

Introduction: The Carbonaceous Asteroid Volatile Recovery (CAVoR) system extracts water and volatile organic compounds for propellant production, life support consumables, and manufacturing in support of advanced space exploration. CAVoR thermally extracts ice and water bound to clay minerals. The extracted water is then combined with small amounts of oxygen to gasify organic matter in carbonaceous chondrite asteroids. CAVoR produces water, hydrogen, carbon monoxide, and carbon dioxide that comprise precursors to produce oxygen and to produce hydrogen or methane fuel for propellant or organic compounds useful for in-space manufacturing.

Pioneer Astronautics designed, built, and successfully demonstrated a small-scale CAVoR system during a NASA JPL SBIR Phase I project. A process model with material and energy balances of the CAVoR integrated with Sabatier-electrolysis for production of methane and oxygen propellant constituents was prepared. The following figure schematically depicts the CAVoR reactor system.

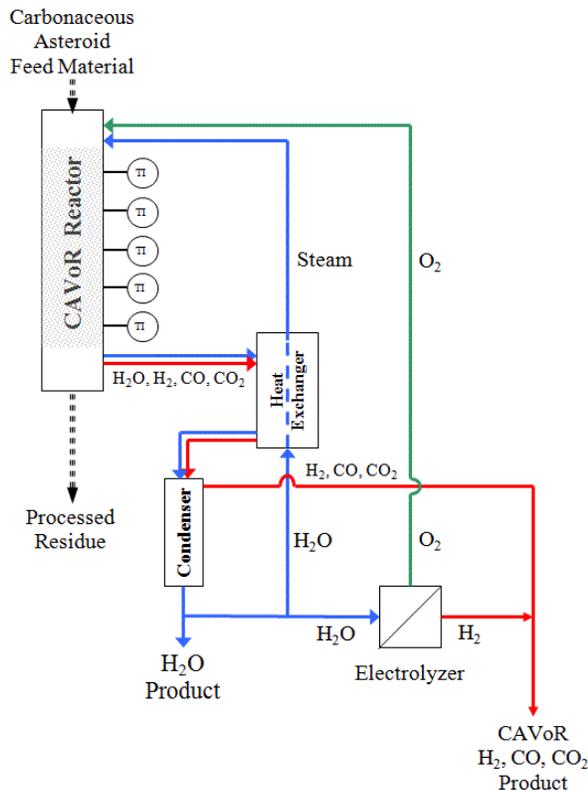


Figure 1: CAVoR reactor system schematic.

Background: Many near-Earth asteroids with diameters up to 40 kilometers are present in orbits that approach or cross that of Earth [1]. Characteristics of these asteroids have been derived by inference from the composition of meteorites and from spectral analysis [2]. Chondrites represent more primitive forms of asteroids, and the subset of carbonaceous chondrites are of most interest in addressing the topic. Carbonaceous chondrites are highly oxidized and contain up to 20 percent bound water and up to 6 percent organic matter [3]. This class of asteroid is thought to primarily contain water-bearing phyllosilicates, or clays [4] with water present as bound water and hydroxyl groups. These asteroids also contain organic matter in the form of kerogen-like material [5], amino acids [6], polycyclic aromatic hydrocarbons such as naphthalene [7], and other organic compounds. Carbon exists primarily in organic matter with only a small fraction as carbonates or more-refractory materials such as graphite and diamond [8]. The water and hydrocarbon contents of carbonaceous chondrite asteroids make them an attractive target for the recovery of resources valuable to advanced space exploration.

Simulant Preparation: Based on literature citations, various inorganic substrates and organic compounds were identified and evaluated for preparation of simulants for use during the Phase I CAVoR program. The goal was to create a simulant with the ability to bind water and to include organic matter of a composition and concentration sufficiently representative of carbonaceous asteroids. Organic matter candidates were selected to represent a range of physical and chemical properties. Target concentrations of 15 percent total water and 5 percent organic matter were chosen for the effort.

Granular montmorillonite, a phyllosilicate mineral, was identified as a suitable inorganic substrate based on the desired characteristics. This material is capable of absorbing significant quantities of both hydrophobic and hydrophilic compounds. A commercial absorbent was used for the Phase I work. Clay particles of less than 8 mesh (2.5 millimeters) were sieved from the bulk material and used as the simulant substrate.

