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Self-Cleaning Boudouard Reactor for Full Oxygen Recovery from Carbon Dioxide

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Oxygen recovery from respiratory carbon dioxide is an important aspect of human spaceflight. Methods exist to sequester the carbon dioxide, but production of oxygen needs further development. The current International Space Station Carbon Dioxide Reduction System (CRS) uses the Sabatier reaction to produce water (and ultimately breathing air). Oxygen recovery is limited to 50% because half of the hydrogen used in the Sabatier reactor is lost as methane, which is vented overboard. The Bosch reaction, which converts carbon dioxide to oxygen and solid carbon is capable of recovering all the oxygen from carbon dioxide, and is the only real alternative to the Sabatier reaction. However, the last reaction in the cycle, the Boudouard reaction, produces solid carbon and the resulting carbon buildup will eventually foul the nickel or iron catalyst, reducing reactor life and increasing consumables. To minimize this fouling and increase efficiency, a number of self-cleaning catalyst designs have been created. This paper will describe recent results evaluating one of the designs.

Nomenclature

<i>CRS</i>	= carbon dioxide reduction system
<i>ml</i>	= milliliters
<i>g</i>	= grams
<i>GC</i>	= Gas Chromatograph
<i>MF</i>	= molar flow rate
<i>VF</i>	= Volume flow rate
<i>sccm</i>	= standard cubic centimeters per minute

I. Introduction

OXYGEN recovery from respiratory CO₂ is an essential aspect of human spaceflight and Mars exploration. Methods exist to capture the CO₂, but production of O₂ needs further development. The current ISS Carbon Dioxide Reduction System (CRS) uses the Sabatier reaction to produce H₂O which is electrolyzed to make O₂ for breathing air. O₂ recovery is limited to 50% because half of the H₂ used is lost as CH₄, which is vented overboard, and supplemental H₂ availability is limited. The Bosch reaction (CO₂ + H₂ → C + H₂O) is a promising alternative to

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the Sabatier reaction that does not consume H₂. The Bosch reaction can be considered to be the combination of the Reverse Water Gas Shift (RWGS) reaction and the Boudouard reaction, as shown in *Figure 1*. However, during the Boudouard reaction step the resulting carbon buildup eventually fouls the nickel or iron catalyst, reducing reactor life and increasing the use of consumables. This has long been the subject of study. An early study developed a Bosch system with catalyst cartridges that could be replaced when they were fouled.¹ More recently, Abney et al.²⁻⁷ have investigated different configurations and catalysts. They demonstrated full conversion of CO₂ into O₂ and carbon using the Bosch reaction with a steel wool Boudouard catalyst using only 0.0019 g of catalyst/g O₂ recovered and showed that other catalysts can improve the kinetics and the capacity to hold carbon before failing. Nevertheless, the catalyst bed is eventually clogged with carbon and the catalyst is not recoverable.

To minimize this fouling, find a use for this waste product, and increase efficiency, we have designed various self-cleaning catalysts and selected a few which we deem the most reliable for conversion and lack of fouling. Criteria that we considered include the estimated mechanical reliability of the cleaning method and its ability to maintain high conversion efficiency. The chemical reactions of the Bosch process are well understood, but reusable self-cleaning Boudouard catalysts have not been investigated before.

As noted above, the current ISS O₂ recovery method utilizes the Sabatier process which is only 50% efficient due to limits on H₂ availability. This means that for a full crew over 3 kg of H₂O/day are used in making O₂ that is not recovered from CO₂. At cargo launch prices of \$10,000-\$40,000/kg, this costs \$30,000-\$120,000/day, depending on the supplier. For deep space exploration missions, in-space resupply is virtually impossible so nearly 100% recovery is essential to reduce launch mass. The carbon product could be used as air or H₂O purification filters, which we will test, as a filler for 3D printing, as a dry lubricant suitable for low-pressure applications, or as a reactant in other processes, such as carbothermal reduction or as consumable electrodes for metal production. By producing a self-cleaning Boudouard reactor the single greatest challenge of the Bosch process is resolved and full O₂ recovery can be realized. The decrease in consumable requirements will be significant for the ISS and enabling for deep space exploration missions. In addition, O₂ production is a limiting factor in ISS population and a system such as this can help improve that situation.

In this paper, results from a novel self-cleaning Boudouard reactor are presented. Yields, carbon collection efficiencies, and lifetime of the reactor will be presented. Exact designs will remain proprietary until determinations are made on their patentability.

