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REVISED DRAFT: PRACTICAL EXPERIENCE WITH A MOBILE METHANOL SYNTHESIS DEVICE

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ABSTRACT

Northern Arizona University has developed a methanol synthesis unit that directly converts carbon dioxide and hydrogen into methanol and water. The methanol synthesis unit consists of a high pressure side that includes a compressor, a reactor, and a throttling valve; and a low pressure side that consists of a knockout drum, and a mixer where fresh gas enters the system. Methanol and water are produced at high pressure in the reactor and then exit the system under low pressure and temperature in the knockout drum. The remaining, unreacted recycle gas that leaves the knockout drum is mixed with fresh synthesis gas before being sent back through the synthesis loop. The unit operates entirely on electricity and includes a high-pressure electrolyzer to obtain gaseous hydrogen and oxygen directly from purified water. Thus, the sole inputs to the trailer are water, carbon dioxide and electricity, while the sole outputs are methanol and water. A distillation unit separates the methanol and water mixture on site so that the synthesized water can be reused in the electrolyzer. Here, we describe and characterize the operation of the methanol synthesis unit and offer some possible design improvements for future iterations of the device, based on experience.

NOMENCLATURE

CH₃OH Methanol
CO Carbon Monoxide
CO₂ Carbon Dioxide
H₂ Hydrogen
H₂O Water
 ΔH Change in enthalpy $\frac{kJ}{mol}$

INTRODUCTION

Methanol (CH₃OH) is the simplest alcohol, consisting of one carbon, one oxygen and four hydrogen atoms. At room temperature it is a colorless liquid that is less dense than water, making it a good solvent and fuel. Methanol is mainly used as a feedstock for other chemicals such as formaldehyde [1], dimethyl ether [2,3], methyl tertiary butyl ether (MTBE) [4], and acetic acid [5], though it is also employed as a fuel in passenger vehicles [6–8], racing cars [9] and direct fuel cells [10, 11].

The worldwide production capacity of methanol reached 100 million metric tons in 2012 [12], with about 60 million metric tons being produced. Demand is expected to more than double in the next decade [13], in part due to China adopting methanol as a transportation fuel [14], with 17% of all methanol being used for this purpose [15]. To meet its own demand, China increased production capacities by 16 fold in 16 years from 1995-2011 [15].

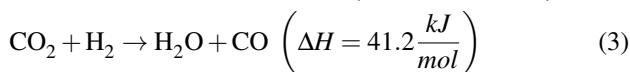
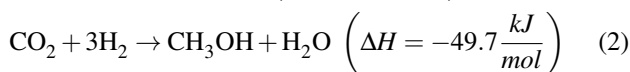
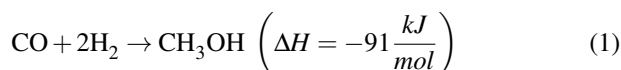
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The United States was historically a major methanol producer with a 20% worldwide market share in 2000 [6]. However, due to changing market conditions in the natural gas industry and the significant reduction in MTBE production due to the Energy Policy Act of 2005 [16], the US produced only 2% of the worldwide market in 2007. Countries in Asia, South America and the Middle East now dominate the market, and the US has become a net importer.

In 2004, ninety percent of industrially produced methanol was synthesized using a steam reforming process to convert methane and water to carbon monoxide and hydrogen [3, 17]. The steam-reforming process is efficient: based on the lower heating value the thermal efficiency of methanol production is typically above 60% [18, 19]. More recently, 64% of all methanol produced in China is synthesized by coal gasification, while methanol via natural gas accounts for only 23% of methanol production [15, 20].

Both steam reforming and coal gasification result in a synthesis gas (syngas) which is a mixture of carbon monoxide, carbon dioxide and hydrogen. All methanol synthesis technologies use syngas with varying proportions of the constituent gases. The earliest methanol reactors built by BASF operated at temperatures of 300 – 400°C with pressures of 100-250 atm over a ZnO/Cr₂O₃ catalyst [21]. Reactors operating at 200 – 300°C and 50-100 bar using a Cu/ZnO/Al₂O₃ catalyst have dominated the market in recent years, and supplanted the higher pressure technologies [22].

There are three main reactions that govern methanol synthesis: the hydrogenation of carbon monoxide and carbon dioxide and the reverse water gas shift reaction:



Early kinetic models assumed the hydrogenation of carbon monoxide (Equation 1) to be the primary source of methanol (see, for example, [23, 24]). It was finally shown through isotope tracing that CO₂ is the likely the major source of carbon in methanol [25]; researchers in the field now generally accept this to be the case [26].

