Demonstration of a Piloted Mars Mission Scale RWGS

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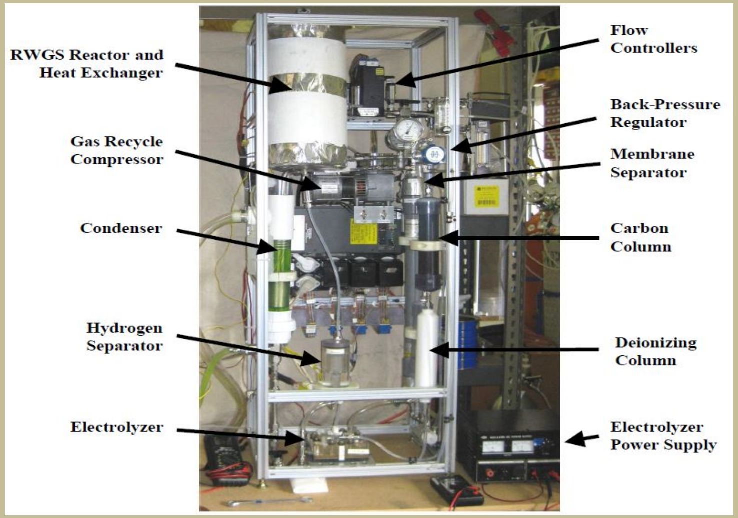
The Reverse Water Gas Shift

$CO_2 + H_2 \Rightarrow CO + H_2O \quad \Delta H = +9$ kcal/mole

- Combined with H_2O electrolysis can produce unlimited O_2 and CO on Mars.
- Endothermic
- Equilibrium constant ~0.1 at 400 C
- Higher equilibrium constant at higher temperatures, but cause coking
- Equilibrium independent of pressure
- Forward gas shift known and used since 19th Century, Keq>10
- RWGS and FGS both catalyzed by Cu-based catalysts
- RWGS single pass yield ~25%. Requires recycling to get good yields.
- High yield recycling RWGS demonstrated by Pioneer Astronautics in 1997

