

FEASIBILITY STUDY OF VENUS SURFACE COOLING USING CHEMICAL REACTIONS WITH THE ATMOSPHERE

Christopher Evans¹
NASA Marshall Space Flight Center

ABSTRACT

A literature search and theoretical analysis were conducted to investigate the feasibility of cooling a craft on Venus through chemical reformation of materials from the atmosphere. The core concept was to take carbon dioxide (CO₂) from the Venus atmosphere and chemically reform it into simpler compounds such as carbon, oxygen, and carbon monoxide. This process is endothermic, taking energy from the surroundings to produce a cooling effect. A literature search was performed to document possible routes for achieving the desired reactions. Analyses indicated that on Venus, this concept could theoretically be used to produce cooling, but would not perform as well as a conventional heat pump. For environments other than Venus, the low theoretical performance limits general applicability of this concept, however this approach to cooling may be useful in niche applications. Analysis indicated that environments with particular atmospheric compositions and temperatures could allow a similar cooling system to operate with very good performance. This approach to cooling may also be useful where the products of reaction are also desirable, or for missions where design simplicity is valued. Conceptual designs for Venus cooling systems were developed using a modified concept, in which an expendable reactant supply would be used to promote more energetically favorable reactions with the ambient CO₂, providing cooling for a more limited duration. This approach does not have the same performance issues, but the use of expendable supplies increases the mass requirements and limits the operating lifetime. This paper summarizes the findings of the literature search and corresponding analyses of the various cooling options.

INTRODUCTION

Surface missions to Venus are extremely difficult due to the harsh environment. Surface temperatures can exceed 460°C (860°F), the ambient pressure is 93 times that of Earth, and the atmosphere itself is corrosive. The high temperatures are perhaps the greatest challenge, as they quickly cause overheating and thermal failure of electronics and other equipment. As such, previous surface missions have been very short in duration, lasting mere hours. There is considerable interest in conducting a longer surface mission to the planet, with a duration of one year or more. Heat pumps can be used for cooling in the Venus atmosphere and have been proposed for such a mission, but because of the extreme conditions, the laws of thermodynamics dictate that such a device would be extremely inefficient. The Carnot limit on

¹christopher.j.evans@nasa.gov

the coefficient of performance for a refrigerating heat pump is a function of the difference in temperatures, as given by the equation:

$$COP_{Carnot} = \frac{T_L}{T_H - T_L} \quad (1)$$

Where T_L is the cold reservoir temperature and T_H is the hot reservoir temperature. For example, if a refrigerating heat pump is used to keep a payload at 50°C against the 460°C outside temperature, the maximum (Carnot) coefficient of performance for a perfect device is less than 0.8, meaning each Joule of electrical energy expended removes less than 0.8 Joules of heat. A real system would attain only a fraction of this maximum performance, removing far less than 0.8 Joules of heat per Joule of electrical energy. For comparison, the Carnot limit for a refrigerator on Earth might be ten times as high, with real devices achieving up to half the theoretical performance limit. Developing a heat pump for Venus is also challenging because of the need to identify suitable materials and working fluids, and to construct a system with sufficient tolerances to withstand the high pressures, high temperatures, and corrosive substances in the Venus environment.