Only two of the three reactions that define methanol synthesis are linearly independent: 2 and 3. This implies that methanol

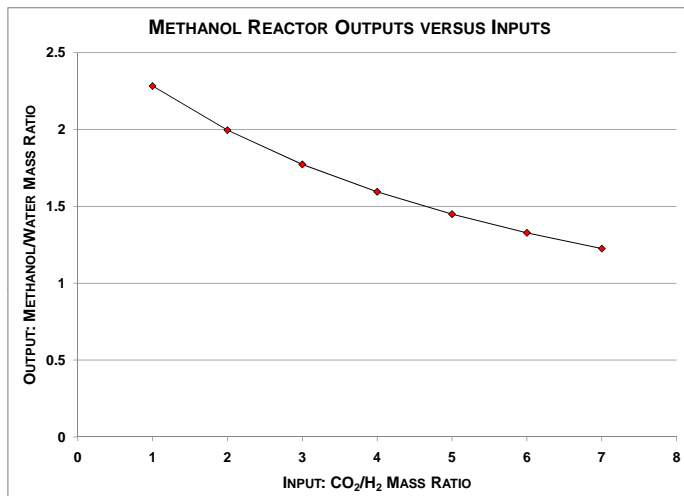
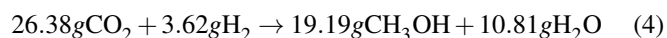


FIGURE 1. Relationship between methanol synthesis inputs and outputs

can be synthesized using only a mixture of CO₂ and H₂. Indeed, significant research on methanol synthesis using only CO₂ and H₂ has been conducted [27–37] in an effort to battle climate change by reusing or sequestering CO₂.

The overall equation for our methanol reactor (inputs → outputs) is given by Equation (2) which can be used to calculate the theoretical stoichiometry of the system. Carbon only appears in one molecule on each side of the equation, so carbon balance can be used to determine production rates based on a mixture of carbon and hydrogen at the inlet. If a 3:1 ratio of hydrogen to carbon is assumed this is usually the case for reactors of this type then equation 2 can be rewritten for a mass input of 30g/h as:



For a given inlet ratio of H₂ to CO₂, the outputs are uniquely defined by the inputs due to the carbon balance constraint. This implies that the mass ratio of inputs is directly related to the mass ratio of the outputs; they all fall on one line. Figure 1 illustrates the relationship between the inlet gases and the output products. Note that the products theoretically must have a mole fraction ratio of 1:1 which is equivalent to a methanol to water mass fraction ratio of about 64:36.

METHANOL AS A FUEL

In 2011, the transportation sector of the United States consumed 71% of the total petroleum demand, accounting for over 25% of all energy consumption [38]. In 2012, the US consumed slightly over 95 quads, of which over 36% were from

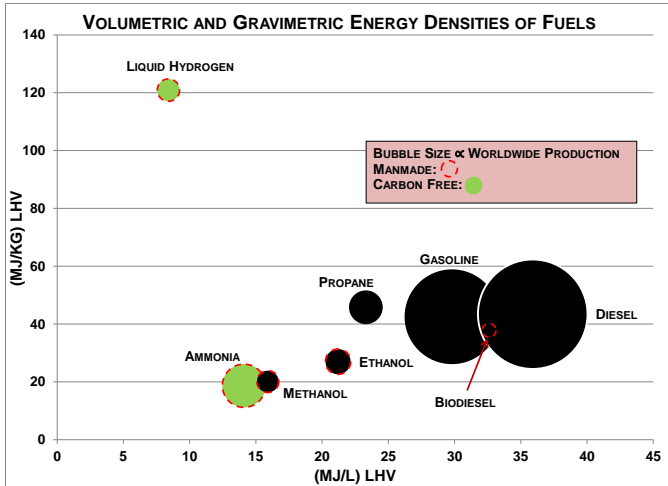


FIGURE 2. Energy densities of common fuels

crude oil or its derivatives [39]. The dependence on crude oil is due entirely to its availability, phenomenal energy density –one gallon of diesel fuel is the equivalent of 10^{15} gallons of peak ($800 \frac{W}{m^2}$) sunlight –and liquid phase stability over the range of temperatures and pressures encountered on Earth. At the end of 2012, the world had an estimated 52.9 years of oil left, based on current consumption and proven reserves. Thus, the US and the world are in desperate need of a drop-in replacement fuel with similar characteristics to gasoline and diesel fuels –the distilled products of crude oil.

The fuel candidates must be energy dense, easily made in an industrial process and, ideally, non-toxic. Figure 2 shows a fuel map of fuels that are industrially mature. The size of the bubble is related to the worldwide production; black indicates carbonaceous fuel; green indicates carbon free fuel; and the red ring indicates a manmade fuel. The ordinate of the plot is the gravimetric energy density of the fuel. Here, hydrogen has a gravimetric density value nearly triple all of the other fuels –it is highly energetic as a molecule. The abscissa shows the volumetric energy density –how much energy can be packed into a space. Liquid hydrogen (the most dense form of pure, non-solid hydrogen) has the lowest value even though it has the highest gravimetric energy density: it is the least dense substance on the fuel chart.

Hydrogen has limited value as a fuel because it requires significant energy to liquefy and requires additional energy to keep in a cryogenic state [40]. Gaseous hydrogen is less dense than liquid hydrogen and therefore requires extreme pressures to become energy dense. Compressing hydrogen is also energy intensive and impractical for widespread use.

Ammonia has been used as a fuel for years in buses, cars [41], and the X-15 rocket jet [42]. Ammonia has a high volumetric energy density, is a liquid at reasonable temperatures and pressures, and contains no carbon. However, exposure to ammonia can cause severe injury or death, so widespread use as a fuel is unlikely despite an extensive transportation infrastructure that exists in the Midwest.