1997



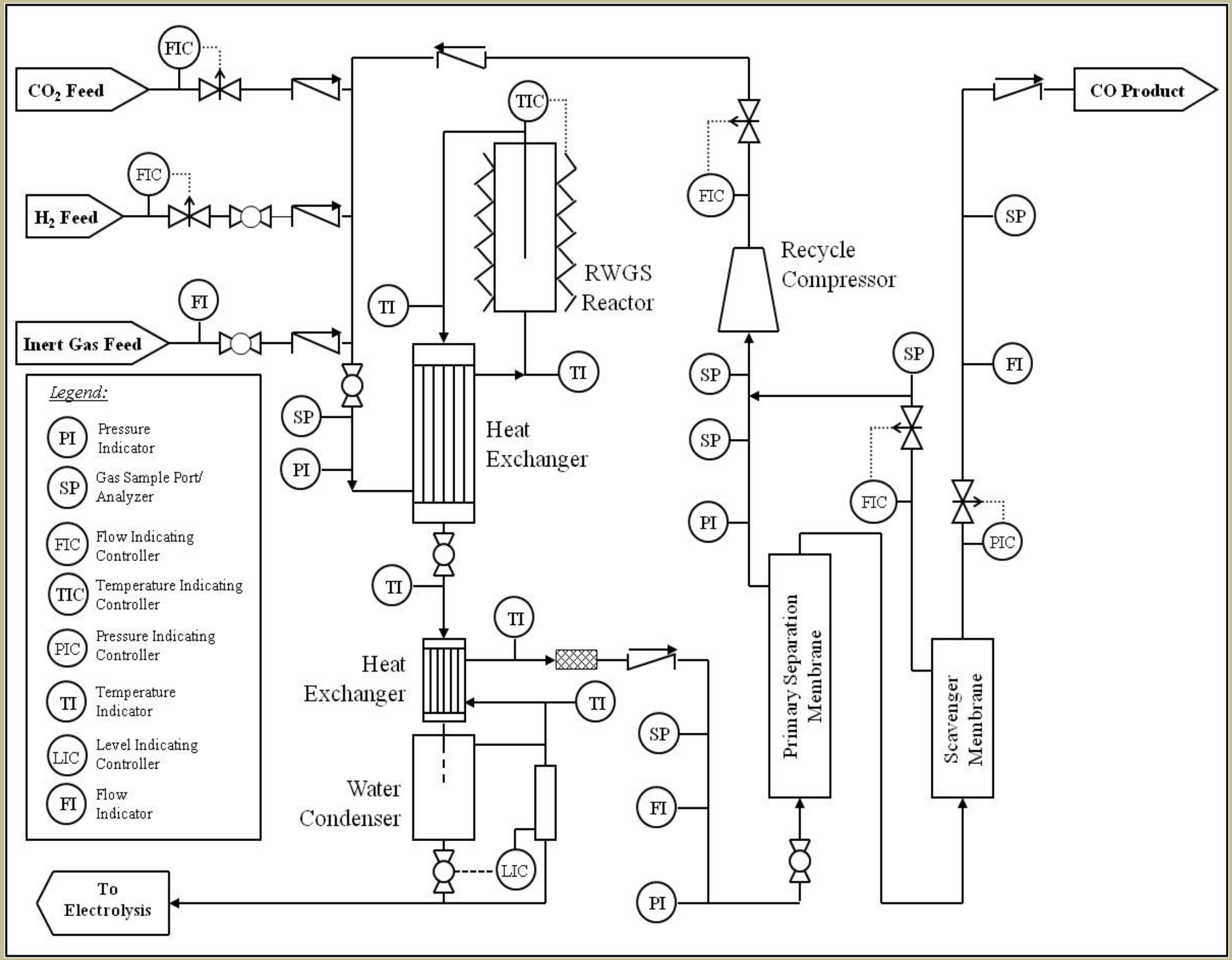
2004

The Commercial RWGS Program

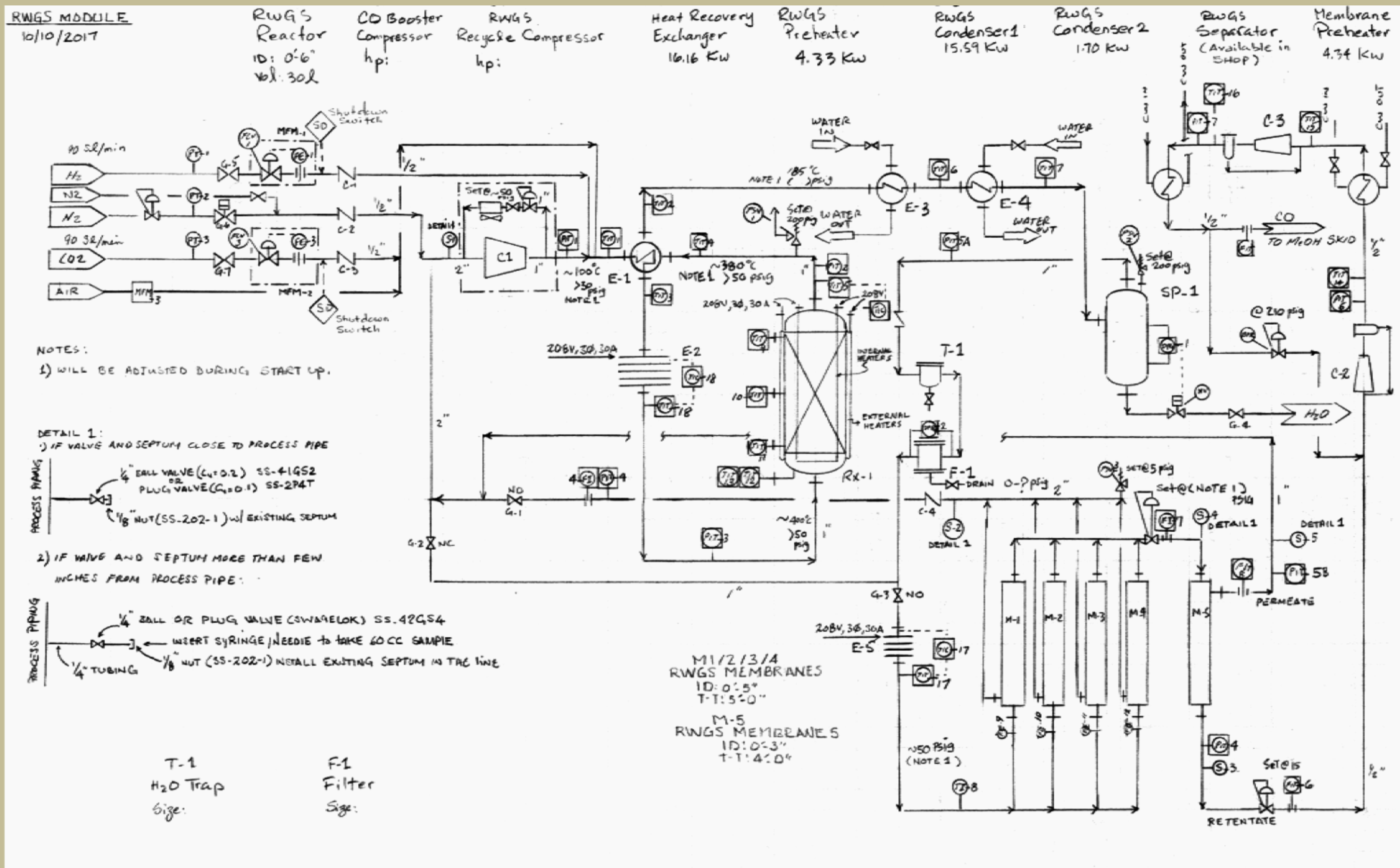
- In 2017 the Canadian company CO_2 Solutions had a technology for capturing CO_2 from flue gas. Quebec government funded them to find utilization for CO_2.
- Pioneer Astronautics' spinoff company Pioneer Energy won contract to turn it into methanol, and then acetic acid and/or DME.
- Assume cheap H_2 available from hydro power or refinery flares
- Desired scale ~200 kg CO_2/day. Equals ~80 kg H_2O/day from RWGS.
- Project led by Robert Zubrin. Mark Berggren served as chief engineer
- Crash program: Award made in May 2017. Needed to demonstrate operation by October to be eligible for Carbon Capture X-Prize.
- Requirement for acetic acid made ultra-high purity CO from RWGS necessary