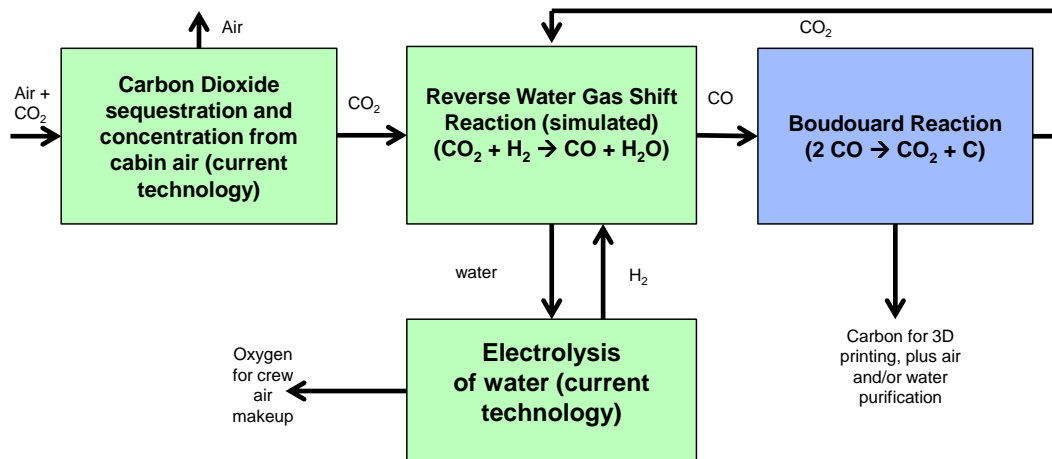


Figure 1. Schematic Representation of the Bosch Reaction by a Combination of the RWGS Reaction and the Boudouard Reaction Followed by Electrolysis of Water to Recover Oxygen from Carbon Dioxide.

II. Materials and Methods

A. Boudouard Reactor Tests

Two reactors with the same self-cleaning mechanism, but with 1 inch or 2 inch diameters have been evaluated. The reaction conditions were as follows. The reactors were operated with two heating zones. The inlet of the

reactor was heated to 600°C while the exit was at 500°C. This was done to promote faster kinetics at the inlet and better thermodynamic conversion at the exit. The reactor volume, catalyst mass, and gas flow rates are given in Table 1. The gas flow rates, were taken to match previous experiments performed by others⁷ and were changed to keep a 9 second residence time in each reactor. The addition of hydrogen helps the Boudouard reaction, but also leads to the methanation of carbon monoxide, via the following reaction: $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$. A schematic of the system is shown in Figure 2.

The gas products of the reaction were sampled by a Varian CP-4900 microGC. The volume percentages of carbon monoxide, carbon dioxide, hydrogen and methane were taken every 5-6 minutes throughout the course of each test. The mass of solid carbon was measured after the test of the 1 inch reactor, and included carbon collected in the carbon capture bag and carbon removed from the reactor body after the test. For the 2 inch reactor, the mass of carbon captured in the collector was recorded periodically during the test.

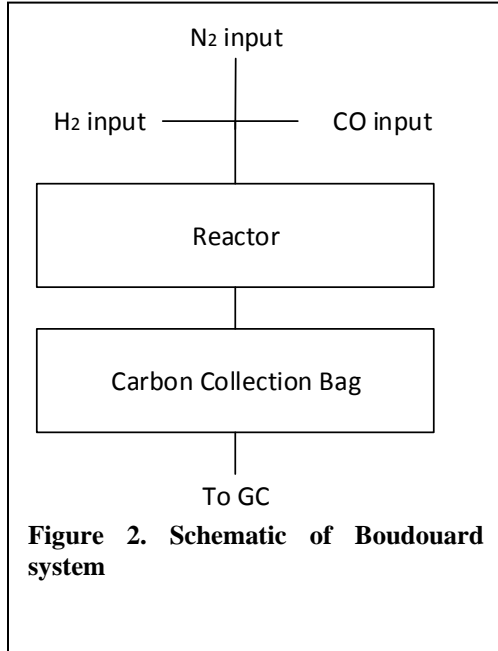


Figure 2. Schematic of Boudouard system

Table 1. Parameters for each reactor.