Several candidate organic materials were identified for the Phase I asteroid simulant. Materials selected for evaluation were based on their compositions and characteristics relative to the kerogen-type material expected to be predominant in carbonaceous chondrite asteroids. The concentration and nature of inorganic

matter in the organic candidate samples, the expected reactivity or release of the organic matter with increasing temperature, and the handling characteristics with respect to preparing repeatable, representative blends were considered in selecting candidate materials. The clay substrate and candidate organic samples were subjected to thermogravimetric analysis by sequential heating up to 800°C. Weight loss, physical properties and residual ash content were measured for each material. After evaluating a number of candidate organic constituents, experiments were conducted using a combination of montmorillonite clay along with organic matter consisting of oil sands, gilsonite, petroleum coke, and oil shale.

Samples were prepared by adding moisture to the clay to achieve the target concentration of 15 weight percent. Next, organic matter was blended into the sample to achieve the target concentration of 5 weight percent. Samples were thoroughly mixed, sealed, and allowed to equilibrate prior to testing. A larger proportion of oil shale and oil sands were required relative to other organic constituents due to their low organic contents (10-12 percent).

CAVoR Proof-of-Concept Demonstration: Experiments were carried out to validate the concept using a 12.5-inch (31.8-cm) long, 1.5-inch (3.8-cm) diameter fixed-bed reactor with downward flow of steam and oxygen as depicted in Fig 1 and a simulant feed charge of about 200 grams. The reactor was preheated prior to initiating flow of steam and oxygen. Variables such as feed type, steam:carbon ratio, oxygen:carbon ratio, temperature, and gas flow rate were investigated. The simulants exhibited only slight reduction in volume upon removal of water and organic matter. The reaction front was monitored by movement of the peak temperature along the reactor length. Temperature profiles, exhaust gas compositions, and water recovery were measured during the course of each experiment, which varied between 20 and 60 minutes depending on the oxygen feed rate. Temperatures as high as 850°C were obtained in the reaction zone as a result of the autothermal steam reforming reaction. Virtually complete removal of moisture and organic matter was achieved. At a steam:carbon molar ratio of 2 and an oxygen:carbon molar ratio of 0.25, CAVoR generated an average dry product gas composition of about 38% H₂, 12% CO, 7% CH₄, and 43% CO₂.

With the addition of a downstream methanation-electrolysis unit, the dry CAVoR product gas can be converted to methane and oxygen propellant constituents as demonstrated by Pioneer during previous work [9]. A comprehensive process model was applied to incorporate a scaled-up, continuous CAVoR reforming system with downstream methanation-electrolysis to generate material and energy balances for prediction of

system performance over a wide range of feeds and operating conditions. Methanation-electrolysis, with its heritage in the ISS microgravity environment, was found to be a very attractive candidate technique to convert CAVoR reforming gases into valuable in-space commodities. Preliminary mass estimates showed CAVoR to provide a rapid breakeven time and high process leverage required to reduce risks of space resource utilization.

Shortcomings of the Phase I batch processing method were identified. However, evaluation of the test results led to a conceptual continuous processing reactor design that is capable of achieving high heat recovery from the spent process material, which leads to reduced thermal and electrical heat inputs while maximizing hydrogen production during reforming (resulting in reduced electrolysis power requirements). Continuous operation, or at least long durations between shutdowns, also minimizes the production of heavier hydrocarbons that are evolved by pyrolysis as the system is preheated. The CAVoR was selected for further development during a Phase II program.

References: [1] Davis D.R., Friedlander, A.L., and Jones T.D. (1993) Chapter in Resources of Near-Earth Space, Lewis, Matthews, and Guerrieri, Editors, University of Arizona Press. [2] Binzel R.P., Bus S.J., Burbine T.H., and Sunshine J.M. (1996) Science 273, 946-948. [3] Lewis J.S. and Hutson M.L. (1993) Chapter in Resources of Near-Earth Space, Lewis, Matthews, and Guerrieri, Editors, University of Arizona Press. [4] Nichols C.R. (1993) Chapter in Resources of Near-Earth Space, Lewis, Matthews, and Guerrieri, Editors, University of Arizona Press. [5] Kerridge J.F. (1993) Proceedings of the National Institute of Polar Research, 6, 293-303. [6] Ehrenfreund P., Glavin D.P., Botta O., Cooper G., and Bada J.L. (2001) Proceedings of the National Academy of Sciences of the United States of America, 98, 5, 2198-2141. [7] Plows F.L., Elsilá J.E., Zare R.N., and Buseck P.R. (2003) Geochimica et Cosmochimica Acta, 67, 7, 1429-1436. [8] Septhon M.A. (2002) Nat. Prod. Rep., 19, Royal Society of Chemistry, 292-311. [9] Carrera S., Zubrin R., Jonscher P., Hinkley C., and Berggren M. (2013) *Lunar Organic Waste Reformer*, NASA Glenn Research Center SBIR Phase II Contract No. NNX11CA76C, Final Report, Pioneer Astronautics.

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