$CO + 2H_2 \Rightarrow CH_3OH$	ΔH= -23 kcal/mole	Methanol
$2(CH_3OH) \Rightarrow C_2H_6O + H_2O$	ΔH = -3kcal/mole	DME
$CH_3OH + CO \Rightarrow CH_3COOH$	ΔH = -40 kcal/mole	Acetic acid

RWGS Block Flow Diagram



RWGS PFD



RWGS MODULE
10/10/2017
RWGS Reactor
ID: 0'-6"
Vol: 30l
CO Booster Compressor
hp:
RWGS Recycle Compressor
hp:
Heat Recovery Exchanger
16.16 Kw
RWGS Preheater
4.33 Kw
RWGS Condenser1
15.59 Kw
RWGS Condenser2
1.70 Kw
RWGS Separator
(Available in SHOP)
Membrane Preheater
4.34 Kw
H2
N2
N2
CO2
AIR
Shutdown Switch
WATER IN
WATER OUT
E-1
E-2
E-3
E-4
E-5
C1
C-2
C-3
SP_1
T-1
F-1
Rx-1
CO
TO MeOH SKID
H2O
PERMEATE
RETENTATE
INTERNAL HEATERS
EXTERNAL HEATERS
208V, 3Φ, 30A
NOTES:
1) WILL BE ADJUSTED DURING START UP.
DETAIL 1:
1) IF VALVE AND SEPTUM CLOSE TO PROCESS PIPE
1/4" BALL VALVE (Cv=0.2) SS-41GS2 OR PLUG VALVE (Cv=0.1) SS-2P4T
1/8" NUT (SS-202-1) w/ EXISTING SEPTUM
PROCESS PIPING
2) IF VALVE AND SEPTUM MORE THAN FEW INCHES FROM PROCESS PIPE:
1/4" BALL OR PLUG VALVE (SWAGELOK) SS-42GS4
INSERT SYRINGE/NEEDLE to take 60 CC SAMPLE
1/8" NUT (SS-202-1) INSTALL EXISTING SEPTUM IN THE line
1/4" TUBING
PROCESS PIPING
M1/2/3/4
RWGS MEMBRANES
ID: 0'-5"
T-T: 5'-0"
M-5
RWGS MEMBRANES
ID: 0'-3"
T-T: 4'-0"
T-1
H2O Trap
Size:
F-1
Filter
Size:

Choosing the Optimum Recyle Rate

Assuming stoichiometric feed ratios and a reactor temperature of 400°C, there is a single pass conversion of about 25%. If the number of passes the average gas molecule makes through the reactor is given by N (the recycle ratio), a good approximation of the CO_2 to CO conversion is:

Conversion = Z = $CO/(CO + CO_2) = 1 - 0.75^N$

So for a single pass reactor, N=1 and Z=0.25. But if we recycle, we have N=2 Z=0.43, N=4 Z=0.68, N=6 Z=0.82, N=8 Z= 0.9, N= 10 Z= 0.94, N=12 Z=0.97, etc.

For maximum conversion, the system optimizes at the highest recycle rate. But higher recycle rates require a larger recycle compressor using more power, and larger membranes, and also increase the heating power required by the reactor, as no heat exchanger can be 100% efficient.

So, for example, if we increase the recycle rate from 6 to 12, the compressor and reactor heating power will double, while the conversion rate will only increase from 0.82 to 0.97, or 18%.

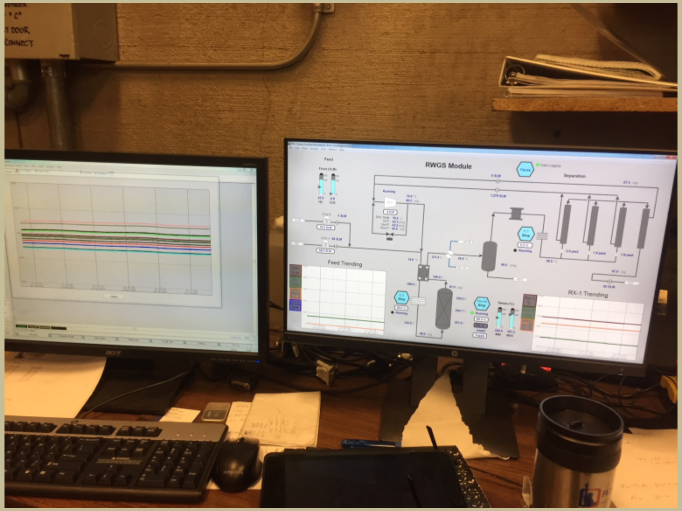
To produce pure CO for fuel synthesis (as for example was the case with the commercial RWGS, which had N=16 Z=0.99), going to such high rates makes sense. But for NASA Mars missions, the primary product of interest is H2O (or O2), which will be pure regardless of the conversion ratio.

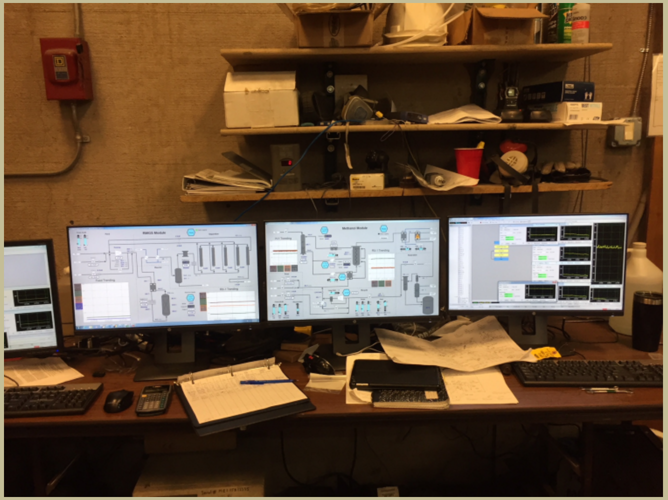
H2 losses can be reduced by running the system CO_2 rich, and by placing a small scavenger membrane on the system outlet, which can recycle much of the CO_2 and H_2 that passes to the primary membrane retentate back to the reactor.

