. Consideration was made of the material strength for operation at reaction pressure and temperature, as well as, corrosion resistance. Finally, the relative importance of reaction kinetics versus thermodynamic equilibrium must be considered.

Preliminary tests of feedstocks and catalysts were made in a small batch reactor. Most of our recent results are from continuous-flow reactor studies with a fixed bed of catalyst in a tubular reactor. These tests demonstrate the scale-up of a useful reactor configuration for industrial application of the technology.

BACKGROUND

The use of high-pressure liquid water at elevated temperatures as a processing environment has recently been reviewed[3]. One application of this processing environment is for catalytic gasification of organics. In this application, catalysts accelerate the reaction of organic compounds with water and produce methane and carbon dioxide. It can be both a means of recovering useful energy from wet biomass and other organics in water and as a water treatment system for more dilute hazardous organic contaminants. Batch reactor test results have demonstrated process applicability to a wide range of organic components[4]. Development of catalysts for this processing environment has also been an important factor in making this technology viable[5].

Low-temperature catalytic gasification involves relatively complex chemistry including pyrolysis, steam-reforming, hydrogenation, methanation and water-gas shift. Specific chemistry varies with the feedstock type. For example, various reaction pathways are suggested by the products that have been identified from carbohydrate feedstocks:

$C_6H_{10}O_5 + H_20 \rightarrow 6CO + 6H_2$	steam-reforming
$CO + 3H_2 \rightarrow CH_4 + H_20$	methanation
$CO + H_20 \rightarrow CO_2 + H_2$	water-gas shift

The overall stoichiometry approximates:

$$C_6H_{10}O_5 + H_20 \rightarrow 3CH_4 + 3CO_2$$

A thermodynamic equilibrium limitation of about 1% residual hydrogen shifts the methane/carbon dioxide product ratio slightly more toward the carbon dioxide than is suggested in the given stoichiometry.

Early gasification tests in supercritical water showed no evidence of catalytic effects[6]. A major component of the continuing development of the low-temperature gasification technology has involved studies on catalyst efficiency and integrity. Nickel catalysts have been used in the system throughout its development and scaleup. Many conventional nickel catalysts developed for steam reforming, hydrogenation, and methanation. (the chemical mechanisms involved) have been evaluated. Many of these catalysts were found to be active for converting organics to methane and carbon dioxide but were not satisfactory for long-term operation. Our past catalyst studies have addressed mass transfer limitations and the active form of the nickel catalyst. Clear evidence was presented on the need for reduction of the nickel catalyst prior to processing[2].

A wide range of catalyst materials and support compositions were also evaluated. The reduced effectiveness of other Group VIII metals (compared to nickel), because of their oxidation (in high-temperature water) or lack of specific activity, was also reported[2]. Evidence of the instability of conventional catalyst support materials when used at the reaction conditions was initially reported by Elliott *et al.*[7] Continuous-flow reactor tests indicated that long-term stability of the nickel catalyst was a critical development requirement.

PROCESSING ENVIRONMENT CONSIDERATIONS

Processing development results addressing the reactor environment considerations can be conveniently separated into catalyst development efforts, material corrosion tests, and reactor system descriptions with results from various feedstock tests.

Catalyst Development

The preliminary catalyst tests were performed in a batch reactor. These experiments tested the activity of the catalyst for the gasification and methanation of a model compound and the long-term stability of the support in the high-pressure water reaction environment. The results of these tests are presented in Table 1. The details of these tests are published elsewhere[5]. Numerous conventional supported nickel catalysts have been tested for low-temperature gasification. The supported nickel catalysts exhibited a wide range of activities in the high-pressure aqueous environment. The various spent catalysts were analysed to determine if any significant changes had occurred. In addition, other samples of some of these catalysts were subjected to long-term batch tests in water. These samples were also analysed to determine changes resulting from exposure to the high-pressure steam/water environment at 350°C. X-ray diffraction analysis of the spent catalysts proved that the nickel metal stayed reduced; however, there were significant changes noted in the composition of some of the support materials.

Noble metal catalysts have also been tested. Particularly interesting are Rh and Ru as these metals have been found by others to be useful methanation catalysts[8]. Catalyst formulations with these metals typically contain much lower levels of metal because of their high activity and cost. Recent Pt and Pd test results confirm our earlier reports of the lack of activity of Pd for low-temperature gasification.