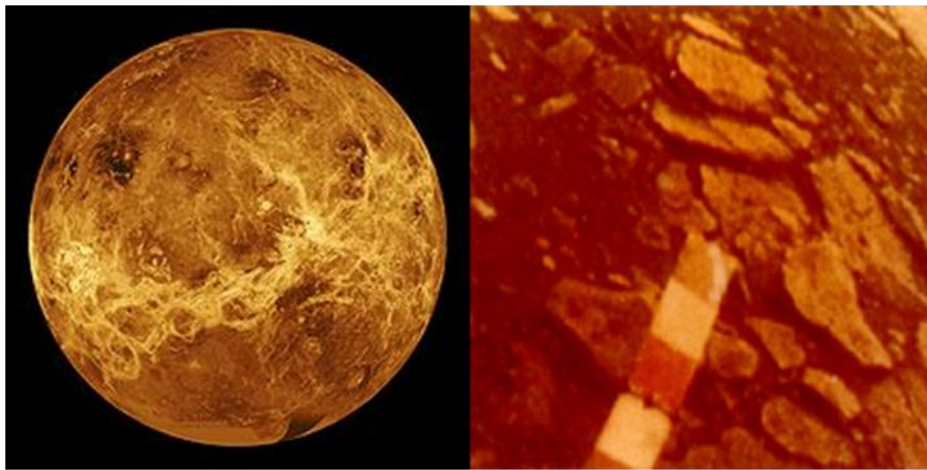


Figure 1. Planet Venus. Left: Magellan radar map. Right: Venera 13 surface image.

A possible alternative is to approach the problem through chemistry. The atmosphere of Venus is composed primarily of carbon dioxide. Carbon dioxide is commonly produced through combustion of carbon-containing compounds, a process which releases thermal energy and heats the surroundings. However, this process can also be reversed: carbon dioxide can be broken apart and reformed into carbon compounds and oxygen. The reaction is endothermic, absorbing energy from the surroundings to give a cooling effect. This "reverse combustion" process could allow the Venus atmosphere to be exploited for the purpose of cooling. Using a chemical process rather than a mechanical one opens the door to a wider variety of system designs, some of which may be easier to implement or more robust in the Venus environment. Chemical processes are also subject to different theoretical limits on performance, as demonstrated by the example of fuel cells. Many fuel cells have efficiencies that far exceed the

Carnot limits for a heat engine using similar fuel, raising the possibility that a chemical cooling system could also exceed the Carnot performance limit for a mechanical heat pump.

The overarching goal of this study was to evaluate the feasibility of cooling a craft on Venus via chemical reformation of the surrounding atmosphere, and to the extent possible to evaluate the feasibility of using this technique for cooling in other environments.

METHODOLOGY

An extensive literature search was performed to examine different methods and processes for chemically reforming CO₂ into other compounds. The idealized concept under investigation for this effort was one in which only materials from the Venus atmosphere would be used. Some quantity of energy would be supplied to drive the process, but no consumable reactants would be used. As such, processes were sought that could produce one of two net reactions:



That is, decomposing carbon dioxide into either solid carbon and oxygen, or carbon monoxide and oxygen. The reaction to solid carbon and oxygen is more endothermic than the reaction to carbon monoxide and oxygen (requiring 393.5 kJ/mol CO₂ vs. 283 kJ/mol CO₂), which gives it greater cooling ability. However, it also has the major drawback of producing solid carbon, which is very difficult to move through a system and tends to form problematic deposits. The reaction to carbon monoxide and oxygen, while not quite as endothermic, still absorbs a great deal of energy and produces only gaseous products, which are much easier to handle. For this reason, the carbon monoxide and oxygen route was preferred, although both were studied. Although the constituent elements of CO₂, carbon and oxygen, can in principle also be combined into other compounds via endothermic processes, the more exotic compounds of these elements are very unstable and therefore unlikely to be useful for this application.

The CO₂ reformation processes found in the search were then evaluated to determine their suitability for use in a cooling system on Venus. Surface conditions on Venus include a pressure of 93 atm, temperature of 460°C, and composition of almost entirely CO₂. The payload of the cooled craft was expected to require a temperature of 50-100°C. To provide the desired cooling, the most viable option is to design the CO₂ decomposition reaction to occur at a temperature lower than that of the surroundings – that is, lower than 460°C. In this way, the reaction zone would provide a lower temperature sink for the heat produced by the payload, which allows for more efficient heat rejection.

In some cases, evaluating the potential of a given process required more detailed thermodynamic data than what was available in the literature. To close this data gap, a basic equilibrium solver was developed in MATLAB. Given reaction parameters and thermodynamic

data for the component species, the solver was capable of calculating the changes in enthalpy, entropy, and Gibbs energy, and to determine the equilibrium composition of a mixture, all for a range of temperatures.

RESULTS & DISCUSSION

Theoretical Analysis

The concept under study is a highly novel application of chemistry; as a result, it was unclear early in the project what the theoretical limits of such a cooling system might be or how to calculate them. Insight into this question was provided in a paper by Nigara and Cales¹, whose analysis we extrapolated to our application.

