

# Dry Reforming: A Unique Flowsheet for Fuel Production on Mars

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## ABSTRACT

A new conceptual flowsheet is presented for Martian *in situ* fuel production. The dry reforming flowsheet incorporates the well-known Sabatier-Electrolysis process with a carbon dioxide / methane reforming step to consume some of the Sabatier methane. By varying the ratio of effluent to reformed methane, any desired methane / oxygen ratio can be produced by the dry reforming process. Such a machine will enable utilization of all imported hydrogen into an optimal methane / oxygen fuel mixture, with copious quantities of surplus oxygen produced for crew consumables.

The reforming process is highly endothermic and requires temperatures above 650 centigrade on precious metal catalysts. Appropriate feed / effluent heat exchange reduces the reformer power requirements, but an increased oxygen / methane ratio increases the power requirements. In addition, the complexity introduced by the reformer and its interactions with the Sabatier system make the system relatively difficult to automate or control remotely. The energy usage and complexity imply that a dry reforming process will not be useful in the early stages of Mars exploration. However, the increased material usage efficiency and oxygen generation capability of the dry reforming technique will make it an attractive technology to consider for second generation ISRU systems. In addition, the potential ease of retrofitting Sabatier / Electrolysis units with a dry reformer provide an important advantage for early adoption of the technology. Minor preinvestment in the Sabatier system – essentially just provision for interconnections – will allow the addition of a reformer, thus extending the useful lifetime of the Sabatier system, instead of replacing early Sabatier systems with entirely new second generation systems. Thus, dry reforming will be an important technology to allow cost effective expansion of early Martian exploration and base building efforts.

## Introduction

The concept of *in situ* resource utilization (ISRU) has been advocated as a means to reduce the amount of mass launched from Earth for Mars missions. Primary resources on Mars include the components of the atmosphere, especially the majority constituent, carbon dioxide. Primary near term utility for this resource includes oxygen for life support and rocket fuel oxidizer, and carbon for hydrocarbon or oxygenated hydrocarbon fuels.

The advantages of an ISRU application are often described by its “mass leverage.” The mass leverage is the ratio of the mass of usable product produced on Mars to the mass of required feedstock and equipment that needs to be flown to Mars. For example, if 5 kg of equipment and feedstock can produce 100 kg of Mars product, then the mass leverage would be 20. First order calculations of the mass leverage can ratio the product to hydrogen feedstock masses only (hydrogen is typically the only feedstock brought from Earth), but more detailed calculations require including all knock-on masses, such as required power systems, refrigeration and storage units, chemical reactors, etc. In turn, the mass required for the complete ISRU system needs to be compared to completed designs of alternative systems that would accomplish the same mission. Such alternative systems should include a “traditional” type mission architecture (i.e., a mission using storable propellants and tankage launched from Earth), as well as suitable alternative ISRU concepts. The comparison also needs to account for various secondary properties of the ISRU products, such as specific impulse or energy density.

The SEDR concept is closely related to the Sabatier / Electrolysis (S/E) ISRU concept, but extends the concept to allow production of any desired fuel / oxygen ratio. This is done by introducing a carbon dioxide reformer, or “dry” reformer, which reforms methane produced by the Sabatier reactor into carbon monoxide and hydrogen. Carbon monoxide can be vented while the hydrogen is recovered to the Sabatier system, thus potentially creating a closed hydrogen loop. Since hydrogen is the feedstock material brought from Earth, this concept allows a significant improvement of the mass leverage of the S/E ISRU system, from a value of 12, to a value of 20 or more. In addition, the SEDR provides a

responsive and flexible product distribution for variable crew demands. This improvement can be accomplished with negligible preinvestment in the S/E system, and only modest marginal cost for the dry reforming system.

### The SEDR Flowsheet – Process Description

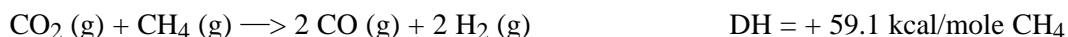
The SEDR flowsheet is shown in Figure 1. In this flowsheet, carbon dioxide is gathered by a freezer or other suitable carbon dioxide acquisition system, and pumped at moderate pressure to the Sabatier reactor. The reforming reaction is favored by low pressure, and the Sabatier reaction can achieve high conversion at moderate pressure, so the entire system can operate at pressures on order of one bar, thus reducing the required performance and power requirement of the carbon dioxide collection system. In the Sabatier reaction, CO<sub>2</sub> reacts with hydrogen from the fresh feed and recycle streams to produce methane and water. Water is condensed from the reactor outlet and electrolyzed. Oxygen from the electrolyzer is condensed and stored, while hydrogen is recycled to the Sabatier reactor feed for further production.

Methane from the Sabatier water condenser is also sent to liquefaction and storage. However, a slipstream from the methane product, and methane boil-off from storage (and any unreacted hydrogen from the Sabatier reactor), can be sent to the reformer with a portion of the carbon dioxide feed gas. Feed gas to the reformer passes through a feed / reformer exchanger to recover heat from the reactor and reduce the heating requirements of the highly endothermic reactor. The feed CO<sub>2</sub> reacts with the methane over an appropriate catalyst to form carbon monoxide and hydrogen. Cooled effluent gas from the reformer has water removed and sent to electrolysis, and then is compressed and separated in a highly selective polymer membrane. Permeable gases, including hydrogen, any produced water, and unreacted carbon dioxide, flow through the membrane and back to the Sabatier reactor, where they can be captured in useful products. Impermeable gases, primarily carbon monoxide, are vented from the system. Such polymer membranes are used in industrial gas separations, and have been demonstrated in Mars ISRU systems built by Pioneer Astronautics.

