



Development of a Catalytic Wet Air Oxidation Method to Produce Feedstock Gases From Waste Polymers

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Abstract

Given the high cost of space launch, the repurposing of biological and plastic wastes to reduce the need for logistical support during long distance and long duration space missions has long been recognized as a high priority. Described in this paper are the preliminary efforts to develop a wet air oxidation system in order to produce fuels from waste polymers. Preliminary results of partial oxidation in near supercritical water conditions are presented. Inherent corrosion and salt precipitation are discussed as system design issues for a thorough assessment of a second generation wet air oxidation system. This work is currently being supported by the In-Situ Resource Utilization Project.

Nomenclature

CWAO catalytic wet air oxidation
GC gas chromatograph
PET polyethylene terephthalate
TCD thermal conductivity detector
TWR transpiring wall reactor
WGSR water-gas shift reaction

Introduction

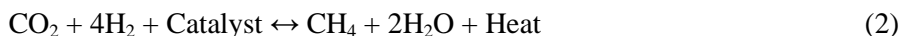
Given the high cost of space launch, repurposing of biological and plastic wastes in order to reduce the need for logistical support is a high priority. Logistical support becomes a greater challenge as missions lengthen in distance and duration. Producing return propellant from waste during a long distance space mission would lessen the required amount of logistical mass. High temperature approaches to transform polymer waste into feedstock gases in order to produce useful products include pyrolysis in inert environments and combustion. Discussed in this paper is a low temperature approach to gasify waste polymers using catalytic wet air oxidation (CWAO).

The conditions required for CWAO approach the conditions of supercritical water, 374 °C with a pressure of 22.1 MPa (Ref. 1). At these conditions, the properties of water change significantly. Due to the reduced effect of hydrogen bonding, water begins to behave as a non polar solvent. In addition, water becomes increasingly miscible with permanent gases. Thus, water provides a nearly homogeneous reaction medium suitable for the oxidation of waste polymers as conditions approach supercritical.

There are advantages of using CWAO for the production of feedstock gases from polymer waste in comparison to pyrolysis or combustion. CWAO can be accomplished with temperature as low as 250 °C as compared to temperatures ranging from 600 to 1000 °C (Refs. 1 and 2). In addition, CWAO produces mostly carbon dioxide, hydrogen and methane. Whereas pyrolysis produces a complex distribution of hydrocarbons dependent on the polymer material and temperature, combustion mostly produces carbon dioxide, carbon monoxide, and water. The occurrence of the water-gas shift reaction (WGSR) explains the lack of carbon monoxide and a significant percentage of carbon dioxide and hydrogen in the product stream of CWAO (Ref. 3).



Methane is then produced from the reaction between, carbon dioxide and hydrogen over a catalyst, referred to as the Sabatier reaction (Ref. 4).



Described in this paper are the preliminary efforts to develop a CWAO method in order to produce useful gases from waste polymers. Preliminary results of CWAO of polyethylene terephthalate (PET) are presented. Important considerations for a continuous system suitable for harsh conditions required for CWAO processing of waste material are discussed.

Preliminary Results

The CWAO of PET was tested with five separate catalyst/supports in a 100 mL tubular batch reactor. A total of 0.4 g of polymer and 0.4 g of catalyst/support were mixed and loaded with 30 mL of deionized water. The reactor was pressurized with 100 psig of dry air in order to achieve a 1.3:1 stoichiometric ratio of oxygen to carbon. The process took place over a 24 hr period with a temperature of approximately 280 °C and a pressure of approximately 900 psig. Two control tests were performed. One test was performed with only polymer and water in air to compare with the catalytic reactions. Another test was performed with PET, 5 percent ruthenium/carbon, and water in air without stirring to determine the effect of stirring on the product stream.

The gas products were analyzed with a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). Analytical separation was achieved with a capillary column (carboplot 27.5-m by 0.53-mm id, film thickness 0.25- μm). The gas flow rate was kept at 1.69 ml/min. The amount of gas injected was 1 mL. The injector was in splitless mode and kept at 50 °C. The oven temperature was held at 26 °C for 10 min then programmed to 100 °C at 3 °C/min and held for 25 min.

Both qualitative and quantitative analysis of the gaseous products were accomplished using standards. The retention times of the eluted components were compared with the known retention times of standards for identification. Linear calibration curves of carbon dioxide, carbon monoxide, methane, and hydrogen were constructed from the known quantities of the standards in order to determine the quantities of said components from each polymer in terms of percentages. For each gas, the calibration curve provided an approximate error of 20 percent. Listed in Table I are the percentages of the gas products from the partial oxidation of PET with the five separate catalyst/supports. The estimated detection limits of the TCD were 0.004 percent for carbon dioxide and carbon monoxide and 0.100 percent for methane and hydrogen.