Methanol and ethanol are both alcohols with high energy densities and favorable liquid phase properties. Both fuels are produced easily on an industrial scale and have widespread distribution infrastructures. However, ethanol forms an azeotrope with water so any contact with humid air reduces its purity because of its high affinity for water. Methanol, on the other hand, does not form an azeotrope with water and therefore does not require airtight piping. Moreover, ethanol has historically been produced from fermentation of sugar –corn sugar in the US and cane sugar in Brazil –and requires a large footprint of agricultural land. Thus, methanol has emerged as a competitor to ethanol as a drop-in replacement for gasoline and other energy dense liquid fuels, and its adoption as a transportation fuel in China is expected to increase its demand as a renewable fuel.

THE METHANOL SYNTHESIS UNIT AT NAU

Here we report on a methanol synthesis unit (MSU) developed at Northern Arizona University (NAU) that was designed not only to use CO₂ and H₂ as feedstocks, but also to be mobile. A detailed picture of the complete mobile MSU inside the trailer is shown in Figure 4. The reactor is capable of producing about 2 liters of pure methanol per day when running at maximum capacity. The reactor mobility enables synthesis of methanol at sites that have free carbon dioxide streams such as breweries, power plants or wastewater treatment facilities. Methanol produced in this way could be carbon-neutral [43] and used for a vehicular fuel or in denitrification of wastewater [44]. However, many state-of-the-art carbon capture technologies use electricity in some form so care must be taken to offset any electricity with renewable energy sources for the methanol to be truly carbon-neutral or carbon-negative.

At present we have no universal interface for utilizing carbon dioxide: integration design must be done on a case-by-case basis. There are a number of carbon sources that could be compatible with our system including carbon capture from sodium hydroxide sprays [45], acidification of seawater [46], or moisture swing sorbents [47].

The purity of the carbon dioxide is paramount because any impurities such as oxygen or sulfur can temporarily or permanently damage the catalyst [48]. Unlike industrial processes which contain impurities in their fossil fuel feed streams, our

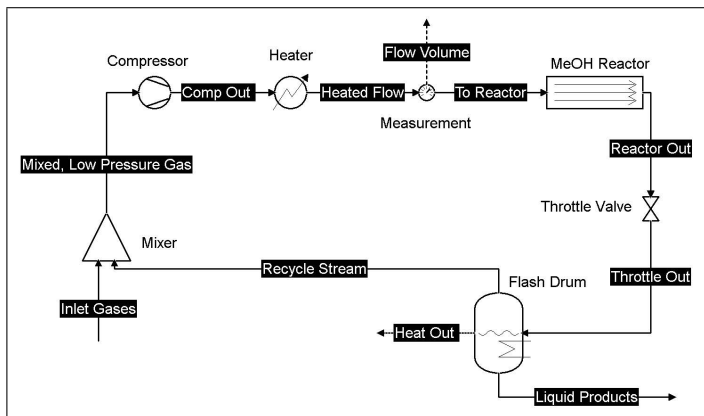


FIGURE 3. A schematic of the NAU reactor

reactor uses only pure carbon dioxide and hydrogen, making it much less susceptible to catalyst poisoning and catalyst deactivation. This approach lowers the overall capital costs in some respects because extensive purification equipment is not required. Moreover, the operations and maintenance costs are also reduced because the catalyst is not subjected to harmful impurities that limit useful lifetime and reduce methanol production.



FIGURE 4. The fully assembled mobile MSU at NAU. Numbers correspond to major pieces of equipment: 1. Electrolyzer 2. Bottled synthesis gases 3. Low pressure buffer 4. Compressor 5. High pressure buffer 6. Methanol reactor/heating elements 7. Throttle valve 8. Condenser 9. Knockout drum 10. Distillation column. Red indicates high pressure (100bar) operation; yellow indicates low pressure (30bar) operation; gradients represent transitional pressure operation in the direction of the gradient. Not shown: pneumatic air compressor.

DESIGN CRITERIA

The original NAU methanol reactor was a proof of concept design based on the Lurgi process from the 1960s. The operating temperature and pressure were chosen to match those found in industrial production. All valves, fittings, and piping were selected to be compatible with not only the temperatures and pressures, but also hydrogen. The original system was a single pass reactor that consisted mainly of the reactor and pressure regulators [31].

The second generation system incorporated a synthesis loop to capture unreacted gases and cycle them back through. The design was again a proof of concept –the reactor was designed produced methanol under the correct conditions.

Finally, it was decided to make the methanol synthesis unit mobile in an attempt to capture either 1) curtailed electricity or 2) free streams of CO₂ from wastewater treatment facilities or other industrial manufacturing or power production facilities.

In order to compensate for unmanned operation and mobility, several features were added to the basic design. First, an electrolyzer was included to obviate the need for hydrogen refilling. The decision to incorporate an electrolyzer was predicated upon the fact that there are few free streams of hydrogen in industry (with the exception of the chloro-alkali process, and some others) while CO₂ is actively being pursued for sequestration. Thus, it was assumed that in most cases NAU would provide the hydrogen and the electricity and CO₂ would be provided by another entity.

A high pressure electrolyzer (30 bar) was chosen so that an additional compressor was not required –the outlet pressure of the electrolyzer was sufficiently close to the low-pressure side of the synthesis loop. The electrolyzer was originally designed to shut off at 30 bar of pressure at the outlet with a manual reset required to restart. The electrolyzer was retrofit with a control system that restarts the electrolyzer after high-pressure shutdown. The addition of a H₂/CO₂ buffer tank enabled an electronic restart (which takes several minutes) of the electrolyzer without compromising the mass flow into the synthesis loop. The excess oxygen was routed through the ceiling of the trailer and into the surrounding environment.