The energy balance for a chemical reaction is described by the equation

$$\Delta H = \Delta G + T\Delta S \quad (4)$$

Here ΔH is the change in enthalpy between the products and reactants, ΔG is the change in Gibbs free energy, T is the temperature, and ΔS is the change in entropy. For an endothermic reaction like the decomposition of CO_2 , ΔH is the energy input needed to make the reaction happen. From the Nigara and Cales paper¹, the amount of energy that can be supplied by heat from the surroundings is given by $T\Delta S$. The remainder must be supplied by ΔG , the Gibbs energy, which represents a more ordered energy input such as electricity or mechanical action. ΔH , ΔG , and ΔS for a given reaction can be calculated via thermodynamics tables by comparing the H , G , and S values for the reactants and products.

This can be extended to provide a method of calculating the potential coefficient of performance for a chemical cooling process, which would allow direct comparison with a conventional mechanical heat pump. The performance of a heat pump is quantified as the coefficient of performance (COP), which is defined as the heat removed per unit of work input. For an endothermic chemical reaction, the heat removed is $T\Delta S$, while the work input needed to make the reaction occur is ΔG . Therefore, the COP can be calculated as

$$COP = \frac{\text{heat removed}}{\text{work input}} = \frac{T\Delta S}{\Delta G} \quad (5)$$

Figure 2 shows the trends in these values over a range of temperatures for the reaction under study, $\text{CO}_2 \rightarrow \text{CO} + \frac{1}{2}\text{O}_2$. This analysis holds whether the reaction occurs in one step or through multiple intermediate steps, as the overall reaction is what matters from an energy standpoint.

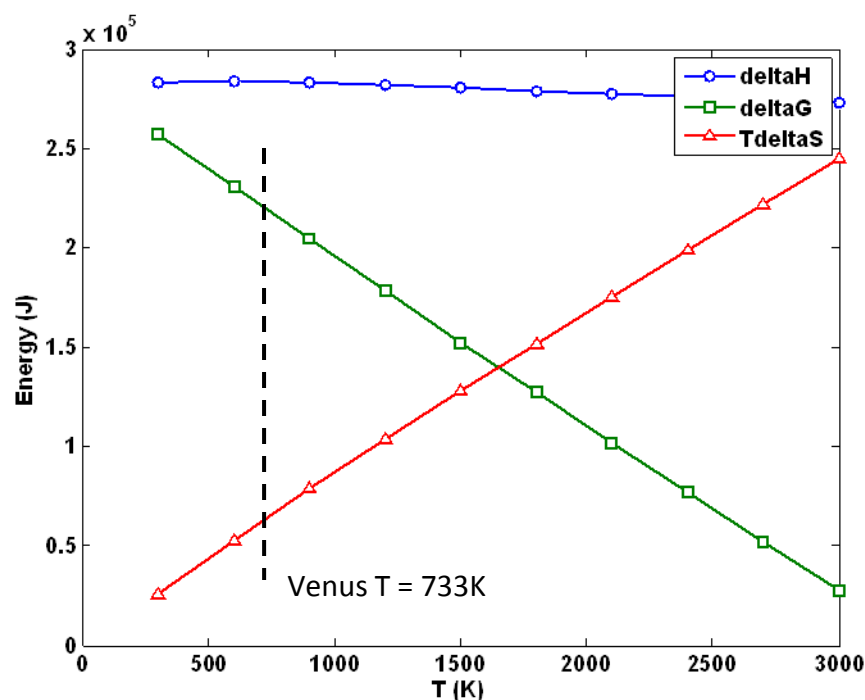


Figure 2. Changes in enthalpy, Gibbs energy, and the product of temperature and entropy over a range of temperatures for the decomposition of carbon dioxide into carbon monoxide and oxygen.

