# Manufacturing from $CO_2$: Acetic Acid Synthesis on Mars


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## ABSTRACT


A reduction in mission costs is critical to increasing the feasibility of long-duration space exploration. Essential supplies, such as biopolymers, food, and pharmaceuticals, are complex products that can be generated in energy-intensive bioreactors. Carbon dioxide ($CO_2$) comprises over 95% of the Martian atmosphere. Leveraging this resource, this project aimed to develop an in-situ chemical process to manufacture acetic acid from $CO_2$. Acetic acid can then be metabolized by bacteria to produce useful products in bioreactors on Mars.


## PROJECT SCOPE

Three generalized pathways currently exist to convert $CO_2$ into a useful product. The project scope was defined as the generation of an intermediate compound to be fed to a biological process.

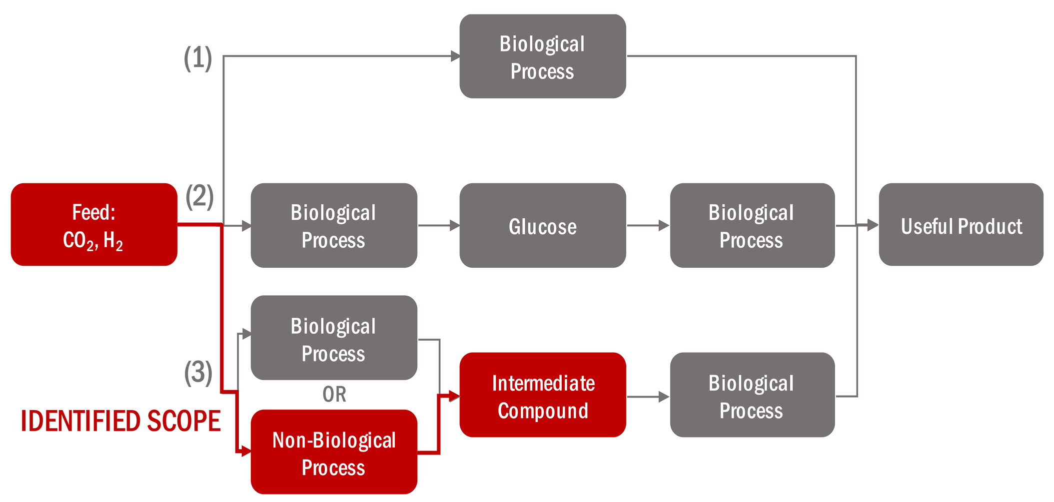


**Figure 1.** Pathways to convert $CO_2$ into a useful product. The project scope is highlighted.

Acetic acid is an ideal intermediate compound as:

- it is easily metabolized by acetanogens into versatile end products, and
- there are currently many well-developed chemical processes to produce it

The system is designed to produce acetic acid at a basis rate of 24 kg/day, minimize crew maintenance and implementation requirements, have a minimum lifetime of 1000 days, and optimize mass, volume, and energy requirements. For eventual deployment on Mars, the following service environment must be considered.