Rates of Flow of the Commercial RWGS

- At 100% conversion, converting 200 kg of CO2/day requires 70 l/min flow each of CO2 and H2
- A recycle rate of 16 therefore requires 2240 l/min recycle flow
- System operated at between 50 and 100 psig pressures.
- So volumetric recycle flow was ~600 l/min
- 70 l/min of CO product needed to be compressed to ~400 psi for methanol system.
- ~9 l/min volumetric flow
- So big recycle compressor (11 kW), small (~1 kW) step up compressors needed.

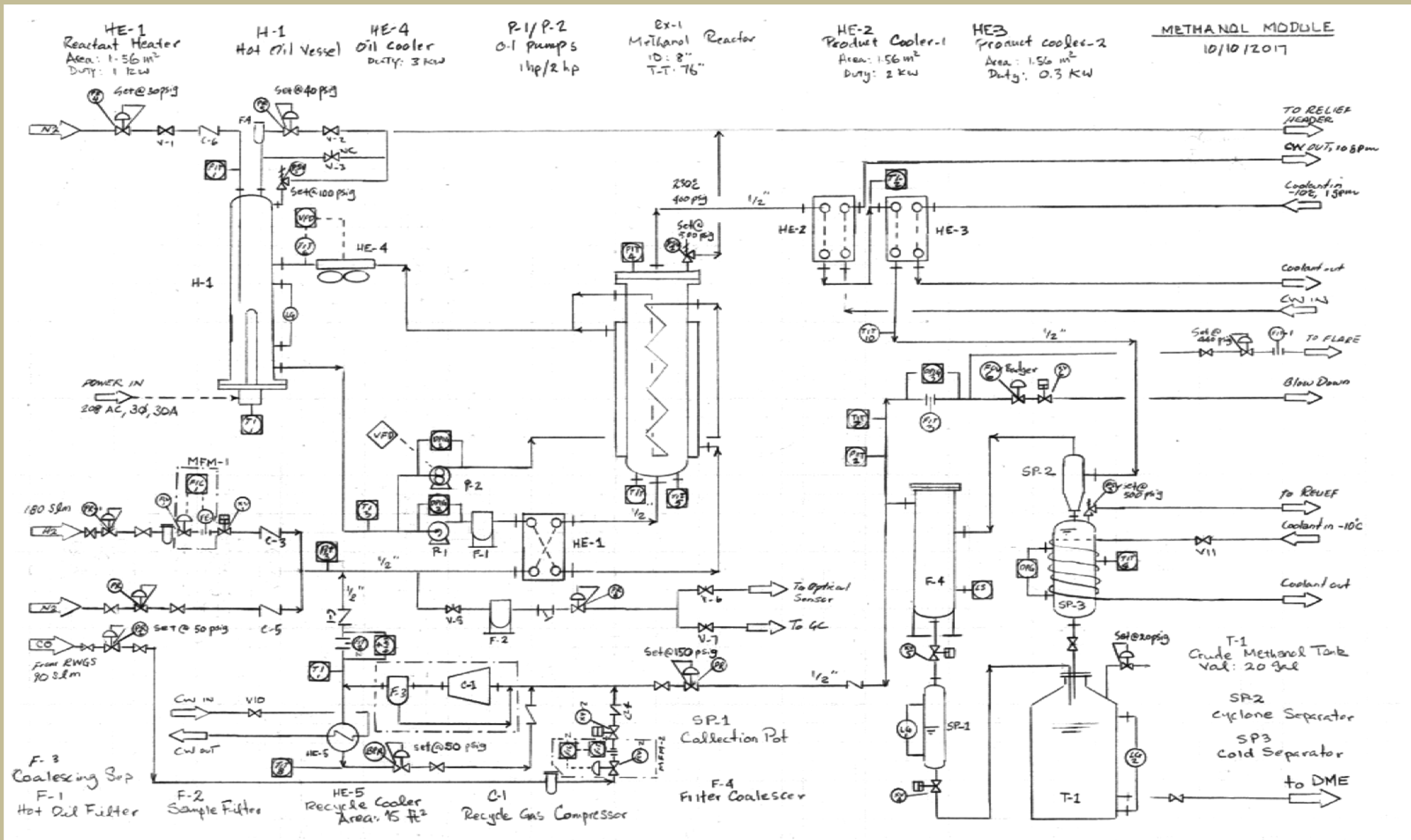
The RWGS Unit





Reactor (at left) is 15 cm diameter, 1.5 m long, 25 liter volume, filled with fixed-bed Cu-on-ZnO pellets

Methanol Synthesis Unit PFD



The Methanol system

System is similar to RWGS except that it operates at high pressure (~400 psi) and lower temperature (240 C) and no membranes are required.
Also, exothermic chemistry means no reactor heating is needed after startup.