The methane slipstream ratio to the reformer is a primary control variable for the system operation. When the slipstream to the reformer is set to zero, the system is simply a standard Sabatier / Electrolysis system, producing a LOX / LCH<sub>4</sub> bipropellant combination in a 1:1 molar ratio, which gives a mass ratio of 12 (first order calculation based on H<sub>2</sub> import). When the slipstream to the reformer is set to 0.5 of the methane flow, the system recovers half the hydrogen in methane product, allowing a 2:1 molar ratio LOX / LCH<sub>4</sub> bipropellant, or a mass ratio of 4, which is the ideal stoichiometric ratio. This provides a net system mass leverage of 20. If all of the methane product from the Sabatier reactor is sent to the reformer, oxygen will be the only net system product and there will be no net consumption of hydrogen, thus giving an infinite ideal mass leverage.

### Carbon Dioxide / Methane Reforming

The SEDR flowsheet seems to offer some definite benefits, but how easy is it to reform methane? Does this process flowsheet have the possibility of turning into a practical process? Fortunately, the CO<sub>2</sub> / methane reforming reaction is well known and widely utilized in the direct iron reduction industry. The basic reforming reaction is:



(Note: all reaction DH's at 298°K, throughout paper)

Since the reaction does not involve water, it is known as dry reforming, and reactor design is simplified by keeping water out to the extent possible. Nevertheless, with three of the four constituents of the water-gas shift reaction present, the system is susceptible to water formation via that reaction pathway. In addition, the reaction is highly endothermic – significantly more so than a standard steam reforming reaction – which means that elevated temperatures are desirable for reasonable equilibrium conversions. However, the elevated temperatures open the possibility of various coking reactions, most predominately the methane dehydrogenation, the Beggs, and the Boudouard reactions. The various competing reactions make dry reforming a complex reactor design problem, and catalyst selection and operating parameters become absolutely critical. A summary of the previously mentioned primary competing side reactions includes:

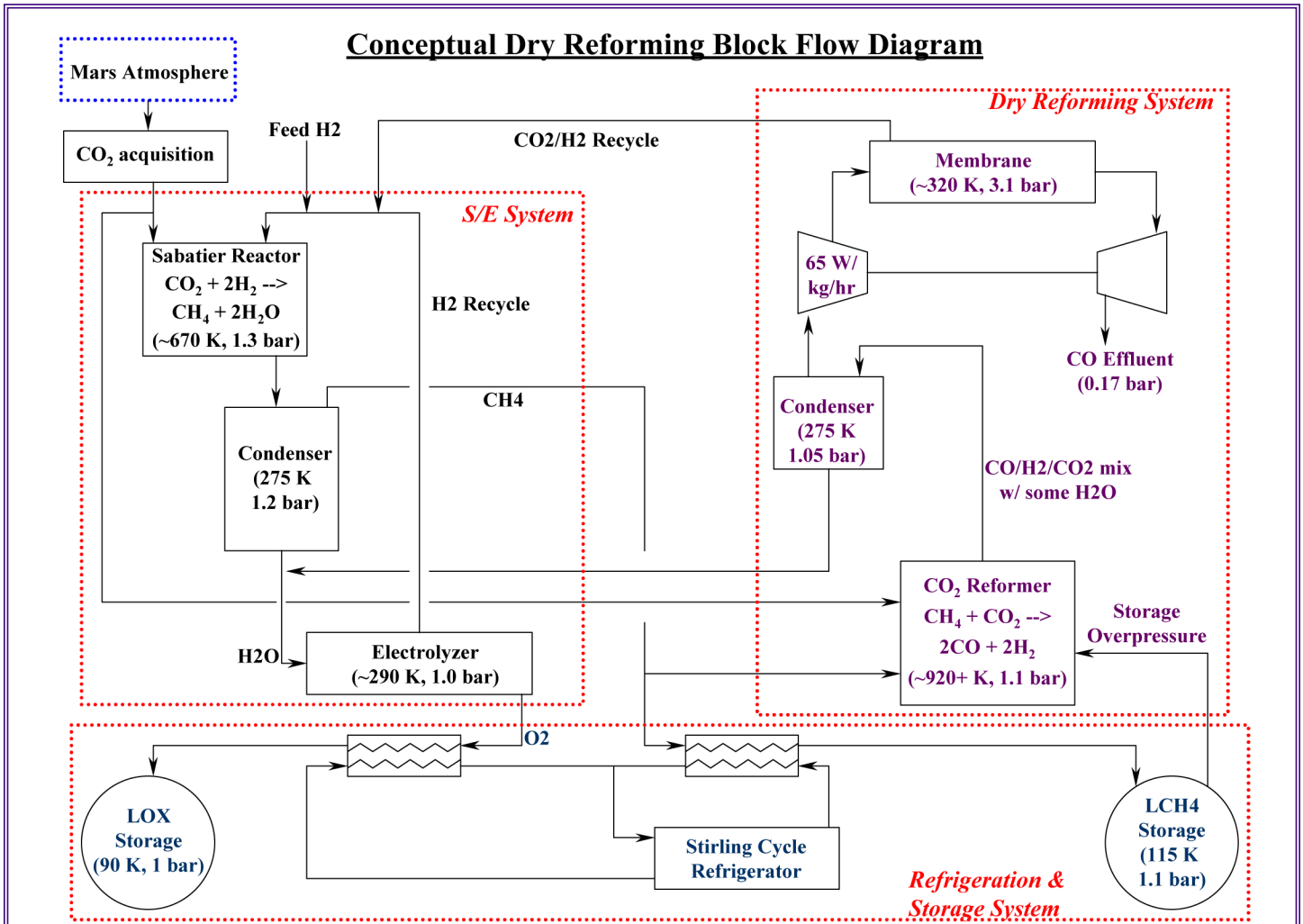
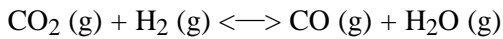