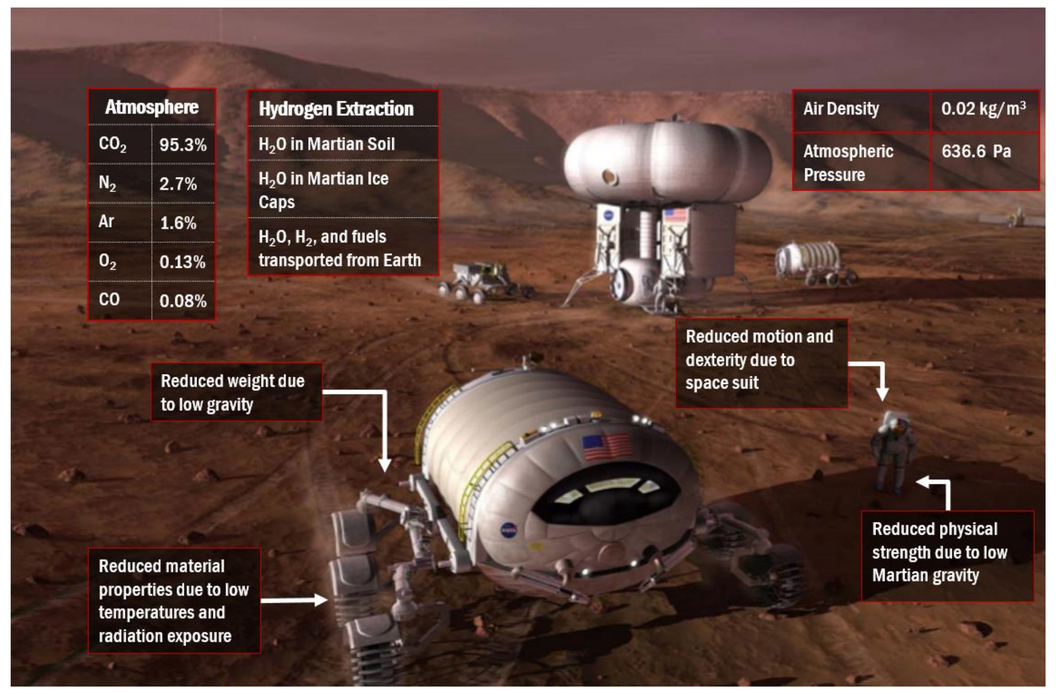


**Figure 2.** Illustration of service environment on Mars, including atmospheric conditions.

## PROCESS SELECTION

A two-stage chemical process was selected to produce acetic acid: (a) carbon dioxide to methanol through a catalytic chemical process and (b) methanol to acetic acid through catalytic carbonylation.