	1"	2"
	REACTOR	REACTOR
REACTOR VOLUME, ML	76	300
CATALYST MASS, G	1.31	11.82
H ₂ FLOW, SCCM	232	909
CO FLOW, SCCM	232	909
N ₂ FLOW, SCCM	52	202

B. Data Analysis

The yield of CO₂ and CH₄ and total carbon balance were calculated for each data point collected by the GC. Since the mole fraction, MF_i, of an ideal gas is proportional to the volume fraction, VF_i, the mole fraction for each product was calculated using the volume fractions of each gas, and the assumption that the number of moles of carbon dioxide equals the number of moles of solid carbon formed, equation 1. The moles of carbon entering the reactor, CO_{in}, is the volumetric flow rate of carbon monoxide, VF_{CO}, multiplied by the time between GC samples, t, and divided by the number of liters of one mole of an ideal gas, 22.4, equation 2. The moles of each product exiting the reactor, Mol_i, is the mole fraction of each multiplied by the moles of CO entering the reactor, equation 3. The yield, equation 4, for the Boudouard and methanation reactions were calculated by dividing the moles of carbon dioxide or methane produced by the total amount that could be produced (n= 0.5 for Boudouard and 1 for methanation).

$$MF_i = \frac{VF_i}{VF_{CO} + 2 \times VF_{CO_2} + VF_{CH_4}} \quad (1)$$

$$CO_{in} = \frac{VF_{CO} \times t}{22.4} \quad (2)$$

$$Mol_i = MF_i \times CO_{in} \quad (3)$$

$$yield = \frac{Mol_i}{n \times CO_{in}} \quad (4)$$

III. Results and Discussion

A. 1 inch diameter reactor

The 1 inch diameter reactor was run twice: a 4 hour and an 8 hour session for a total of 12 hours. The reactor was not opened, nor was any carbon removed, in between the two sessions. The gas composition exiting the reactor and the yield are given in Figure 3 and Figure 4. The gas concentrations continued to change throughout the 12 hours, indicating the reactor never reached steady state. It is unknown if the void spaces were completely filled at the end of 12 hours. The yield increased during the test, reaching a maximum of 51% and averaging 40% over the duration of the run. The reactor also produced a small amount of methane. The methane yield also increased over the course of the reaction, reaching a maximum of 4.6% and an average of 3.1%.

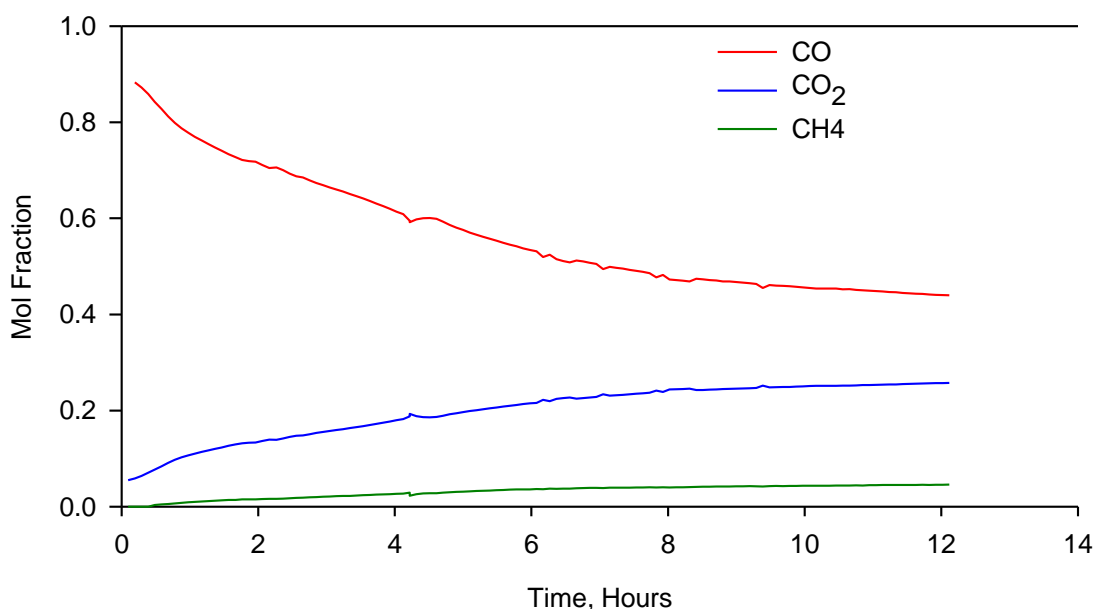


Figure 3. Mole fraction of gas exiting the 1 inch reactor.

A total of 20.5g of solid carbon were collected from the 12 hours of operation. Assuming the molar amount of solid carbon formed is equal to the amount of carbon dioxide measured by the GC, there should have been 18.0 g of carbon. The values are in good agreement, and the discrepancy is likely due to propagation of errors between the flow controllers and measured GC values.