Unmanned operation requires rudimentary control systems to 1) alert operators of any emergencies 2) shut the system down when in danger 3) to ensure no mass accumulation within the loop and the knockout drum. The emergency measures that were incorporated included 1) normally closed solenoid valves on the feed gas tanks as well as the mass flow controllers to minimize gas leaks during unexpected power outages 2) float controls for the knockout drum and the distillation column to

maintain a maximum liquid level 3) alarms and emergency shutdown controls in case of hazardous gas leaks (H_2 , CO_2 , CO) and/or fires 4) additional gas storage was required to provide constant hydrogen output from the batch process electrolyzer. Finally, all storage components including the water tank, for the electrolyzer, the CO_2 tank and the methanol and water tanks at the distillation column were sized for one week of unmanned operation.

The electrical system in the trailer was designed with a 50 foot exterior extension cord and 220V plug so that any location with 220V service and a CO_2 stream could provide both 220V and 110V power inside the trailer. Thus, the trailer could simply drive up to a site, plug in, and produce methanol. The interior electrical wiring was a combination of 110V and 220V standard outlets; no custom wiring was done. The mobile methanol trailer therefore requires only electricity for input power.

DETAILED EQUIPMENT DESCRIPTION

The MSU has gone through several stages of design and, as a consequence, several operational topologies are possible. The initial MSU was a proof-of-concept, single-pass reactor that was capable of converting CO_2 and H_2 into methanol and water [31]. While, the reactor converted 15-20% of the synthesis gas into methanol, the unconverted gases including carbon monoxide, carbon dioxide and hydrogen were vented. To avoid venting, the single-pass reactor was modified into its current form with the addition of a recycle loop that mixes the unreacted gases with fresh synthesis gas.

The inlet synthesis gas flow for the MSU was initially from a steel tank of premixed gases 75 mol% hydrogen and 25 mol% carbon dioxide prepared by Praxair. The tanks from Praxair typically had an initial pressure of about 150 bar; the mixed gas was supplied to the MSU at about 30 bar. The single steel tank has subsequently been replaced by three steel tanks: one tank from Praxair containing pure CO_2 ; one hydrogen tank that receives hydrogen from an ACTA EL300R electrolyzer; and one mixed gas tank that contains both CO_2 and H_2 .

The CO_2 tank is fitted with a 100W heater to prevent icing during tank discharge; an solenoid valve; and a pressure regulator which is capable of low pressure discharge down to 7 bar. The solenoid valve is normally closed and requires power to open the valve. Thus, if no power is being provided to the CO_2 tank, there will be no gas flow.

The H_2 tank and the mixed-gas tank are also equipped with the solenoid valves and pressure regulators, but neither requires heating at the outlet; hydrogen warms upon expansion at temperatures above the inversion temperature of 205K. The

mixture of hydrogen and carbon dioxide neither discharges at roughly room temperature due to the combined effects of the hydrogen and carbon dioxide.

The molar ratio of hydrogen to carbon dioxide that flows into the mix tank is controlled through two mass flow controllers; the mixed gas tank has a single flow controller that controls the synthesis gas flow into the synthesis loop. Thus, the typical ratio of 3 moles of hydrogen to one mole of carbon dioxide can be altered by setting the volumetric flow rates out of the pure hydrogen and carbon dioxide tanks. An instantaneous change in the ratio of hydrogen to carbon dioxide would not fully affect the reactor until the contents of the mixed tank fully turn over.

When the fresh mixed gases (H_2 and CO_2) flow from the tank, they are mixed with the recycle gases (H_2 , CO_2 and CO) at a T-mixer fitting. Once the fresh and recycle gases are mixed in the synthesis loop, they flow through a low pressure buffer tank that compensates for any disturbances such as surging that might occur. The gases are then compressed to about 100 bar using a gas booster which is driven by an two-stage, single phase reciprocating air compressor. A high-pressure, one gallon cylinder is installed directly after compression as a buffer tank to stabilize the gas flow. Instability is an issue in some industrial processes, such as ammonia production, that resemble methanol synthesis [49]. All flow is control using a digital mass flow controller.

The reactor itself was custom-built using 316 stainless steel, and has an overall length of 30.5cm (12 inches), an internal diameter of 2.5cm (1 inch), and an external diameter of 4.5cm (1.75 inches). The entrance and exit assemblies of the reactor are both approximately 12.5cm (5 inches) long and contain various fittings to connect the reactor to the gas lines. The interior of the reactor contains solid cylindrical $Cu/ZnO/Al_2O_3$ catalyst pellets with a packing density of $1190 \frac{kg}{m^3}$ as well as 3mm glass balls that occupy the initial (top) 10cm (4 inches) of the reactor length for heat transfer purposes. The reactor is enclosed in a custom made rectangular aluminum casing (measurements: 10cm by 10cm by 26cm) that houses four 125W, 1.25cm (0.5 inch) diameter heaters to maintain the reactor jacket temperature at the desired level using temperature controller. As the inlet gas flows through the reactor, it is brought up to temperature by the heating jacket and glass balls. The reactor pressure is controlled using a 316 stainless steel, 135 bar max, spring-loaded back pressure regulator (BPR) located at the outlet of the reactor.