As seen in the figure, $T\Delta S$ is small at low temperatures, but increases with increasing temperature. For ΔG the trend is opposite: large at low temperatures, and decreasing as temperature increases. The clear trend is that the higher the temperature, the higher the potential COP. At the surface of Venus, the temperature is 460°C , or 733K . Unfortunately, this is a relatively low temperature for this reaction. At 733K , the COP for cooling by chemical reformation is calculated to be only 0.29. For comparison, a mechanical heat pump keeping a craft payload at 100°C against an atmospheric temperature of 460°C has a Carnot or maximum COP of about 1. Even in the best case, the theoretical analysis indicates that the chemical cooling system would be outperformed by a conventional heat pump. Moreover, it should be noted that this maximum COP is for a reaction continually maintained at 733K - the same temperature as the atmosphere. This would reform the CO_2 passing through it, but would not provide a cooling benefit to a lower-temperature payload. To provide a cooling benefit, the reaction would need to be run at a lower temperature than the atmosphere, so that it can provide a lower temperature region for heat rejection. Lowering the reaction temperature would reduce the COP, so a practical system would have a maximum theoretical COP of less than the already poor value of 0.29, even before inefficiencies are considered. Since a conventional heat pump has greater potential performance, the theoretical analysis indicates that a chemical cooling approach is not an ideal strategy at Venus conditions. However, the analysis shows that the core concept, of driving an endothermic chemical reaction to provide

cooling, is indeed possible. The next section examines the benefits this method might offer as a tradeoff for the poorer performance.

Beyond the issue of cooling on Venus, this analysis also helps answer the more general question of whether chemical cooling can be useful given the right circumstances. The analysis suggests that given appropriate conditions, chemical cooling can indeed be a viable, high-performance technique. Consider a planet with an atmosphere of CO₂, but with a much higher temperature than Venus. As Fig. 2 shows, at high temperatures ΔG can be much larger than $T\Delta S$, enabling a high COP for the chemical approach. Different atmospheric compositions would also allow for other endothermic reactions, which would have their own ranges of temperatures at which they could provide efficient cooling. There are environmental conditions under which chemical cooling can be viable and efficient, but they may be rare, as particular combinations of atmospheric composition and ambient temperatures are required. The applicability of chemical cooling for a particular environment must be determined on a case by case basis, but with the analysis methodology used here it can be a relatively simple process.

Reformation Processes

Theoretical analysis shows that providing cooling by forcing the decomposition of CO₂ is possible; the next question is how it could be achieved in practice. CO₂ can be chemically reformed into CO and O₂ via numerous methods and processes. A few of the most applicable techniques uncovered during our literature search are highlighted here.

Thermal decomposition

Thermal decomposition occurs when molecules have sufficient kinetic energy to break their molecular bonds through collision or simply vibration. As the CO₂ molecules break apart, they absorb energy from the surroundings, providing cooling. Thermal decomposition occurs at any temperature, but only to the point of chemical equilibrium – at low temperatures, few molecules have enough energy to decompose, while at higher temperatures more do. Catalysts can speed up the rate of reaction, but will not affect the equilibrium composition. By itself, this method is unlikely to be useful for cooling on Venus or elsewhere. Mechanical compression and expansion could be used to elevate the gas temperature and promote decomposition, but this type of manipulation works in essentially the same way as a mechanical heat pump while giving poorer performance, as noted above. However, there is potential for use if the CO and O₂ products were highly desired. A system engineered to produce them could also be designed to provide a small amount of cooling as a side benefit.

Separation of products

This technique is in some ways an augmentation to thermal decomposition. By removing the products of reaction as they are formed, a reaction can be made to proceed past the normal equilibrium. Chemical reactions are normally limited by equilibrium. As reactants are consumed to form products, the rate of reaction gradually slows down, and finally stops completely when the composition of reactants and products in the mixture matches the equilibrium composition for the system's temperature and pressure. If the reactants are separated out, however, the system will no longer be at equilibrium, and the reaction can continue. Separation can be active (e.g. a centrifuge) or passive (e.g. a selectively permeable membrane). In either case, there must be a "sink" to which the products can be rejected (for example, a purge gas flow). If the sink has a lower concentration of the product species, separation can be fully passive as diffusion will cause the product molecules to flow out to an area of lower concentration of their own accord. If the sink does not have a lower concentration of the product species, work must be done to force the products out of the system, for example via compression. Assuming separation can be accomplished, the reaction itself will proceed to completion with only heat input.