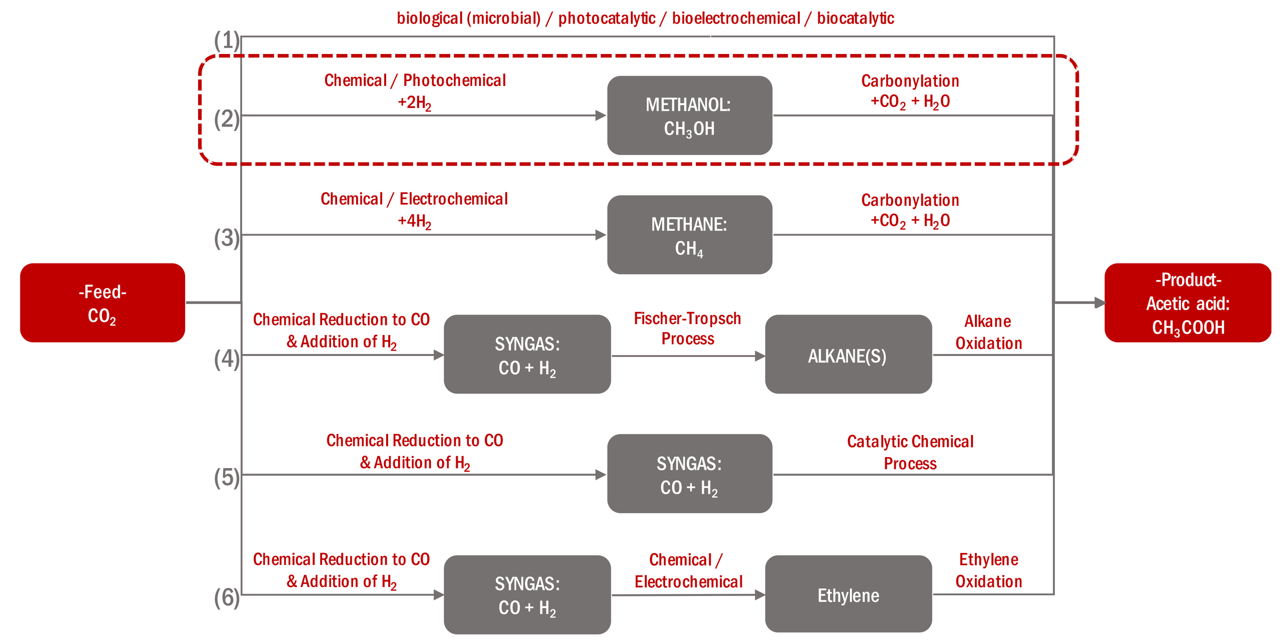


**Figure 3.** Possible pathways from carbon dioxide to acetic acid, identified through a literature review. This selection was iteratively narrowed by elimination based on the state of development (i.e. research or industry) and availability of reaction information.

A complete process was developed to link Reactors 1 and 2, and to purify the acetic acid product from the system. An ASPEN simulation was used to model the process and optimize separation components. Both ASPEN and manual Excel equilibrium calculations were completed using the Soave-Redlich-Kwong equation of state.