The operating pressure drops across the BPR from about 100 bar on the high pressure side to about 30 bar on the low pressure side. The large pressure drop is implemented for two reasons. First, operating the flash drum at modest pressure was advanta-

geous because the drum was hand welded steel with flat flanges in the top and bottom. During a high pressure (100 bar) test with no BPR installed, one of the flanges began to plastically deform and risked failure. Second, the premixed inlet gases enter the recycle loop from the holding tank at about 30 bar. In order to have a driving force through the reactor loop, the BPR was chosen to be close to the inlet gas pressure. Moreover, the pressure drop across the throttle alleviates the installation of a second compressor at the inlet. The low pressure gases then flow through a tube-in-tube heat exchanger and are cooled to room temperature with antifreeze that cycles through a simple air-cooled loop. Upon cooling, the methanol and water condense and are then sent to a custom-built knockout drum while the unreacted gases are sent back to the T fitting mixer. The liquids in the knockout drum are sent to a custom-built, atmospheric pressure distillation column that includes controllable heaters. The temperature of the distillation column is maintained between the boiling points of water (100°C) and methanol (64.7°C) so that only methanol evaporates. The separated liquids are collected in plastic jugs.

ELECTRICAL SYSTEM

The electrical system in the trailer is sized to accommodate a maximum of 22kW of power. A 220V, 100amp service enters the trailer via a main breaker box that is connected to an exterior 50 foot extension cord with a male-type plug; a 220V outlet is required at the site for the trailer to produce methanol. The electrical system contains 10 breakers including two 30amp breakers and eight 20 amp breakers. The two 30 amp breakers are meant for powering the air compressor which draws nearly 5kW at 220V; and the electrolyzer which draws about 1.4kW at 220V. The other 20 amp circuits are for auxiliary equipment such as heaters, computers, control systems and data acquisition.

The trailer is also outfitted with emergency alarms including a smoke alarm, and detectors for CO, CO₂ and H₂. Each alarm is wired to the main breaker box such that an alarm event on any of the devices shuts down the entire system immediately. The normally closed valves on the fresh synthesis gas tanks ensure that no gas will flow into the system, or out of the tanks. After an alarm event, the ceiling fan, emergency lights, and alarms are powered along with some dedicated outlets. A ceiling fan is sized to exhaust the trailer volume in under an hour.

RESULTS AND DISCUSSION

The methanol reactor operated under formal test conditions for a total of about 21 hours in the laboratory, prior to being moved into the trailer. The MSU also operated at other times during the design and build process in both the lab and trailer, but no formal performance records were kept. Testing was mostly done after small device modifications or hardware replacements

as a system check.

We calculated the energy requirements of the methanol reactor during typical operational conditions during the formal testing. We used a reactor pressure of 90 bar, a jacket temperature of 240°C and a space velocity of 2.5 normal liters per minute (NLPM). Under these conditions, the methanol reactor produced 29.32 grams of total product (methanol and water) in a one hour period. We measured the volume of the liquid product so that we could easily determine the mass fraction of methanol and water, which deviated from theory. We assumed that no major impurities were present, based on results from the single pass reactor output [31]. We determined that the mass fraction of methanol was 0.58, meaning that we produced 17g of methanol, and 12.32g of water.

We ran the methanol reactor at steady state and recorded the total time that the air compressor operated during that interval. The results showed that the compressor typically operates for about 7.5% of the time meaning that over a one hour period, the air compressor operates for about 4.5 minutes. Since the compressor draws an assumed 4.9kW over a one hour period it consumes 0.3575kWh of energy.

The electrolyzer requires 1.4kWh to produce 300 normal liters of hydrogen gas. We assume a hydrogen balance across the entire reactor inlet to outlet and find that we require 3.52g of hydrogen per hour. This equates to 1.746mol of H₂, or 42.69 normal liters per hour. Therefore, the energy consumed to produce the H₂ using the electrolyzer is approximately 0.2kWh. Neglecting the power for the auxiliary components and taking the lower heating value of methanol to be 19.93 $\frac{MJ}{kg}$ the overall efficiency is calculated to be 16.5%.

The MSU was operated at using two jacket temperatures of 240°C and 260°C with space velocities ranging from 1.5NLPM to 30NLPM. During the tests, the steady state catalyst temperature was recorded and the liquid methanol and water mixture from the reactor was collected at the completion of the test. The results from twenty three of the testing runs are presented in a bubble chart in Figure 5. Note that the ordinate is in \log_2 space for convenience. There are several notable trends that emerge from the plot. First, there is a bifurcation of measured catalyst temperature values for the same flow rate due to the difference in jacket temperature set points during different tests. This implies either that the exothermic methanol reaction could not be sustained under low jacket temperature conditions, or that the endothermic water-gas shift reaction was dominant. In either case, there the heat was not adequate. Second, as the volumetric flow rate increases, the catalyst temperature decreases. The relationship held for both jacket temperature set points. The decrease in temperature is likely due to cold feed gases entering the system and cooling the reactor. More cooling is expected at higher