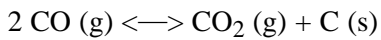
Figure 1. The proposed SEDR flowsheet.



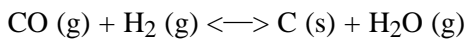
$$\text{DH} = + 9.85 \text{ kcal/mole}$$



$$\text{DH} = + 17.9 \text{ kcal/mole CH}_4$$

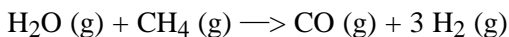


$$\text{DH} = - 41.2 \text{ kcal/mole CO}_2$$



$$\text{DH} = -31.4 \text{ kcal/mole}$$

Water formed from the gas shift will also promote the steam reforming reaction. This will be a secondary reaction since water content of the reactor is fairly low, and will also help convert feed methane to product. The equation for steam methane reforming is:



$$\text{DH} = +49.3 \text{ kcal/mole CH}_4$$

It's clear that the desired reaction system is very complex, which makes it difficult to design a reactor that achieves high and selective yields. Fortunately, we have a long history of Earthly industrial dry reforming practice and research to draw upon to help design a functional reactor, and to narrow the possible desirable operating regimes. In fact, several vendors offer commercial dry reformers for direct iron reduction industrial application. One of the leading vendors for this process is Midrex, a subsidiary of Kobe Steel Co., which produces dry reformers of up to 500 tons/day capacity.

These reformers use 510 tubes, each 250 mm diameter x 8 m length, filled with sulfur-passivated nickel-based heterogeneous catalyst. At tube temperatures in excess of 1,020°C (1,293°K), low pressure, and in the presence of the catalyst, the feed gases are reformed into hydrogen and carbon monoxide. These reducing gases are then sent to the shaft furnace for the reduction of the iron ore. A picture of the entire direct reduced iron process is shown in Figure 2.