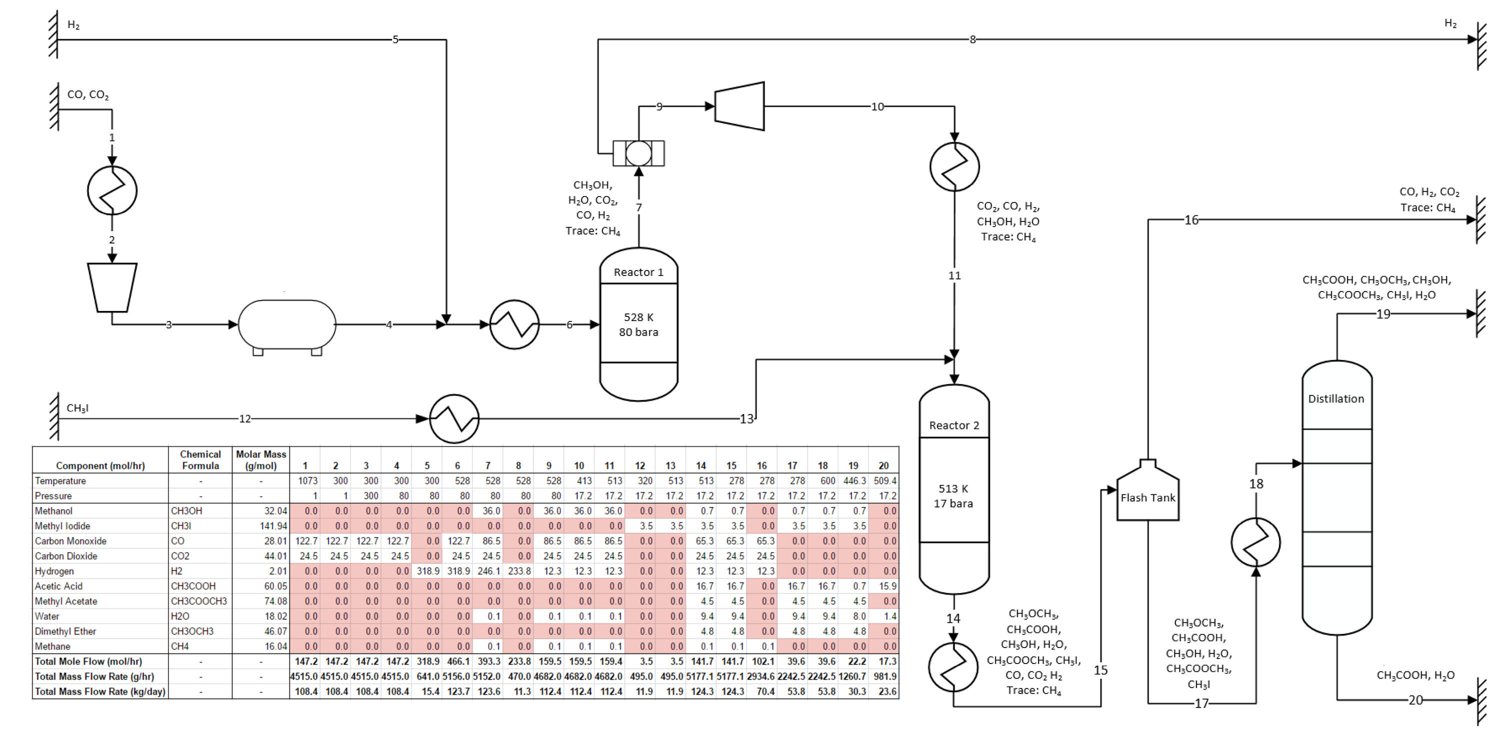

**Figure 4.** Process flow diagram for the step-wise reactor system to produce acetic acid. The accompanying stream table shows the flow of the material in each stream (mol/hr) as well as the temperature (K) and pressure (bar).

## REACTOR DESIGN

### Reactor 1

An Integrated Micro-Packed Bed Reactor Heat Exchanger (IMPBRHE) with a $Cu/ZnO/Al_2O_3$ catalyst is proposed to synthesize methanol from syngas. Preceding the reactor system, $CO_2$ is converted to syngas using a solid oxide electrolysis system (i.e. MOXIE). Pillars in the reaction slits redistribute flow, enhance mixing, and prevent heat accumulation.

| PREDOMINANT REACTIONS | ENTHALPY OF REACTION ($\Delta H_{298K}$) |
|---|---|
| $CO + H_2O \rightleftharpoons H_2 + CO_2$ | -41 kJ/mol |
| $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$ | -49 kJ/mol |
| $CO + 2H_2 \rightleftharpoons CH_3OH$ | -91 kJ/mol |
| $CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$ | -165 kJ/mol |

**Microstructure Reactor**
8 reaction slits sandwiched between 2 cross-flow oil channels for heat transfer

**Catalyst**
$Cu/ZnO/Al_2O_3$
Cu/Zn/Al (mol%): 0.28/0.28/0.44

**Feed Gas Composition**
$H_2/CO/CO_2$ (68.4/26.3/5.3 mol%)

**Pressure**
80 bar

**Temperature**
528 K

**CO Conversion**
29.515%

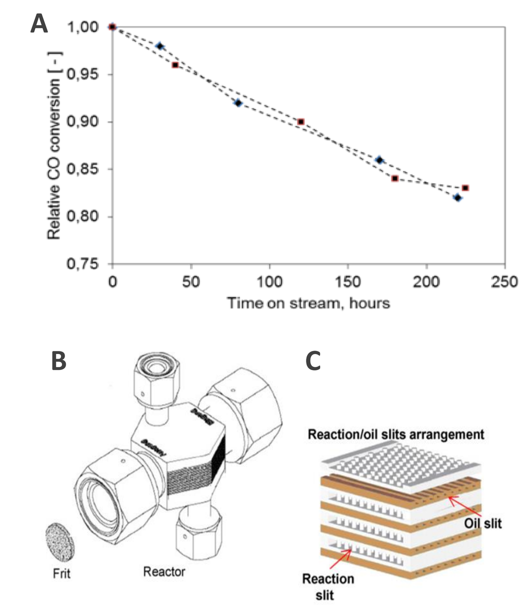


**Figure 5.** (A) Relative CO conversion versus time for a Cu-ZnO-based catalyst in IMPBRHE over two runs. (B) IMPBRHE module, (C) Schematic of reaction slits and oil channels.