The percent yield for each carbon-containing gas product was determined by dividing the number of moles of each gas product by the total number of moles of carbon in the reactor, Table II. The number of moles of each component was determined from the percentages multiplied by the total moles of the gas product which was estimated using the ideal gas law.

TABLE I.—GAS PERCENTAGES

Catalyst/support	Carbon dioxide %	Carbon monoxide %	Methane %	Hydrogen %
%5 ruthenium/carbon	19	0.03	3.0	12
%5 ruthenium/carbon without stirring	14	0.08	6.0	11
%5 ruthenium/alumina	11	0	2.0	8.0
%5 platinum/carbon	5.0	0	0.3	2.0
%5 palladium/carbon	2.0	0.02	0.4	2.0
%5 rhodium/carbon	13	0	0.4	7.0
Without catalyst	12	0.05	0	0.2

TABLE II.—CARBON YIELD

Catalyst/support	Carbon dioxide %	Carbon monoxide %	Methane %	Total carbon yield %
%5 ruthenium/carbon	44	0.1	6.0	50.1
%5 ruthenium/carbon without stirring	35	0.3	16	51.3
%5 ruthenium/alumina	25	0	5.0	30.0
%5 platinum/carbon	8.0	0	0.5	8.5
%5 palladium/carbon	3.0	0.1	0.7	3.8
%5 rhodium/carbon	24	0	0.7	24.7
Without catalyst	19	0.1	0	19.1

Design Considerations

Of the five catalyst/supports tested, ruthenium on carbon provided the largest carbon yield. Ruthenium is active as both a water-gas shift and Sabatier catalyst. Interestingly, the control test involving ruthenium on carbon without stirring provided the most methane. The result can be explained by the fact that without stirring there were temperature gradients throughout the reactor. The hot spots were allowed to reach higher temperatures than were possible in the comparatively isothermal conditions brought on by stirring. The effect of the support on the performance of the catalyst was observed by comparing ruthenium on carbon with ruthenium on alumina. Ruthenium on carbon provided significantly more carbon dioxide and hydrogen yet both provided approximately the same amount of methane. Both platinum and palladium showed little water-gas shift and hydrogenation activity.

A future goal is to design a continuous CWAO system that converts various waste polymers into methane. The occurrence of corrosion and salt precipitation are major issues for the system design due to the aggressive oxidizing environment, the complex chemical nature of waste material, and the non-polar properties of water in near-supercritical conditions (Ref. 5).

The corrosiveness of aqueous systems up to supercritical temperatures is dependent on several factors: density, temperature, pH, electrochemical potential, and reactivity of anions in solution (Ref. 6). Since supercritical water behaves like a nonpolar solvent at low densities, corrosion due to aggressive anions is reduced drastically if the pressure is kept at a minimum. Interestingly, corrosion at supercritical temperatures near 500 °C is lower by orders of magnitude than subcritical temperatures near 300 °C (Ref. 7). This is primarily due to ionic reactions that occur at higher density subcritical conditions even at 300 °C. The type and quantity of electrolytes is also very important as well because the protective oxide layer on the reactor surfaces is stable within a particular window of pH and electrochemical potential (Ref. 5). The most destructive anions are chloride, bromide, and sulfide (Ref. 5).

The most widely used reactor materials are stainless steel and nickel alloys (Ref. 5). With its high chromium content stainless steel alloys are appropriate for highly oxidizing acidic solutions at moderately high temperatures between 300 and 500 °C. However, the tendency towards dissolution of the protective layer through chromate formation increases with temperature and is significant above 500 °C. Nickel is

appropriate in alkaline solutions at moderately high temperatures. Other metals such as niobium and tantalum have excellent corrosion resistance in high density subcritical solutions but show fast corrosion at higher temperature due to a phase transformation of the protective layer (Refs. 8 and 9).

The solubility of inorganic salts in water decreases drastically near the critical point of water from 100 g/L to less than 0.1 g/L (Ref. 5). The precipitated salt can lead to plugging of the equipment and is one of the main reasons for delay of the commercialization of processes involving supercritical water (Ref. 10). Plugging can be reduced by limiting the quantity of salt present in the reactor. This can be achieved using solid-fluid separation methods such as cyclonic separation (Ref. 11) or microfiltration (Ref. 12). Reactor design can also reduce plugging (Ref. 5).