Run History

Oct 1 2017	5 hrs	Methanol from CO_2	1.7 kg/hr
Oct 4	10 hrs	Methanol from CO_2	2.04 kg/hr
Oct 5	7.25 hrs	Methanol from CO	2.7 kg/hr
Oct 6-7	29.5 hrs	Methanol from CO and CO_2	1.5 kg/hr
Oct 8	7.5 hrs	RWGS/Methanol	0.8 kg/hr
Oct 9	14 hrs	RWGS/Methanol	1.2 kg/hr RWGS ~99% efficient
Nov 4	3.6 hrs	Methanol to DME	5.2 kg/hr methanol processed
Nov 6	3.0 hrs	Methanol to DME	7.2 kg/hr methanol processed
Nov 7	3.0 hrs	Methanol to DME	5.7 kg/hr methanol processed
Nov 8	2.0 hrs	RWGS	RWGS 99% eff @40 l/m CO_2
Nov 9	3.0 hrs	Methanol from CO_2	1.4 kg/hr
Nov 10	3.0 hrs	RWGS	RWGS 99% eff @70 l/m CO_2
Nov 11	7.5 hrs	RWGS/Methanol	4.7 kg/hr during final 3 hrs
Nov 12	4.0 hrs	Methanol to DME	7.2 kg/hr methanol processed
Nov 13	3.0 hrs	Methanol to DME	3.8 kg/hr methanol processed
Nov 14-15	24 hrs	RWGS/Methanol	4.6 kg/hr ave RWGS 98.5% eff
Nov 15	5.5 hrs	Methanol to DME	4.1 kg/hr methanol processed
Dec 14	3.9 hrs	Methanol to DME	12 kg/hr methanol processed
Dec 15	1.9 hrs	Methanol to DME	24 kg/hr methanol processed

Typical efficiencies: RWGS 98.5 %, Methanol 75%, DME 73% w/o recycle, 93% w recycle

The November 24 hour run

On November 14, 2017, the integrated RWGS/Methanol System was run for 24 hours non-stop.

RWGS Performance

Rate of Feed	70 l/min H_2 and CO_2
Recirculation Rate	1300 l/min
Pressure	45 psi low/ 90 psi high
Reactor exit temperature	350 C
CO_2 conversion	~98.5% (97.8 to 99.1)
Power	~21 kW (12 pumps, 9 heaters)

Methanol System Performance

Rate of Feed	69 l/min CO, 1 CO_2, 140 H_2
Recirculation Rate	780 l/min
Pressure	395 psi
Reaction temperature	~240 C
Methanol produced	110 kg
CO to methanol efficiency	75%
Power	~2 kW (1.5 pump, 0.5 heater)

Mars Mission Application

Approximately 81 kg of water was produced by the RWGS in the course of the 24 hour run.

The CO from the RWGS was then fed into the methanol synthesis unit, where it was reacted with hydrogen to produce approximately 110 kg of methanol in the course of the 24 hour run.

If the water produced by the system were electrolyzed, it would produce 72 kg of oxygen/day, or 36 metric tons over a 500 day period. The methanol system would produce 55 metric tons of methanol. The DME system would produce 28.5 tons of DME.

Oxygen burns with DME at a stoichiometric ratio of 2.09. So if the 28.5 tons of DME produced were combined with 59.5 tons of oxygen, a total of 88 tons of useful bipropellant would result.

If the oxygen product were used in a LOX/RP engine burning at 2.8:1, at total of 49 tons of useful bipropellant would be available.

More propellant would be produced by such a system than that required for the ascent vehicle in the NASA design reference mission.

If the RWGS system were run in parallel in a Sabatier Electrolysis (S/E) system sized to produce 48 kg of CH_4 and 96 kg of O_2 per day, a total of 24 tons of methane and 84 tons of oxygen would be produced, which is sufficient to fly the Mars Direct mission.

ISRU has entered a new world.

The Team