### Reactor 2

The selected plug flow reactor contacts methanol vapor with carbon monoxide in the presence of a heterogeneous catalyst consisting of iridium deposited on an activated carbon-catalyst support mesh. Acetic acid is produced in the vapour phase, enabling lower operating pressures and avoiding leaching of the catalyst support that commonly occurs in liquid-homogeneous-catalytic systems.

| PREDOMINANT REACTIONS | ENTHALPY OF REACTION ($\Delta H_{298K}$) |
|---|---|
| $CO + CH_3OH \rightleftharpoons CH_3COOH$ | -117 kJ/mol |
| $CO + 2CH_3OH \rightleftharpoons CH_3COOCH_3 + H_2O$ | -131 kJ/mol |
| $2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$ | -16 kJ/mol |

**Reactor Structure**
Tubing with inside diameter of 6.35 mm, length of 850 mm, & quartz catalyst support

**Catalyst**
Iridium and at least one second metal (0.1 to 2 wt%) between atomic numbers 57-71

**Feed Gas Composition**
$H_2/CO/CO_2/CH_3OH/CH_3I$ (8/53/15/22/2 mol%)

**Pressure**
17.2 bar

**Temperature**
513 K

**Methanol Conversion to Acetic Acid**
46.3%

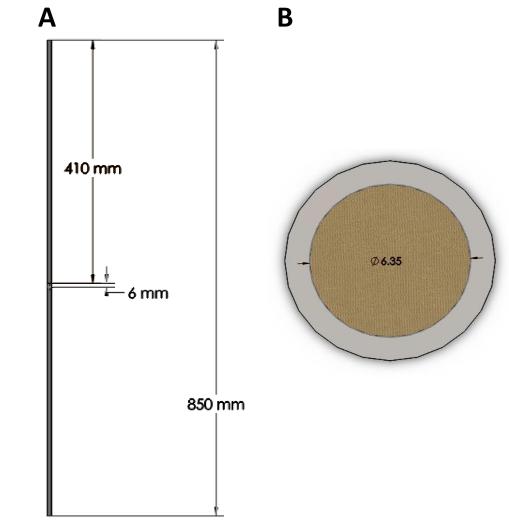


**Figure 6.** (A) Dimensions of the reactor tube. 410 mm from the top, a ~6 mm length of quartz wool pad supports the catalyst. (B) Cross-sectional view of the reactor tube.

75 g of catalyst is required.

## PROTOTYPING

A valuable next step would be to prototype the system in a lab-scale setup to provide a proof-of-concept. Thereafter, experimental production rates can be correlated back to the design. A 10% scale model of a possible lab configuration is presented below.

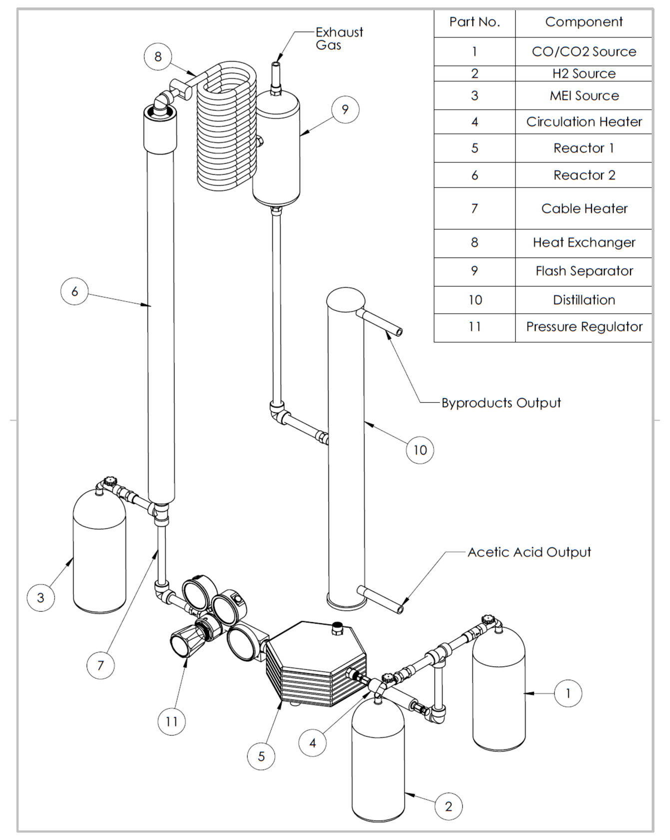


**Figure 8.** 3D representation of lab-scale setup.

## ENERGY OPTIMIZATION

There are many areas where energy utilization could be further optimized through the use of heat exchangers. For example, by implementing two cross-flow heat exchangers, energy savings of up to 1 kW can be obtained, which reduces overall system costs.