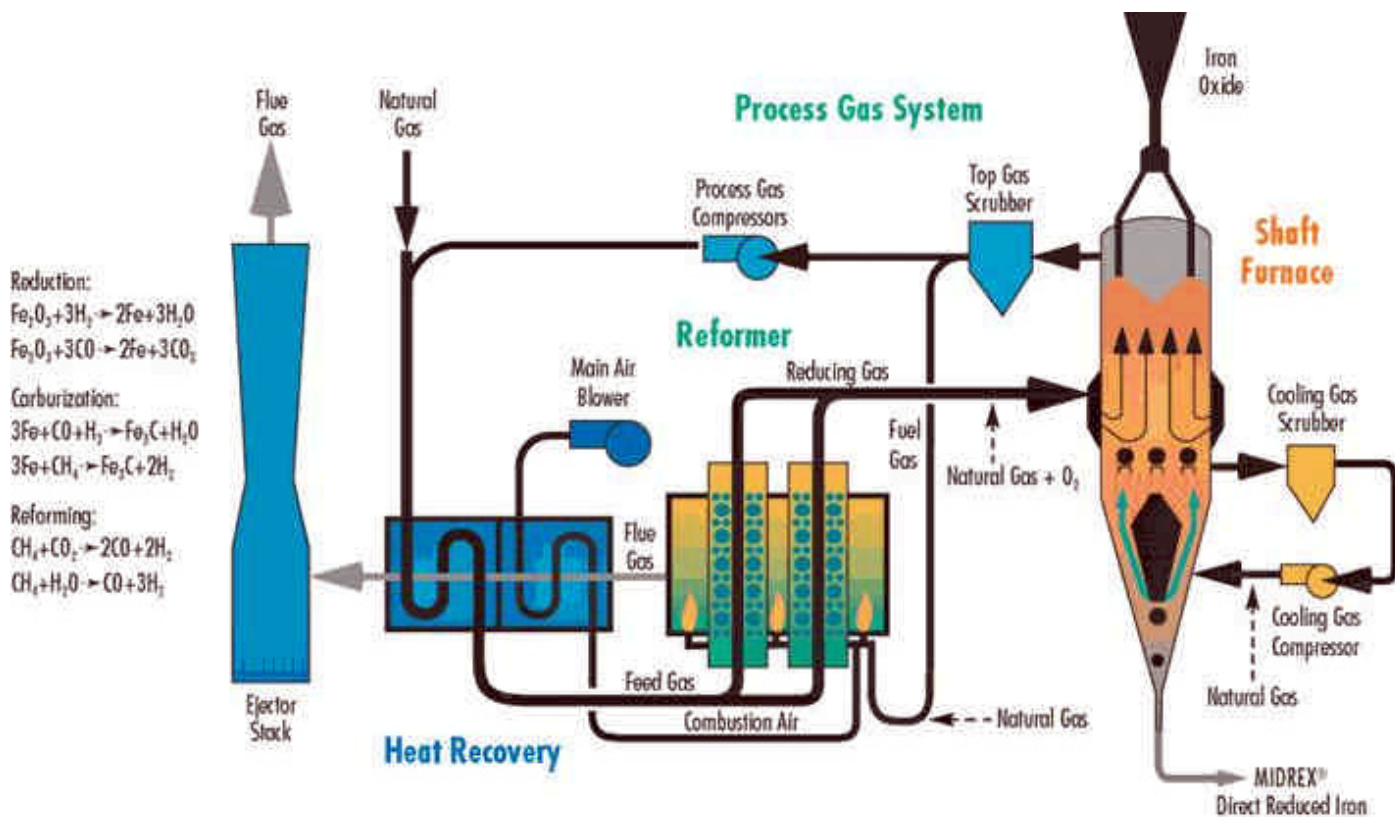


Figure 2. Direct Reduced Iron Process from the Midrex web site. The SEDR process can use a reformer based on that used in the Midrex process. The Midrex reformer is direct fired, which is not appropriate for the Mars ISRU system, but since the thermal energy in the ISRU reformer outlet is not required for iron reduction (as is the case in the Midrex process), this energy can be recaptured in the feed, allowing electrical heaters to supply the modest trim heating duty.

### Nickel Catalysts

The use of nickel catalyst is widespread for methane reforming reactions in industry, where the relatively low cost of the catalyst is a prime concern. However, nickel is very susceptible to coking reactions at modest temperatures. Typically, a small amount of sulfur is allowed to poison the nickel catalysts, which reduces the coking reactions substantially, while not interfering significantly with the reforming reactions. Nickel is also active for the water-gas shift reaction, so this reaction can be assumed to be at equilibrium. Midrex notes that there are two separate mechanisms for carbon deposition – thermal cracking of hydrocarbons (methane dehydrogenation) and dissociation of adsorbed carbon monoxide (the Boudouard and Beggs reactions). These two mechanisms have very different characteristics. Thermal cracking reactions are very endothermic and slow. They are favored by high temperature, long residence times of the base hydrocarbons at the elevated temperature, and acidic catalyst supports, such as alumina. Coke from these reactions tends to form along the wall of the tubes in fired reformers, where the temperature is highest. In contrast, the carbon monoxide deposition reactions are exothermic, tend to occur quickly in low temperature regions near the center of the tubes, and are inhibited by acidic catalyst supports. A chart of the equilibrium constants for the coking reactions over the typical reactor operating temperature range, along with the constants for the reforming and water gas shift reactions, is shown in Figure 3.