From the perspective of providing cooling, product separation is perhaps the most promising method of reforming CO₂. All of the energy needed to make the reaction happen can be supplied by heat, and in principle the reaction can be done at any temperature. Unfortunately, a few issues prevent this method from being feasible for use on Venus. One issue is technological. For this to work, membranes which can selectively and passively separate CO and O₂ from a CO₂ stream would be required. Such devices are permitted by physics, but the technologies are not yet mature and may never reach the needed level of performance. The other issue that holds back this option is the lack of an effective sink for the products of reaction. According to equilibrium, CO₂ decomposition and CO/O₂ concentration will increase with increasing temperatures. The atmosphere of Venus is essentially all CO₂ at 460°C, whereas the cooling system would operate its CO₂ reaction at a lower temperature. As a result, the concentration of products in the atmosphere is higher than what would be produced by our reaction in the cooling system, so the reaction products will not passively flow out through diffusion. Work would be required to separate and force the products out. The energy needed for this work input would likely erase the cooling benefits from the reaction. On Venus, providing cooling through product separation would only be possible if a purge gas were somehow available from other components on the craft, for example the exhaust from an engine. In that case a small amount of cooling could be realized. Outside of Venus, product separation could be a viable method of cooling in environments with access to regions of different chemical composition – for example, with gas pockets like those commonly found underground, or perhaps at a gas/liquid interface.

Electrochemical

Here a direct input of electricity supplies the energy needed to break CO₂ apart. In electrolysis, the electricity is delivered by means of electrodes inserted into a conductive solution of reactants. As current is applied, O₂ is formed at one electrode, and the other product (CO or solid carbon) forms at the other electrode. This has the added benefit of separating the products from each other as they are formed. Devices such as regenerative fuel cells also fall into this category.

A cooling system built around reforming CO₂ with this technique could be far more simple and robust than a conventional heat pump. The system could be entirely solid state, with no moving parts or concerns about seals and working fluids. In principle, it could be as simple as a pair of electrodes. The ease of separation makes harvesting pure CO or O₂ for other uses possible as well. Current electrolysis systems suffer from poor efficiency, often wasting more electricity as heat than what is used to break molecules – an even more major fault for a cooling system. Future advances may improve the technology, perhaps through microscale fabrication or developments in regenerative fuel cells. If so, this might enable an alternative cooling system that offers simplicity and reliability as a trade-off for lower performance.

Revised Approach: Finite-use System with Expendable Reactants

Since the theoretical analysis showed that our intended strategy would have poor performance, we revised our approach to achieving chemical cooling. The original goal was to have a fully reusable system with no expendable materials, which would be capable of running as long as it had an energy source. For our revised approach, we allowed for a limited supply of additional reactants which would be consumed during operation of the system. This makes the system operable for a limited duration rather than the indefinite period originally envisioned, but opens the door to a wider selection of chemical reactions that may allow for easier and more efficient cooling.

In order to limit the quantity of reactants that would need to be carried, as well as make a system suited to Venus, we attempted to devise a setup that would require only one carried reactant and would be able to use CO₂ from the atmosphere of Venus. This led us to the reverse water gas shift reaction:



This reaction is endothermic and would only require a hydrogen supply to be carried along, which could be combined with CO₂ taken from the atmosphere. Like most endothermic reactions, it is not favored by equilibrium at the temperatures we might consider. However, equilibrium principles can be used to get around this issue: by using uneven ratios of the

reactants (for example, a 10:1 ratio of H_2 to CO_2), the reaction can be made to occur even at low temperatures, as equilibrium would favor consumption of the scarcer reactant.