**Table 2. Processes and heat flows of interest**

| | Process | Net Heat Transfer | $\dot{Q}$ [W] |
|---|---|---|---|
| 1 | *Cooling MOXIE Input* | Loss | 1078 |
| 2 | *Heating Methyl Iodide Input* | Gain | 34 |
| 3 | *Heat Adjustment into Reactor 1* | Gain | 685 |
| 4 | *Heat Adjustment for Reactor 2* | Gain | 102 |
| 5 | *Cooling output of Reactor 2* | Loss | 657 |
| 6 | *Heating into Distillation Column* | Gain | 663 |

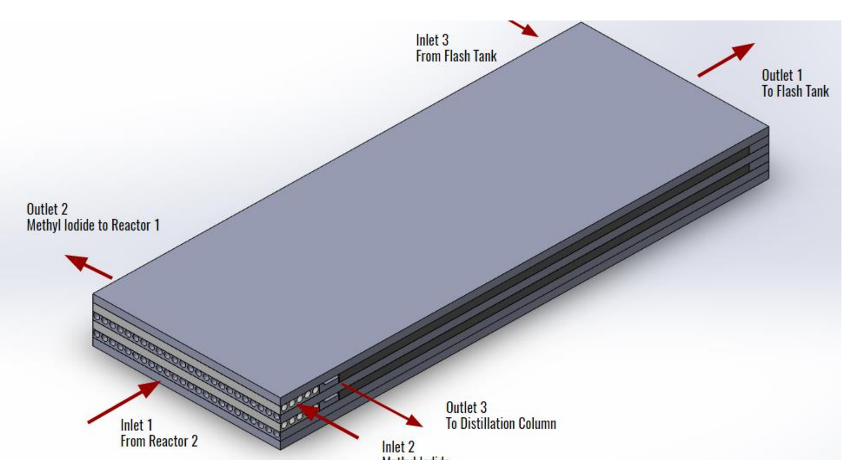


**Figure 7.** 3D representation of proposed heat exchanger.

## ECONOMIC ANALYSIS: ESM

Equivalent System Mass (ESM) methodology converts 5 design factors – mass, volume, power, cooling and crew time – into a single mass cost [kg] from which systems may be compared. The cost of space missions is most directly determined by the transportation costs associated with the weight of the payload. This system also reflects that space travel is an international endeavor: by eliminating currency from the cost calculations, missions costs may be analyzed on an S.I. basis. Table 1 illustrates a cost analysis of one of several potential products from the system.

$$ESM = Mass \times \gamma_m + Volume \times \gamma_v + Power \times \gamma_p + Cooling \times \gamma_C + Crew\ time \times \gamma_{ct}$$

| Parameter | | Traditional Method | Proposed Design | |
|---|---|---|---|---|
| Parameter | Conversion Factor | Shipped Food | Two 2000 L *Spirulina* - producing bioreactors | 24 kg/day Acetic Acid Production |
| ***Mass*** | 1.15 kg/kg | 2,506 kg | 1,588 kg | 552 kg |
| ***Volume*** | 216 kg/m³ | 12.7 m³ | 9.9 m³ | 1.02 m³ |
| ***Power*** | 228 kg/kW | 1.5 kW | 0.01 kW | 3.7 kW |
| ***Cooling*** | 145 kg/kW | 1.5 kW | 0.01 kW | 2.4 kW |
| ***Crew Time*** | 1.25 kg/h | 0 h | 30 h | 225 h |
| ***ESM Launch*** | | 5,816 kg | 3,765 kg | 2,327 kg |
| ***ESM per Mission*** | | 5,816 kg | 783 kg | 932 kg |

**Table 1. ESM Cost Analysis of Shipped and Proposed System for Food Production**