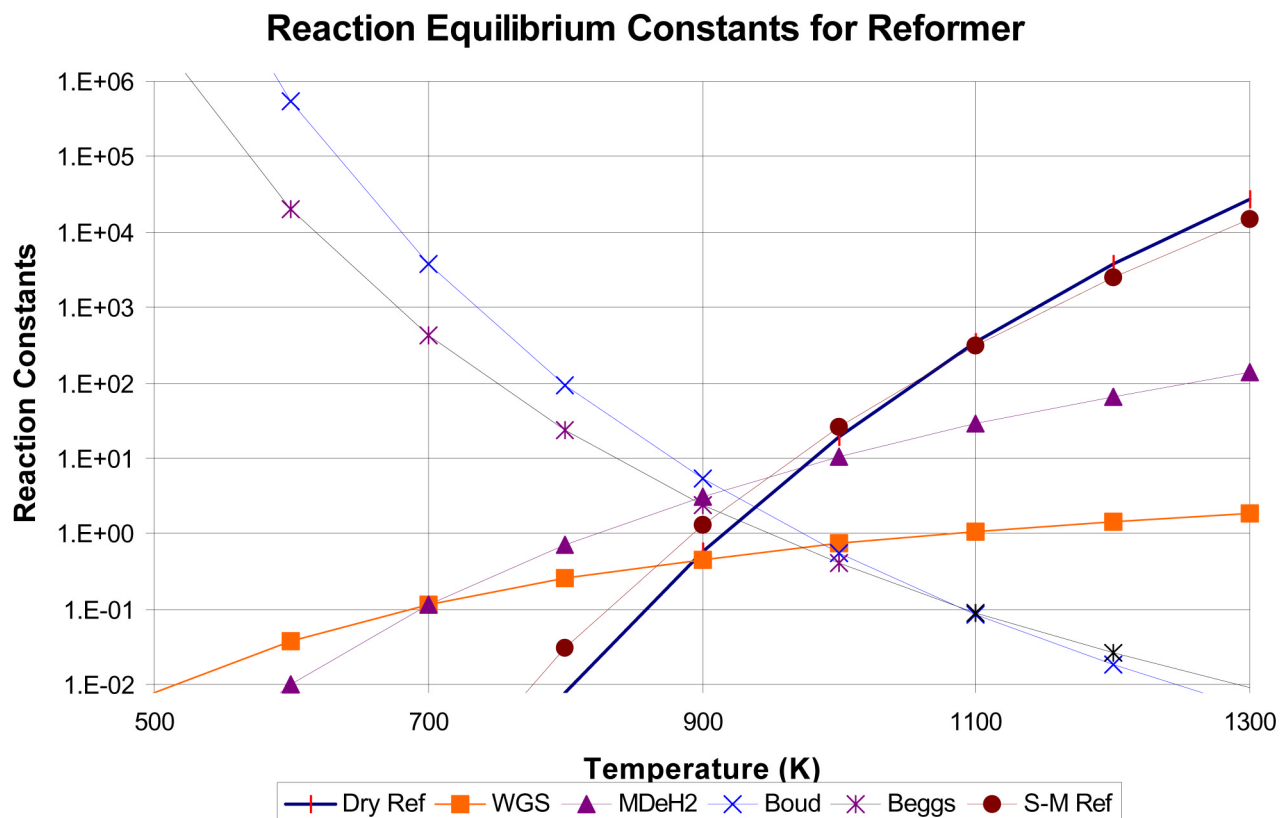


Figure 3. The equilibrium constants for reactions expected to impact the reformer design. Clearly this is a complex reaction system, with all six reaction equilibria of the same order at ~900°K. The two different types of potential coking reactions are also apparent, with the exothermic Beggs and Boudouard reactions quickly falling to insignificance above 900°K, while the endothermic dehydrogenation reaction competes with the desired reforming reactions. The water gas shift is only a weak function of temperature, barely varying over the temperature range of interest.

The characteristics of the reactions give strategies for eliminating the formation of coke in the reactor more than can be accomplished with simple sulfur passivation. To eliminate the dehydrogenation reaction, the catalyst should be maintained active so that hydrocarbons are reformed quickly and the production of cracked products is thermodynamically impossible. To eliminate the formation of carbon monoxide deposition products, the reactor temperature should be maintained high enough to make the thermodynamics unfavorable whenever there is carbon monoxide present.

In Midrex’ commercial reactors, elimination of carbon deposition is accomplished by two reaction stages in the tubes. The inlet of the reactor tubes heats up the feed gas very quickly over a low activity catalyst on a magnesia (basic) substrate. Thus, the region where carbon monoxide dissociation can occur is traversed very quickly over a catalyst that is not active enough for these reactions, and where there is a very low partial pressure of CO, since the reactants have not had time to reform. When the reactants reach a temperature high enough for hydrocarbon cracking to occur, the basic substrate inhibits this reaction, and the low activity nickel catalyst produces enough reforming reaction products quickly enough that cracking reactions become thermodynamically unfavorable – i.e., the partial pressure of methane falls and hydrogen increases, inhibiting this reaction pathway. However, the low catalyst activity prevents the endothermic reforming reactions from occurring fast enough to cool the reactor back into the CO deposition temperature range.

The second stage of the Midrex bed uses a high activity nickel-on-alumina catalyst. This allows the reforming reactions to proceed arbitrarily close to equilibrium, but there isn’t enough reactant left at the start of this zone for the reactions to cool into the CO deposition temperature range. In addition, the acidic substrate inhibits carbon deposition from CO dissociation.

Midrex' methodology, in effect, allows a near constant reaction rate through the length of the reactor tube, balancing the reforming reactions in a narrow temperature and reaction rate region between the exothermic CO deposition and endothermic cracking reactions. One of the disadvantages of this technique is that very fast heating is required in the inlet zone of the reactor tubes. Midrex accomplishes this with a direct fired heater, which is obviously impractical for a Mars apparatus. Solutions for a Mars reformer using nickel catalyst would be an enhanced heat transfer feed / effluent exchanger, such as the microchannel devices being developed at Pacific Northwest National Laboratory. However, the 1000+ degree C temperature required in the reformer makes the design of a microchannel exchanger a difficult technical challenge. A rigorous R&D effort would be required to solve the material concerns and verify that coking is prevented using the designed reaction profile over a nickel catalyst.

### **Precious Metal Catalysts**

If the technical challenges of a high temperature nickel based reformer prove too formidable, an alternative solution for a Mars system would be to scrap the nickel catalyst entirely in favor of a more selective catalyst. Numerous academic laboratories have studied carbon dioxide / methane reforming reactions over noble metal catalysts such as rhodium, rhenium, iridium, ruthenium, and platinum. Many variants have been found to be very active and selective for the reforming reactions at modest temperature, while resisting any carbon deposition. For example, an iridium on alumina catalyst allowed equilibrium reforming at 650 degrees C, without any carbon deposition. Iridium or ruthenium have also been found to be active on europium oxide supports without coke formation. Rhodium on alumina has displayed a high activity without carbon formation at low methane / CO<sub>2</sub> ratios. Platinum is also very active for the reforming reactions, but tends to coke readily. However, promotion of platinum with rhenium enhances the resistance to carbon deposition reactions without substantially impacting the reforming reactions, apparently by ensemble control of Pt site groupings that are required for carbon polymerization. In some respects, the Pt/Re combination resembles the performance of sulfur passivated nickel, but, of course, it is active at a much lower temperature. Overall, rhodium and ruthenium tend to display the highest selectivity for reforming reactions over carbon deposition reactions, although they are also the most expensive catalysts.