Most recently, long term catalyst lifetime testing has been performed in a microscale tubular reactor system. New catalyst formulations based on extensive catalyst testing are proving to be economically viable catalysts. Catalyst lifetimes of >6 months have been demonstrated for these proprietary formulations

Material Corrosion Concerns

Review of corrosion issues was part of an earlier report on low-temperature catalytic gasification. The major concerns identified included:

- Chemical Corrosion—caused by either transient organic acids or carbon dioxide dissolved in the water.
- Hydrogen Embrittlement—caused by high partial pressure of hydrogen gas.
- Stress Corrosion Cracking—caused by either chloride or alkali.

The chemical corrosion concern was determined to impact all applications of the technology; however, at these processing conditions oxide coatings do form on steels without the oxidation being severe enough to be a corrosion problem itself. Hydrogen embrittlement is controlled in low-temperature catalytic gasification by maintaining active catalyst which results in a low hydrogen partial pressure in the product gas. Analysis suggests that only low alloy steels are required to avoid hydrogen embrittlement when the gasification process is operated effectively. Stress corrosion cracking can be avoided by working with feedstocks containing aqueous organics only. In reality, potential feedstocks will have chloride and/or alkali in most cases. Direct evaluation of the effects of these materials is not possible based on the literature. It appears that proper stress relief in the

Table 1 Summary of conclusions on catalysts and catalyst support.

Useful Catalytic Metals	Inactive Metals	Metals Oxidized at Conditions	Stable supports	Unstable Supports	Hydrolyzable Supports
Ru	Pt	Co	α-Al_2O_3	MnO_2	γ-Al_2O_3
Rh	Pd	Fe	ZrO_2	SiO_2	δ-Al_2O_3
Ni*	Cu	Cr	C	Ca/aluminate	η-Al_2O_3
	Ag	Mo	TiO_2	Kieselguhr	SiO_2/Al_2O_3
	Re	W			$9Al_2O_3 \bullet 2B_2O_3$
	Pb	Zn			

* subject to sintering

systems is a key factor for avoiding alkali cracking while exclusion of oxygen is a key factor in eliminating chloride cracking.

To evaluate the corrosion potential of the high-pressure aqueous environment, stressed coupon tests were performed with an organochloride containing environment. Over a three month period the stressed coupons were exposed to the low-temperature gasification environment, 350°C in a sealed autoclave (static conditions) with 1000 ppm trichloroethylene in water. Corrosion was reasonably low ($<10\,\mu m/yr$) for all materials tested, including 1020 mild steel, 2.5 Cr/1 Mo steel, 347, 316L and 304L stainless steels, Inconel 600 and 625. The mild steel and the CrMo steel formed black oxide coatings which would likely abrade in a non-static environment leading to increased corrosion. The advantage of the higher cost Inconels (0.1 vs. 0.01 $\mu m/yr$) was judged to be minimal with the conclusion that the 316L was the most useful candidate for construction.

Continuous-Flow Reactor Systems

Gasification tests were carried out in three scales of fixed-bed catalytic tubular reactor. The bench-scale unit was described in detail in an earlier report[7]. The unit consisted of a 2 m long × 0.025 m I.D. 304SS tube which was fed by a reciprocating plunger pump. The reactor was heated by an electrical resistance furnace and essentially served as both the preheater and the reactor. Pressure was controlled in the reactor by a dome-loaded, back-pressure regulator. The pressure regulator was followed by a condenser/separator system in which liquid samples were recovered. Uncondensed product gas was passed through flow meters and vented.

A microscale version of this reactor system was used for catalyst lifetime studies. All the components of the bench-scale unit were incorporated into the microscale tubular reactor system. A smaller pump was used to feed a reactor consisting of 0.37 m of 0.013 m 316SS tubing. In addition to the reactor, there was a preheater section consisting of 6 m of 0.0032 m tubing. Both the reactor and the preheater were contained in the electrical resistance reactor furnace.