Of the total carbon, 5.5g or 27% of the carbon was collected in the collection bag. The reactor has void space where carbon can build up and is not subjected to the carbon removal mechanism. It is likely that this void space needs to be filled before the carbon collection mechanism becomes completely effective. No attempt was made to measure the carbon captured in the bag in between the 4 and 8 hour runs, so it is not known if the rate of carbon capture in the bag changed over the course of the run. Tests with the 2 inch reactor measured carbon collection efficiency over time. An electron microscope image of the carbon is shown in Figure 5. Trace amounts of iron identified with the carbon. The iron could be from the catalyst or the reactor body.

After the 12 hours of test time, the reactor was opened to evaluate the state of the catalyst and cleaning mechanism. Unfortunately, the cleaning mechanism jammed and was destroyed while the reactor was being opened, so the catalyst could not be evaluated. Whether the jam occurred during reactor opening, or was a result of reactor operation could not be determined.

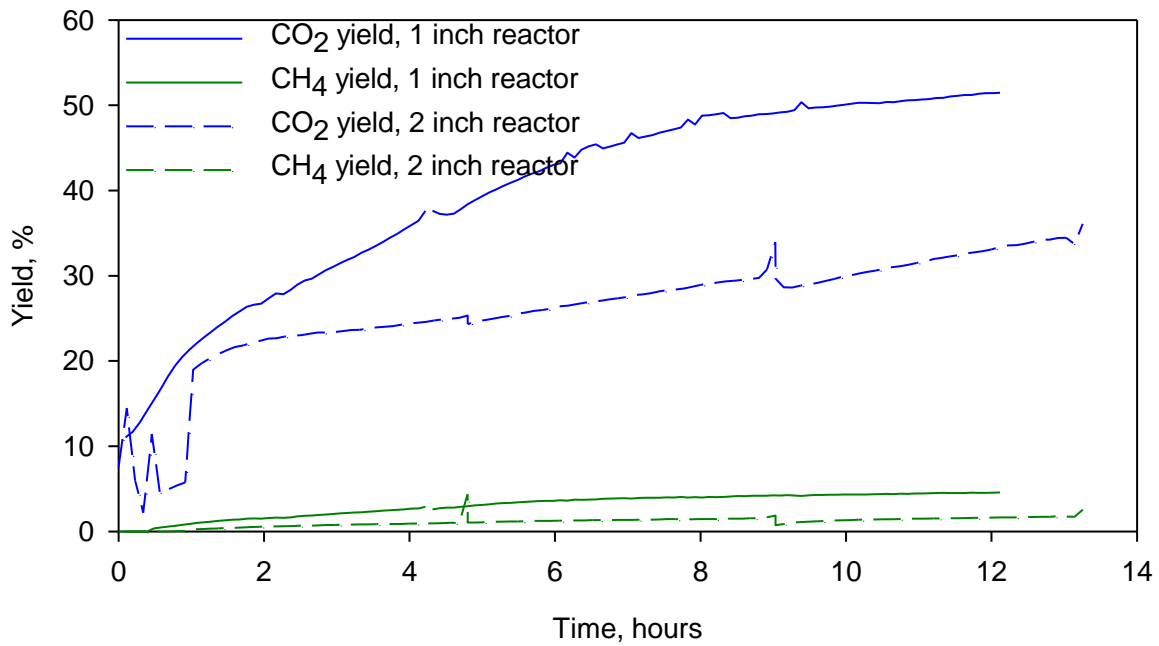


Figure 4. CO₂ and CH₄ yields for both reactors.

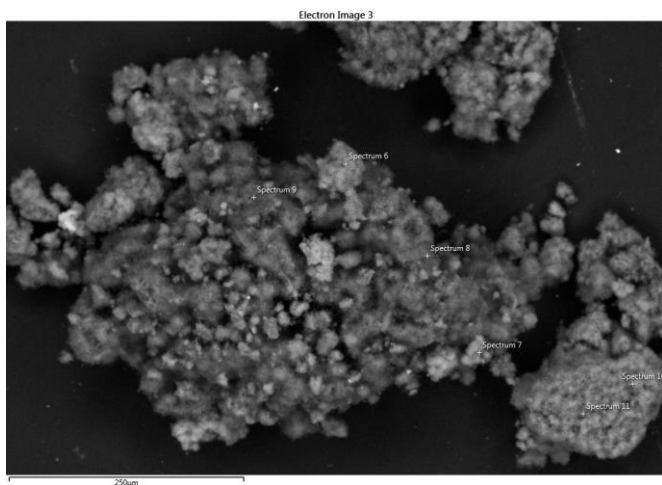


Figure 5. Scanning electron microscope image of carbon collected during the 1 inch diameter reactor test.