The issue of expense is significant; the precious metal catalysts are much more expensive than the nickel catalyst. However, since relatively small volumes will be required for even a massive Mars exploration effort, and since high transportation and development costs dominate the overall mission cost anyway, the catalyst cost may well be a secondary consideration. The lower temperatures from the precious metal catalysts will also benefit the Mars system, reducing maintenance and increasing the lifetime of reformer tubes, electrical heaters, and instrumentation in the furnace.

Thus, the question of whether carbon dioxide / methane reforming is a practical solution for a Mars ISRU mission architecture seems to have a positive answer. It is clear that there are techniques on Earth that allow this reforming reaction to be used in industrial applications with standard nickel catalyst. In theory, these techniques can be adapted to Mars ISRU applications. There are also experimental results that show promise for noble metal catalysts. A R&D effort is required to develop an optimal reactor design for a Mars ISRU application. At this time, it does not appear that any of the technical obstacles to a CO<sub>2</sub> / methane reformer for Mars will be intractable.

### **Other Process Unit Operations**

The reformer provides the majority of the technical challenge in the dry reforming system. However, a couple of other unit operations need to be mentioned.

### **Membrane**

A separation of the reformer products is required to allow produced carbon monoxide to exit the system. Numerous separation technologies are available, but the one that is likely to be most suitable for a Mars ISRU is a polymeric membrane. In previous work done at Pioneer Astronautics and Kennedy Space Center, polymer membranes provided efficient separation of CO from more permeable gases including CO<sub>2</sub> and hydrogen. The relative permeabilities (?) of these gases in commercially available polyimide membranes are order of 10 for CO<sub>2</sub> / CO and better than 25 for H<sub>2</sub> / CO. When the feed stream is compressed to a sufficient pressure to allow permeation, the desired species will preferentially

pass through the membrane to the low pressure permeate side. The residual stream (retentate) will be almost entirely carbon monoxide. Multiple membranes can be used in series to increase the purification of the permeate or retentate.

Note that methane typically also has a very low permeability in polymeric membranes, so any unreformed methane in the reactor effluent will be likely to vent with the carbon monoxide. As methane is an extremely valuable product, this makes it desirable to boost the reformer conversion as high as possible. A small amount of excess CO<sub>2</sub> in the reformer feed should effectively scavenge any methane in the reformer outlet, as well as reducing any tendency to coke.

### **Compression / Expansion**

Compression work is required to increase the reformer effluent to a pressure that will allow permeation of desirable products at a pressure high enough to return to the Sabatier system. However, the residual stream from the membrane will still be at high pressure. The available energy in the membrane retentate can be recovered in an expansion turbine and used to power the compression of the reformer effluent. Since the membrane retentate is being released at Martian atmospheric pressure (approximately 10 mbar), there is plenty of expansion work available, which can provide all the power necessary for the compression, with some excess generated power. This will reduce the amount of power required for the system, at the cost of increasing the complexity and number of moving parts. In addition, the easiest way to achieve the combined compression / expansion is with a centrifugal machine, which may not be appropriate at low ISRU flow rates.

The approximate power required to compress 1 kg/hr of reformer effluent is 69 Watts. To achieve the same power via an expansion turbine, about 0.937 kg/hr of carbon monoxide would be expanded to an outlet pressure of 0.17 bar. Both numbers assume 75% polytropic efficiency.

### **Energy Balance**

The SEDR system is a relatively modest consumer of power. The major portion of power is consumed in the water electrolysis and product liquefaction steps. The dry reformer is an endothermic reactor and requires some heat input, but only consumes a fraction of the power of the Sabatier system. For a system that produces 1 kg/hr of stoichiometric LOX / LCH<sub>4</sub> output (i.e., 4:1 mass ratio), the power required will be:

### **CO<sub>2</sub> Acquisition:**

The CO<sub>2</sub> acquisition system is difficult to estimate because there are many different techniques for acquiring CO<sub>2</sub>, which have widely varying energy requirements. Nevertheless, assuming some sort of carbon dioxide freezer is used, approximately 350 W will be used to collect 1.65 kg/hr of CO<sub>2</sub>, which will be used to manufacture 1.0 kg/hr of net LOX / LCH<sub>4</sub> product.

### **Sabatier:**

The Sabatier will have some startup heating requirements, but since the Sabatier reaction is exothermic, there will be net thermal energy production at 670°K from this unit. This thermal energy can be utilized elsewhere in the process, or can be used to generate power via thermoelectric generators. The Sabatier reactor will produce a total of 1.13 kW per kg of net LOX / LCH<sub>4</sub> product.

### **Electrolysis:**

Assuming 85% efficiency, the electrolyzer requires 6.58 kW electrical power per kg/hr of liquid oxygen production, or about 5.26 kW per kg/hr of net LOX / LCH<sub>4</sub> product.