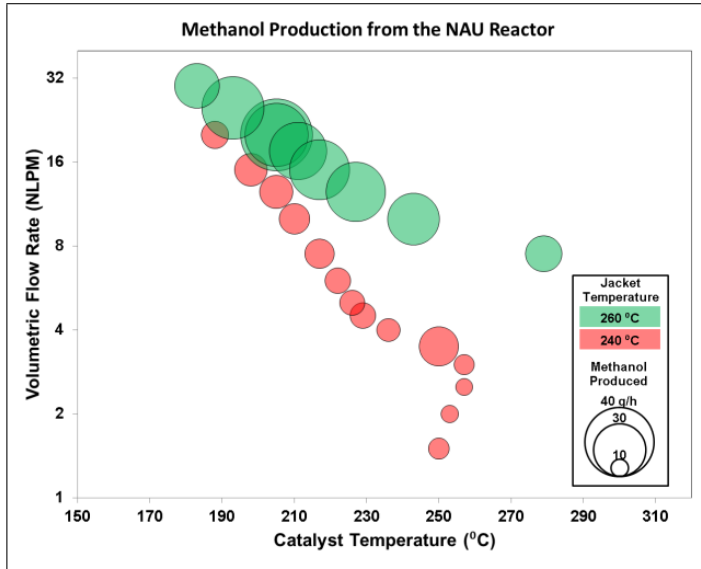


FIGURE 5. Bubble plot of reactor outputs

flow rates due to convective heat transfer from the catalyst and reactor to the flowing gas. A cooled reactor responds by producing less methanol and therefore less heat from reaction, further cooling the reactor. Third, the testing with a high jacket temperature yielded higher outputs of methanol from the reactor. The high outputs were likely due to the significant volumetric flow of synthesis gases through the externally heated reactor. The external heat was enough to sustain the exothermic methanol reaction while enabling ample methanol production. To better understand the response of the reactor under different operation conditions three, data was taken from three thermocouples that each take 0.5Hz data: one at the inlet stream, one inside the reactor bed, and one at the reactor exit. We measured the temperature profiles at these locations during a typical reactor test during August, 2013. The space velocity was set to 2.5NLPM and the reactor pressure was set to 90 bar. We took several hours of data under these conditions. Figure 6 shows the temperature profiles for a half-hour period as the system reached steady state. The reactor temperature is essentially constant over the entire interval while the inlet temperature exhibits low frequency oscillations and the outlet exhibits high frequency oscillations. However, due to some system feedback, the inlet temperature to the reactor ranges from 40.8°C to 46.1°C with a mean of 44.28°C and a standard deviation of 1.53°C. The reactor outlet temperature was much more variable with a maximum value of 104.8°C, a minimum of 88.3°C, a mean of 101.1°C and a standard deviation of 3.18°C.

The oscillating temperature at the reactor outlet was also observed during another characteristic test run two days later, as shown in Figure 7. In this case, the average outlet temperature was 115.9°C with a standard deviation of 5.67°C. The tem-

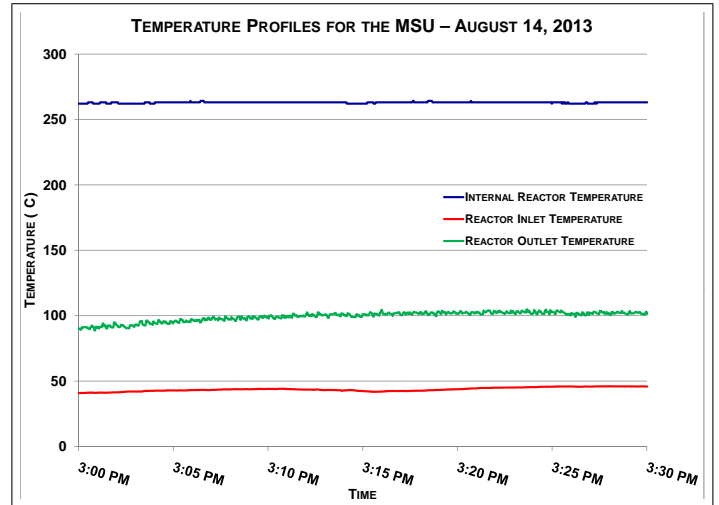


FIGURE 6. Reactor temperature profiles during typical operation

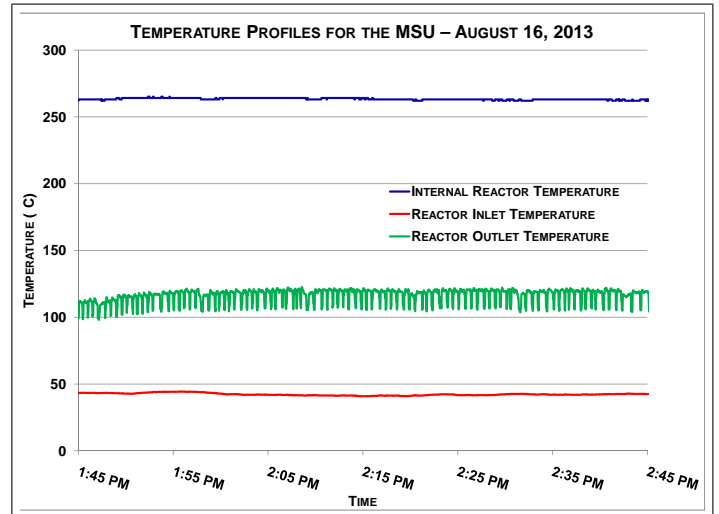


FIGURE 7. Reactor temperature profiles during typical operation, showing abnormal temperature behavior

perature profiles for the reactor outlet resemble those reported in [49], but are much faster, on the order of seconds. The temperature oscillations could be caused by several phenomena within the reactor loop, including surging. During surging events, it is possible that the pressure at the outlet goes through rapid expansion and compression cycles causing the temperature to fluctuate. This behavior could be from the spring-loaded back pressure regulator.