Two scaled-up reactor systems were based on the bench-scale design. One was designed at a scale for obtaining engineering data for further scale-up. This unit was mounted on a single 2.4 m × 3 m skid platform that could be transported on a single flat-bed truck. Equipped with three 2 m × 0.05 m I.D. fixed-bed tubular 304SS reactors and supporting equipment to achieve conversion, the test system's capacity was one-half ton per day liquid feed with a design flow rate of 20 litre/hr. The system included a tube-in-tube, feed/effluent heat exchanger for heat recovery and reuse. Design working conditions for the reactors were 350°C at 24MPa. This system is described in detail by Elliott *et al.*[9]

A second scaled-up reactor system is the 10 litre/hr mobile Industrial Onsite Demonstration Unit. The mobile system can be moved from site to site to maximize exposure of the process to industry. The unit was constructed by the process licensee for North America, Onsite *Ofsite, Inc. Onsite*Ofsite markets the low-temperature catalytic gasification technology under the tradename of Thermochemical Environmental Energy System (TEES.®) The unit is a fifth-wheel trailer-mounted processing system. The Industrial Onsite Demonstration Unit will allow the actual users, the plant managers and operators, to convince themselves of the utility of the process and the operability of the equipment. TEES is an innovative application of high-pressure processing, and is therefore viewed as a high-risk option. Hands-on experience with the Industrial Onsite Demonstration Unit will help reduce the perceived amount of risk involved in the implementation of this process.

Bench-Scale Reactor Tests with Industrial Wastes

Bench-scale reactor tests of low-temperature catalytic gasification were performed with a number of waste materials from commercial processes. Processing data for three of these materials, olive wash water, polyol manufacturing wastewater, and brewer's spent grain, are described in Table 2. The test with the olive wash water had good results in terms of COD destruction. There was a significant ammonia product in the effluent water from nitrogen in the organic feed. Further treatment for ammonia removal may be required or incorporated into the process. One potential process modification for ammonia removal compatible with low-temperature catalytic gasification is another high-pressure aqueous process, the reaction of the ammonia with stoichiometric amounts of nitric acid[4]. The low gas recovery in the olive wash tests was probably as a result of carbonate formation with the ammonia. Alkali in the olive feedstock would also form carbonates at these conditions and further sequester carbon dioxide product gas.

The spent grain sample was ion exchanged prior to gasification. The ion exchange was used to remove primarily calcium (but, in fact, all multi-valent cations would have been removed) by sodium substitution so that calcium phosphate deposits would not form in the catalyst bed. The spent grain was first hydrolyzed with a mild nitric acid treatment to make the calcium available for the ion exchange. The hydrolyzed spent grain was then filtered prior to the ion exchange treatment. Analysis showed that the calcium level in the spent grain was reduced from 130 ppm to below 60 ppm by the treatment. Much higher conversion was achieved with the spent grain (4 wt% dry solids) than has been reported earlier[9].

The polyol wastewater was also treated following ion exchange pretreatment. The ion exchange involved passing the waste through a column filled with the proton form of a resin which exchanged protons for the potassium. In this process, the pH was reduced from 12.75 to 4.5. With this potassium-stripped wastewater, sufficient COD destruction could be accomplished at about 8 times the rate achieved in the earlier tests, and these later tests used a waste at about twice the concentration. Another important difference is the use of the proprietary catalyst which may be somewhat more active.

Table 2. Experimental results with industrial waste streams

	Olive Wash Water	Polyol Wastewater Ion stripped	Spent Grain Ion Exchanged
Catalyst	Ni-0750	Proprietary	Proprietary
Results			
Reduction of COD,%	99.9	97.0	98.3
Feed, L/hr	1.5	1.9	2.0
LHSV, L/L/hr	2.5	4.3	3.5
Gas Yield, L/hr	7.3	4.8	25.3
Effluent COD, ppm	30	335	905
Effluent NH_4^+, ppm	350	NA	3600
Effluent pH	6.9	5.5	7.9
Gas Composition, volume %			
Methane	62	57	60
Carbon dioxide	35	32	35
Hydrogen	2.1	10	2.4
Ethane	0.5	0.8	0.4
Backflush	0.0	0.2	1.9
MJ/m^3	24.2	23.5	25.7

Catalyst bed conditions. 350°C and 21 MPa

CONCLUSIONS

Low-temperature catalytic gasification as performed in a high-pressure aqueous environment has now been demonstrated in continuous-feed, fixed-bed catalytic reactor systems on four scales of operation ranging from 0.03 litre/hr to 33 litre/hr. The systems have been operated with consistency at conditions of 350°C and 21MPa. Aqueous effluents with low residual COD and a product gas of medium-heating value have been produced. Catalysts have been demonstrated for up to 6 months of operation with reasonable stability. A wide range of waste have been processed effectively.

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