### **Reformer:**

The reformer is an endothermic reactor that requires thermal energy at more than 920°K. Assuming this is provided with resistive heaters with near 100% efficiency, the reformer needs 1.14 kW electric power per kg/hr processed through the reformer. Since the reformer only needs to process 0.75 kg per kg of net LOX / LCH<sub>4</sub> production at a 4:1 LOX / LCH<sub>4</sub> mass ratio, only 0.85 kW electric power are required per kg/hr of net LOX / LCH<sub>4</sub> product.

**Compression:**

As mentioned in the previous section, the compression power is about 69 Watts per kg/hr processed in the reformer. For the desired mass ratio, this means about 52 Watts of shaft work per kg/hr of net LOX / LCH<sub>4</sub> product. However, this amount of power will be recovered in the expansion turbine, leaving no net power consumption by the reformer compressor.

**Refrigeration:**

A Stirling cycle refrigerator is used for both the LOX and LCH<sub>4</sub> liquefaction, and the Stirling can achieve 20% of Carnot efficiency at the condensing temperatures of these two components. Assuming negligible heat leak, the power consumption of the refrigeration system will be 0.95 kW of power per kg/hr LOX production and 1.30 kW of power per kg/hr of LCH<sub>4</sub> production. The overall net power consumption for one kg/hr of LOX / LCH<sub>4</sub> in a 4:1 mass ratio is 1.02 kW.

The results of the energy balance are shown in Table 1.

Table 1. Power consumption of SEDR subsystems operating at 4:1 LOX / LCH<sub>4</sub> mass ratio

Subsystem	Energy Usage (kW-hr/kg net production)	Energy Form
CO <sub>2</sub> acquisition	0.35	Thermal and electrical power
Sabatier reactor	- 1.13	Thermal energy at 670 K
Electrolysis	5.26	Electrical power
Reforming reactor	0.85	Thermal energy at 920+ K
Recycle compressor	0.052	Shaft work
Waste product expander	- 0.052	Shaft work
Refrigeration	1.02	Electrical power
<b>Total</b>	<b>7.48</b>	

**Scaling of SEDR System**

The entire SEDR system is highly scalable, by simply adjusting the volume of the reformer, the size of the flow passages in the compressor, and the area of the membrane separator. The largest dry reformers currently in operation process more than 500 tons/day. Considering that the first generation Mars ISRU systems being considered for robotic missions are potentially going to generate on order of 1 kg production per day, it's apparent that it will be a long time indeed before capacity constraints are a problem.

But is it possible to scale the system down? Large industrial units generally operate much less effectively at extremely small scales. However, the case is probably not as extreme as that suggested above for the robotic scale ISRU systems. It's likely that the additional complexity of the SEDR system, relative to the S/E, will require human attention, at least on occasion. Thus, the dry reformer will probably only be of use for the first ISRU systems that support a human presence on the Red Planet – second generation systems. The human support ISRU systems should produce on order of 10's of kg per hour, or 100 times the scale of the robotic precursor ISRU systems. This will be a perfectly suitable scale for the dry reformer system, particularly as one dry reformer might process the output of several Sabatier systems.

**Retrofitting a Reformer in an Existing S/E System**

As noted in the previous sections, the SEDR flowsheet is significantly more complex than a simple Sabatier / Electrolysis flowsheet, which is currently one of the leading candidates for a first generation Mars ISRU system. However, the SEDR overcomes many of the objections to the S/E system, most particularly the low mass leverage caused by a less-than-optimum product stoichiometry, and the inability of the S/E to effectively produce oxygen. These factors suggest that a working dry reformer is a likely candidate for an early second generation ISRU system. Retrofitting one or more S/E systems with a dry reformer offers an intriguing means to dramatically increase the flexibility and usefulness of the ISRU concept by adding lightweight modules as Mars efforts grow more ambitious. In effect, the SEDR can grow as the Mars program effort grows.

The task of retrofitting a S/E unit with a dry reformer can be accomplished with minimal preinvestment. Only five physical tie ins are required:

- 1) The CO<sub>2</sub> feed from the acquisition unit to the reformer
- 2) The methane slipstream from the S/E condenser to the reformer
- 3) The methane overpressure from LCH<sub>4</sub> storage to the reformer
- 4) The recycle stream returning CO<sub>2</sub> and H<sub>2</sub> to the Sabatier unit
- 5) Water from the reformer system condenser to the electrolyzer

The control systems for the Sabatier unit will require a small amount of prework to prepare for a reformer extension unit. Extra connections on the S/E control system bus will allow the reformer to be tied in with minimal fuss. And the control software should be written to allow operation of the fully integrated SEDR system from the start of operation. The software will still operate normally before the SEDR system is added, as this will simply be the special case of zero flow to the methane slipstream.

A slight physical oversizing is desirable for the Sabatier / Electrolysis unit, relative to the base case without preinvestment for the dry reformer. Such an oversizing of the electrolyzer and Sabatier reactor will allow the SEDR system to operate at the same overall mass throughput as the S/E system, despite the fact that the product slate is switched to a higher LOX / LCH<sub>4</sub> ratio. If the electrolyzer (in particular) is not oversized, then it will be the overall process bottleneck, and the addition of the dry reformer will merely decrease the methane production rate while maintaining constant LOX production. Note that the refrigerator does not have to be oversized, as the overall production of the SEDR is approximately the same as the S/E system. However, some of the refrigeration duty will be switched from the LCH<sub>4</sub> to the LOX.