We deployed the trailer in Northern Arizona with the full methanol synthesis unit for several weeks during late fall 2013 and early winter 2014. The trailer was left unattended and unplugged for the first two weeks and encountered subzero

(Fahrenheit) temperatures. When power was brought into the trailer it was found that the electrolyzer had failed due to loose connections and that the mass flow controllers were stuck. The electrolyzer failure was likely due to the bumpy drive (10 miles) from NAU campus to the final destination. The mass flow controllers were likely frozen, as they are not designed for sub-zero operation.

The trailer was retrieved after the initial deployment so that the mass flow controllers and electrolyzer could be repaired. A 2kW heater was added to the trailer to maintain modest temperatures when not in operation.

FUTURE WORK

The methanol reactor at Northern Arizona University is fully functional, and has been for a number of years. The next steps are to improve the design of the reactor itself and the synthesis loop that surrounds it. In order to optimize the design, more real-time system information is necessary. At present, we do not know the exact composition of the inlet gas because the flow rates are controlled by mass flow controllers. A better approach would be to have an inline gas analyzer for the inlet gases so that the feed could be controlled more precisely. Moreover, a liquid analyzer at the output coupled with the inline gas analyzer would enable real-time adjustments to the feed to optimize the output. A governing control system that takes temperature information from the reactor, feed gas composition from the mixed tank and from the reactor outlet, and liquid composition from a refractometer would not only increase efficiency, but also help us understand how the various set points interact.

We need to develop a thermal model of the reactor based on the jacket temperature and the temperature profile in the reactor. This type of model would be relatively simple to implement in a software package such as OpenFoam and could prove useful in designing a new reactor. At present, we have a single temperature reading within the reactor and a single control system that controls the jacket temperature. A full three-dimensional thermal model would aid in the design of a more thermally efficient reactor.

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REFERENCES

- [1] Hader, R. N., Wallace, R. D., and McKinney, R. W., 1952. "Formaldehyde from methanol". *Industrial & Engineering Chemistry*, **44**(7), pp. 1508–1518.
- [2] Hosseininejad, S., Afacan, A., and Hayes, R. E., 2012. "Catalytic and kinetic study of methanol dehydration to dimethyl ether". *Chemical Engineering Research and Design*, **90**(6), pp. 825–833.
- [3] Olah, G. A., Goepfert, A., and Prakash, G. K. S., 2009. "Chemical recycling of carbon dioxide to methanol and dimethyl ether: from greenhouse gas to renewable, environmentally carbon neutral fuels and synthetic hydrocarbons". *The Journal of organic chemistry*, **74**(2), pp. 487–98.
- [4] Adams, J., Clement, D., and Graham, S., 1982. "Synthesis of methyl-tbutyl ether from methanol and isobutene using a clay catalyst". *Clays and Clay Materials*, **30**(2), pp. 129–134.
- [5] Singh, A. D., and Krase, N. W., 1935. "Synthesis of acetic acid from methanol and carbon monoxide". *Industrial & Engineering Chemistry*, **27**(8), pp. 909–914.
- [6] Bromberg, L., and Cheng, W., 2010. Methanol as an alternative transportation fuel in the us: Options for sustainable and/or energy-secure transportation. Tech. Rep. UT-Battelle Subcontract Number: 4000096701, Sloan Automotive Laboratory.
- [7] Nichols, R. J., 2003. "The methanol story: A sustainable fuel for the future". *Journal of Scientific and Industrial Research*, **62**(January-February), pp. 97–105.
- [8] Nowell, G. P., 1994. On the road with methanol: The present and future benefits of methanol fuel. Tech. Rep. Report 2474, Acurex Environmental, May.
- [9] Powell, T., 1975. Racing experiences with methanol and ethanol-based motor-fuel blends. Tech. Rep. SAE Paper No. 750124, Society of Automotive Engineers.
- [10] Bahrami, H., and Faghri, A., 2013. "Review and advances of direct methanol fuel cells: Part II: Modeling and numerical simulation". *Journal of Power Sources*, **230**(0), pp. 303–320.
- [11] Li, X., and Faghri, A., 2013. "Review and advances of direct methanol fuel cells (dmfcs) part i: Design, fabrication, and testing with high concentration methanol solutions". *Journal of Power Sources*, **226**(0), pp. 223–240.
- [12] Methanol Institute, 2013. The methanol industry - methanol institute.
- [13] IHS Media Relations, 2013. Driven by China, global methanol demand rises 23 percent in two years, unprecedented demand growth expected for 2012 to 2022, says new IHS study — IHS online pressroom.
- [14] Yang, C.-J., and Jackson, R. B., 2012. "China's growing methanol economy and its implications for energy and the environment". *Energy Policy*, **41**(0), pp. 878–884.
- [15] Su, L.-W., Li, X.-R., and Sun, Z.-Y., 2013. "The consump-