B. 2 inch diameter reactor

The 2 inch diameter reactor has been run for about 13 hours, in three sessions, as of the writing of this paper. The mole fractions of gas in reactor effluent are shown in Figure 6. Similar to the 1 inch reactor, the mole fractions of each product are changing over the entire time the reactor has been run. The yield, **Error! Reference source not found.**, also continues to increase. The maximum CO₂ yield was 34% and the average over the entire run time was 26%. The maximum CH₄ yield was 1.7% and the average was 1.1%.

The amount of carbon produced was estimated from the GC data, and the amount was collected in the carbon collection bag was measured and is given in Table 2. The percentage of carbon collected compared to the amount produced increases over the course of the test. Low collection efficiencies early in the test are expected, as this is the time the reactor void space is being filled. The reactor will continue to be tested, hopefully reaching steady state where the reactor effluent composition no longer changes and all of the carbon generated is captured in the collector.

A couple of modifications were made to the cleaning mechanism after the 1 inch diameter reactor jammed. The cleaning mechanism has operated without issue during this test after the modifications were made.

Table 2. Carbon generated and collected from the 2 inch reactor.

	C collected, g	Carbon estimated from GC, g	Percent Carbon Collected
Hours 1-5	Not measured	14.2	
Hours 5-9	9.4	17.5	54%
Hours 9-13	15.0	20.1	74%

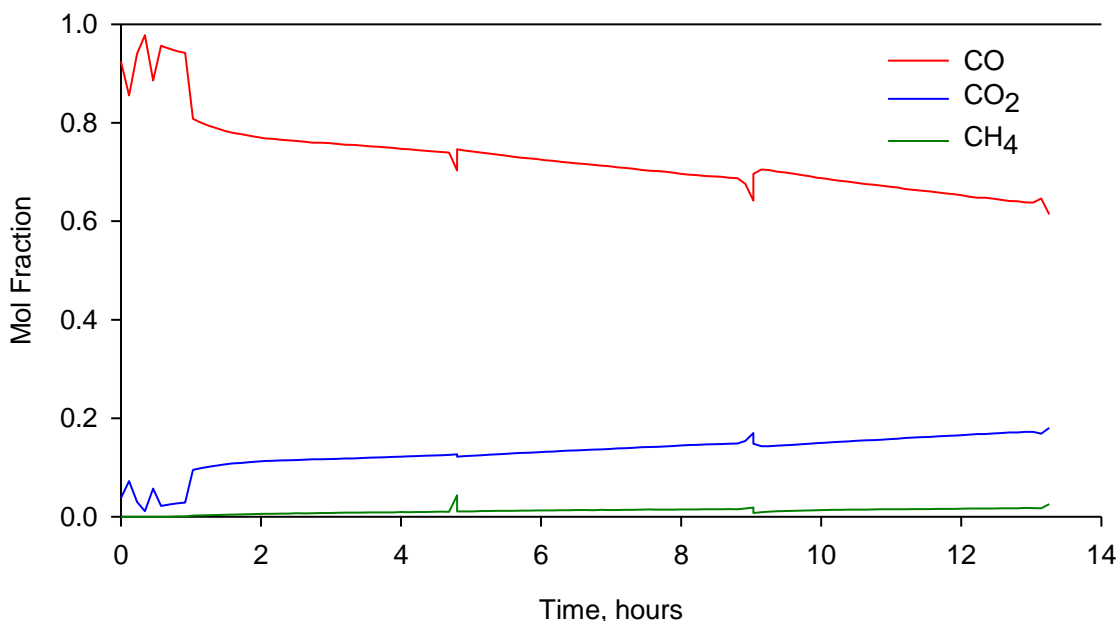


Figure 6. Mole fraction of gas exiting the 2 inch reactor.

IV. Conclusion

The initial testing on this self-cleaning Boudouard reactor were promising. The yield of CO₂ continued to increase for the entire duration of tests with both the 1 and 2 inch diameter reactors. In the case of the 2 inch reactor, the carbon collection efficiency increased over the course of the run, reaching a maximum of 74%. The system must recover 100% of the carbon for the self-cleaning concept to work indefinitely. Iron, either from the catalyst or the reactor body, was identified in the carbon. At this point, it is not known if the iron is a sign that the catalyst is eventually degrading, or if the iron forms at the beginning of the reaction, and then stops forming after carbon has coated the catalyst and internal surfaces of the reactor. The two inch reactor will continue to be operated until the end of the project.

Acknowledgments

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