### Process Extensions

The dry reformer is a logical extension to add to the base Sabatier / Electrolysis unit. However, it is not the final say in process extensions. The SEDR system allows extraction of oxygen from CO<sub>2</sub>, with venting of the resulting CO. But CO will be a valuable product on Mars in the future. With an additional source of hydrogen, it can be used to produce Fischer-Tropsch hydrocarbons or alcohols. It can also be used as a reducing agent for the direct reduction of iron. These types of units can be added to the SEDR system in a modular fashion as Mars base requirements and resources expand. These process additions will allow a SEDR system to be a flexible ISRU option far into the future.

The fundamental difference in the dry reformer is that it allows mission planners to start thinking of an *integrated* series of Mars missions, rather than a series of *standalone* Mars missions. This is enabled by thinking of ISRU units on the Martian surface as valuable, extendible assets, rather than as use-and-abandon hardware. With appropriate preplanning, these assets can be utilized far into the future, tremendously increasing the cost effectiveness of Mars exploration and base building programs.

### Conclusion

The SEDR provides a technology for application to second generation (first human support capacity) Martian ISRU fuel production systems based on the Sabatier reaction. The advantages of the dry reformer added to the Sabatier reactor are many, including increased mass leverage and the ability to vary the product slate on the fly to produce excess quantities of oxygen.

The dry reformer has a complex set of reactions occurring in it, including a troubling set of carbon deposition reactions. However, there is a well-proven heritage of reformer operation on Earth that provides an excellent basis for design of the reactor. Existing reactors utilize nickel based catalysts with numerous design features to reduce carbon deposition. These features include sulfur passivation, and division into different reaction zones to control the concentration of reactants and the rate of reaction. In addition to the standard nickel-based industrial catalysts, a considerable amount of academic work has been performed on noble metal catalysts. Although too expensive for terrestrial use, a modest size Martian ISRU unit would be able to afford these catalysts, which are active for reforming at modest temperatures while providing excellent resistance to coking.

Integration of the reformer into an existing Sabatier unit will be quite easy with minimal preinvestment. A number of physical tie ins and control system modifications will be required, but the total effort will be a small percentage of the complete Sabatier design. In addition, the reformer will prove to be easily scalable, and further process units can extend its usefulness.

Planning to incorporate a dry reformer into a Sabatier system should take place immediately. Provision for retrofitting the Sabatier unit used in NASA's Mars Design Reference Mission with a reformer would be a minor engineering effort and would provide significant returns. The engineering effort would involve revision of existing Sabatier unit drawings and a change in the control software. A further R&D effort to determine the proper design of the reformer should be implemented. With this modest effort, the usefulness of the Sabatier ISRU concept would be tremendously extended, and ISRU could finally start to realize its promise to open the Martian frontier.

### Technical Appendix

Thermodynamic properties of reformer reactions.

Enthalpy of Reaction (cal/mol)						
Temp (°K)	Dry Ref	WGS	MDeH2	Boud	Beggs	S-M Ref
298	59140	9852	17890	-41250	-31398	49288
400	60041	9739	18610	-41431	-31692	50302
500	60755	9551	19282	-41473	-31922	51203
600	61334	9322	19901	-41433	-32111	52012
700	61792	9069	20458	-41334	-32265	52724
800	62137	8800	20950	-41187	-32387	53337
900	62371	8523	21374	-40997	-32474	53848
1000	62498	8243	21728	-40770	-32527	54255
1100	62519	7963	22012	-40507	-32543	54555
1200	62434	7689	22225	-40209	-32520	54745
1300	62245	7422	22367	-39878	-32456	54823

Gibbs Free Energy of Reaction (cal/mol)						
Temp (°K)	Dry Ref	WGS	MDeH2	Boud	Beggs	S-M Ref
298	40800	6825	12140	-28660	-21835	33975
400	34378	5803	10060	-24317	-18514	28575
500	27876	4840	7844	-20032	-15192	23036
600	21244	3918	5498	-15746	-11828	17326
700	14524	3037	3052	-11472	-8435	11487
800	7747	2194	531	-7216	-5022	5553
900	933	1385	-2047	-2981	-1596	-452
1000	-5901	607	-4669	1232	1838	-6508
1100	-12743	-143	-7323	5419	5276	-12600
1200	-19582	-868	-10000	9582	8714	-18714
1300	-26410	-1570	-12692	13718	12147	-24839

Reaction Equilibrium Constants						
Temp (°K)	Dry Ref	WGS	MDeH2	Boud	Beggs	S-M Ref
298	0.000	0.000	0.000	1.049E+21	1.035E+16	0.000
400	0.000	0.001	0.000	1.939E+13	1.308E+10	0.000
500	0.000	0.008	0.000	5.711E+08	4.376E+06	0.000
600	0.000	0.037	0.010	544640.12	20358.29	0.000
700	0.000	0.113	0.111	3820.74	430.26	0.000
800	0.008	0.252	0.716	93.645	23.552	0.030
900	0.593	0.461	3.142	5.295	2.441	1.287
1000	19.489	0.737	10.485	0.538	0.396	26.45
1100	340.387	1.068	28.521	0.084	0.089	318.8
1200	3686.644	1.439	66.290	0.018	0.026	2561.7
1300	27555.792	1.836	136.110	0.005	0.009	15004.8

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