Using an expendable reactant supply in this manner is conceptually similar to using a phase change material. In each case, the craft carries finite amount of material that undergoes a transformation, absorbing heat in the process, and is then discarded. This similarity allows a performance comparison to be made. Consider a craft on Venus which uses a tank of water for phase-change cooling. The water tank might start at 25°C and 93 atm (the ambient pressure), and be released as steam when it reaches ambient conditions (460°C , 93 atm). In the process, the water absorbs 3.17 kJ of heat per gram of water. Now consider a tank of hydrogen used for cooling instead. The H_2 tank starts under the same conditions, 25°C and 93 atm, and undergoes the chemical process above: it is combined with CO_2 from the atmosphere to form H_2O and CO , which are released when they reach ambient conditions (460°C , 93 atm), just like the water case. With the chemical process, 18.75 kJ of heat are absorbed per gram of H_2 used. This is nearly six times the heat absorption of water, for an equal mass of material. It should be noted that while the hydrogen option is attractive on a mass basis, this option would likely not trade as well on a volume basis since hydrogen is much more difficult to compress and store than water. However, it helps to illustrate the potential of a chemical cooling process that utilizes local atmospheric materials.

Two design concepts were developed around this approach. One was intended to be feasible with current technology, while the other was intended to be an optimum implementation of chemical cooling (which unfortunately requires technologies that are not mature). The method that can be implemented with current technology is an enhancement to a heat pump. The optimal implementation uses the hydrogen supply as a close analogue to a phase change material.

Enhancement to heat pump – possible with current technology

Figure 3 shows the conceptual design for this implementation, in which an endothermic reaction is used to improve the performance of a heat pump by creating a low-temperature sink for heat rejection. Here a conventional heat pump is used to reject heat from the craft's payload. Rather than rejecting heat to the environment, however, it rejects heat to a gas stream which is given a reduced temperature by means of an endothermic reaction.

The system works as follows. CO_2 is drawn in from the environment, and mixed with a small flow of H_2 from the onboard tank. The flow rate of CO_2 is much larger than the flow rate of H_2 , so that equilibrium will favor reaction to products. The reactants pass through a catalyst, which causes reaction to CO and H_2O and decreases the temperature of the gas stream. The gas stream then passes through a heat exchanger, where it receives heat rejected from the payload, and is expelled back into the environment.

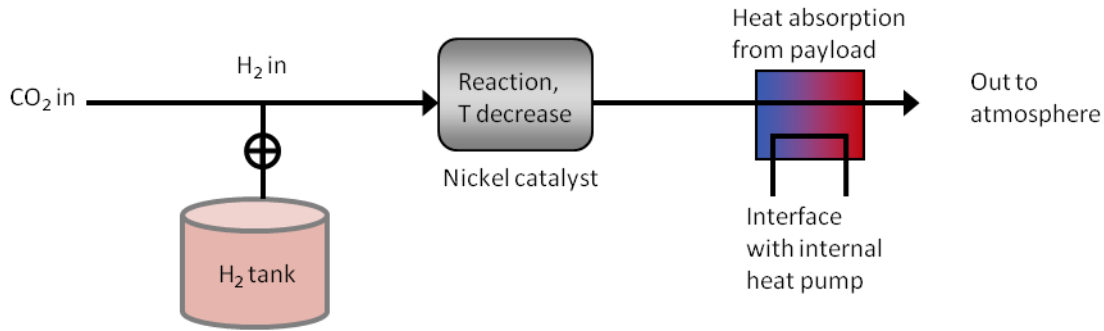


Figure 3. Conceptual design for a system that uses a supply of hydrogen to fuel the reverse water-gas shift reaction and improve the performance of a heat pump.

While this design is feasible with current technology, it has some drawbacks. One is that the performance benefits are relatively small. Since an excess of CO_2 relative to H_2 is needed to force the reaction to occur, only a small amount of the incoming CO_2 actually reacts to form products. This means the heat absorption and associated temperature drop will be relatively small. The other disadvantage is that even with an excess of CO_2 present, not all of the H_2 will react, meaning this system will not make the most efficient use of its H_2 supply.

Analogue to phase-change material – technologies not yet mature

Figure 4 shows the conceptual design for this implementation, in which a hydrogen supply fuels an endothermic reaction that directly absorbs heat from the payload.