Tubular reactors are popular particularly in research laboratories due to their simplicity. However, they are particularly susceptible to plugging from salt deposition and are typically designed with small diameters to obtain high fluid circulation. Nonetheless, precipitated salts have a tendency to adhere to the reactor walls. The plugging problem can be solved with multiple reactors and alternating heat exchangers. When one reactor is in operation, the other can be cleaned.

The transpiring wall reactor (TWR) is a promising reactor developed to overcome both problems of corrosion and salt precipitation. The reactor has a porous element that serves as the walls of the reaction chamber. Cooler water circulates outside of the porous element preventing the contact of corrosive agents and salt precipitation with the reactor wall. Many TWR designs have been developed, resulting in patents that are thoroughly analyzed by Bermejo et al. (Ref. 13).

Conclusion

CWAO is a low temperature alternative for gasification of waste polymers. Preliminary tests of CWAO were conducted using five different catalyst/supports with PET as the waste material. Ruthenium on carbon provided the largest carbon yield. Both the WGS and Sabatier reaction occur during the process. The resultant methane can be used as return propellant for long duration space missions. Corrosion and salt precipitation present major challenges for CWAO systems and can be reduced by considering novel reactor materials and designs.

References

1. Osada, M., Sato, T., Watanabe, M. et al., "Low-Temperature Catalytic Gasification of Lignin and Cellulose with Ruthenium Catalyst in Supercritical Water," *Energy & Fuels*, Vol. 18, No. 1, 2004, pp. 327–333.
2. Maldonado-Santiago, E., Captain, J., Devor, R. et al., "Creating Methane from Plastic: Recycling at a Lunar Outpost," 48th AIAA Aerospace Sciences Meeting (2010).
3. Savage, P.E., "A perspective on catalysis in sub- and supercritical water," *J. of Supercritical Fluids*, Vol. 47, No. 3, 2009, pp. 407–414.
4. Lunde, P.J. and Kester, F.L., "Carbon Dioxide Methanation on Ruthenium Catalyst," *Ind. Eng. Chem. Res.*, Vol. 13, No. 1, 1974, pp. 27–33.
5. Bermejo, M. and Cocero, M.J., "Supercritical Water Oxidation: A Technical Review," *AICHE*, Vol. 52, No. 11, 2006, pp. 3933–3951.
6. Kritzer, P., "Corrosion in high-temperature and supercritical water and aqueous solutions: a review," *J. of Supercritical Fluids*, Vol. 29, No., 2004, pp. 1–29.
7. Hayward, T.M, Svishev, I.M., and Makhija, R.C., "Stainless steel flow reactor for supercritical water oxidation: corrosion tests," *J. of Supercritical Fluids*, Vol. 27, No. 3, 2003, pp. 275–281.
8. Kritzer, P., Boukis, N., Franz, G. et al., "The Corrosion of Niobium in Oxidizing Sub- and Supercritical Aqueous Solutions of HCl and H₂SO₄," *J. Mater. Sci.*, Vol. 18, No. 1, 1999, pp. 25–27.
9. Friedrich, C., Kritzer, P., Boukis, N. et al., "The Corrosion of Tantalum in Oxidizing Sub- and Supercritical Aqueous Solutions of HCl, H₂SO₄ and H₃PO₄," *J. Mater. Sci.*, Vol. 34, No. 13, 1999, p. 3137.

10. Kritzer, P. and Dinjus, E., "An assessment of supercritical water oxidation (SCWO): Existing problems, possible solutions and new reactor concepts," *Chem. Eng. J.*, Vol. 83, No. 3, 2001, pp. 207–214.
11. Dell'Orco, P.C., Li, L., and Gloyna, E.F., "The separation of particles from supercritical water oxidation processes," *Sep. Sci. Technol.*, Vol. 28, No. 1&3, 1993, pp. 625–642.
12. Goemans, M.G.E, Li, L., and Gloyna, E.F., "Separation of inorganic salts from supercritical water by cross-flow microfiltration," *Sep. Sci. Technol.*, Vol. 30, No. 7&9, 1995, pp. 1491–1509.
13. Bermejo, M., Fdez-Polanco, F., and Cocero, M.J., "Effect of the transpiring wall on the behavior of a supercritical water oxidation reactor: Modeling and experimental results," *Ind. Eng. Chem. Res.*, Vol. 45, No. 10, 2006, pp. 3438–3446.

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