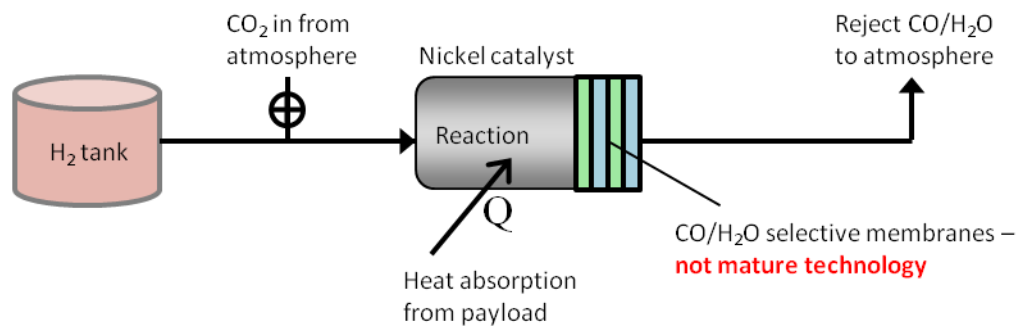


Figure 4. Conceptual design for a system that uses a supply of hydrogen to fuel the reverse water-gas shift reaction and absorb heat like a phase-change material.

This system works as follows. Hydrogen flows from the tank and is mixed with a small flow of CO_2 taken from the atmosphere. The flow rate of H_2 is much larger than the flow rate of CO_2 , so that equilibrium will favor reaction to products – this is the opposite setup of the previous case, but achieves the same result of pushing formation of CO and H_2O products. The mixture

reacts in a catalyst, absorbing heat from the payload as products are formed. The only method of passing out of the system is through membranes that are permeable only to the products of the reaction: CO and H₂O. Unreacted H₂ and CO₂ are retained. After passing through the membranes, the products flow out to the environment. Passive membrane separation is possible in this case because the CO and H₂O products will be much more concentrated inside the reaction zone than they are in the environment. Only trace amounts of CO are present on Venus, and H₂O is nonexistent, so the products of reaction should reliably flow out to the environment.

This system has the advantage of making full use of the H₂ supply, since only products and no unreacted H₂ are rejected to the environment. In principle this system could be also designed to operate at a wide range of temperatures. However, as the reaction temperature gets lower, the size of the catalyst and membranes will likely need to increase. Unfortunately, the membranes needed to produce this system are not a mature technology. While the necessary selective membranes are permitted by physics, it may be many years before useful examples are produced, and even then they may not be well-suited to the Venus environment.

CONCLUSIONS

Theoretical analysis indicates that cooling via chemical reformation of materials from the atmosphere is not a viable method of cooling on Venus. While it is possible to produce cooling this way, the performance is much lower than a conventional mechanical heat pump. However, a chemical cooling system does have the capability to be simpler and more robust than a conventional heat pump.

Looking beyond Venus to a more general case, our analysis showed that it is indeed possible to use materials from an atmosphere to provide cooling through endothermic chemical reactions. The performance of such systems depends on the ambient temperature and the composition of the atmosphere, and the suitability of this method for specific environments must be evaluated on a case by case basis. Where the right environments exist, cooling via chemical reformation of the atmosphere can be a viable strategy, though in practice this may be rare. Chemical cooling can in principle be implemented with fewer components and moving parts than a mechanical heat pump (for example through electrochemistry), which could improve reliability. Though generally inferior from a performance standpoint, a cooling system employing chemical reformation has attributes that may make it preferable to a conventional heat pump in a few situations: where the local environment is favorable, when the products of reaction are valued, or when design simplicity and robustness are valued enough to sacrifice some performance.

Design concepts were developed for systems in which an expendable supply of reactants is used to fuel an endothermic reaction with CO₂ taken from the Venus atmosphere. Since chemical changes can often absorb much more energy than phase changes, such systems have the potential to outperform phase change materials. A concept which used H₂ and atmospheric

CO₂ to produce the reverse water-gas shift reaction was found to have a heat rejection capacity several times larger than water, on a mass basis.

ACKNOWLEDGEMENTS

Funding for this work was made possible through Marshall Space Flight Center's Center Innovation Fund for 2012.

REFERENCES

1. Yutaka Nigara and Bernard Cales, "Production of Carbon Monoxide by Direct Thermal Splitting of Carbon Dioxide at High Temperature", *Bulletin of the Chemical Society of Japan*, Vol. 59 (1986) 1997-2002.