- tion, production and transportation of methanol in China: A review". *Energy Policy*, **61**.
- [16] Environmental Protection Agency, 2012. Methyl tertiary butyl ether (MTBE) — US EPA.
- [17] Lange, J.-P., 2001. "Methanol synthesis: a short review of technology improvements". *Catalysis Today*, **64**(12), pp. 3–8.
- [18] Lemonidou, A. A., Valla, J., and Vasolos, I. A., 2003. "Methanol production from natural gas: Assessment of CO₂ utilization in natural gas reforming". In *Carbon Dioxide Recovery and Utilization*, M. Aresta, ed. Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 379–394.
- [19] Agency, I. E., 2007. *Tracking Industrial Energy Efficiency and CO₂ Emissions: In Support of the G8 Plan of Action : Energy Indicators*. Energy indicators. International Energy Agency.
- [20] Su, L.-W., Li, X.-R., and Sun, Z.-Y., 2013. "Flow chart of methanol in China". *Renewable and Sustainable Energy Reviews*, **28**(0), pp. 541 – 550.
- [21] Lee, S., 1990. *Methanol Synthesis Technology*. CRC Press, Boca Raton, FL.
- [22] Olah, G. A., Goepfert, A., and Prakash, G. K. S., 2006. *Beyond Oil and Gas: The Methanol Economy*, 1st ed. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.
- [23] Graaf, G., Stamhuis, E., and Beenackers, A., 1988. "Kinetics of low-pressure methanol synthesis". *Chemical Engineering Science*, **43**(12), pp. 3185–3195.
- [24] Klier, K., Chatikavanij, V., Herman, R., and Simmons, G., 1982. "Catalytic synthesis of methanol from CO/H₂. Part IV: The effects of carbon dioxide". *Journal of Catalysis*, **74**, pp. 343–360.
- [25] Chinchin, G. C., Denny, P. J., Parker, D. G., Spencer, M. S., and Whan, D. A., 1987. "Mechanism of methanol synthesis from CO₂/CO/H₂ mixtures over copper/zinc oxide/alumina catalysts: use of ¹⁴C-labelled reactants". *Applied Catalysis*, **30**(2), pp. 333–338.
- [26] Grabow, L. C., and Mavrikakis, M., 2011. "Mechanism of methanol synthesis on cu through CO₂ and CO hydrogenation". *ACS Catalysis*, **1**(4), pp. 365–384.
- [27] Saito, M., and Murata, K., 2004. "Development of high performance Cu/ZnO-based catalysts for methanol synthesis and the water-gas shift reaction". *Catalysis Surveys from Asia*, **8**(4), pp. 285–294.
- [28] Kubota, T., Hayakawa, I., Mabuse, H., Mori, K., Ushikoshi, K., Watanabe, T., and Saito, M., 2001. "Kinetic study of methanol synthesis from carbon dioxide and hydrogen". pp. 121–126.
- [29] Saito, M., 1998. "R & d activities in Japan on methanol synthesis from CO₂ and H₂". *Catalysis Surveys from Japan*, **2**, pp. 175–184.
- [30] Toyir, J., Miloua, R., Elkadri, N. E., Nawdali, M., Toufik, H., Miloua, F., and Saito, M., 2009. "Sustainable process for the production of methanol from CO₂ and H₂ using Cu/ZnO-based multicomponent catalyst". *Physics Procedia*, **2**(3), pp. 1075–1079.
- [31] Doss, B., Ramos, C., and Atkins, S., 2009. "Optimization of methanol synthesis from carbon dioxide and hydrogen: Demonstration of a pilot-scale carbon-neutral synthetic fuels process". *Energy & Fuels*, **23**(9), pp. 4647–4650.
- [32] Yang, Y., White, M. G., and Liu, P., 2011. "A theoretical study of methanol synthesis from CO₂ Hydrogenation on metal-doped Cu(111) surfaces". *J Phys Chem A*(111), pp. 248–256.
- [33] Van-dal, E. S., and Bouallou, C., 2012. "CO₂ Abatement through a methanol production process". pp. 463–468.
- [34] Gallucci, F., Paturzo, L., and Basile, A., 2004. "An experimental study of CO₂ hydrogenation into methanol involving a zeolite membrane reactor". *Chemical Engineering and Processing: Process Intensification*, **43**(8), pp. 1029–1036.
- [35] Gallucci, F., and Basile, a., 2007. "A theoretical analysis of methanol synthesis from CO₂ and H₂ in a ceramic membrane reactor". *International Journal of Hydrogen Energy*, **32**(18), pp. 5050–5058.
- [36] Zhang, Y., Fei, J., Yu, Y., and Zheng, X., 2007. "Study of CO₂ Hydrogenation to methanol over Cu-V/ γ -Al₂O₃ catalyst". *Journal of Natural Gas Chemistry*, **16**, pp. 12–15.
- [37] Chinchin, G. C., and Spencer, M. S., 1991. "Sensitive and insensitive reactions on copper catalysts: The water-gas shift reaction and methanol synthesis from carbon dioxide". *Catalysis Today*, **10**, pp. 293–301.
- [38] Energy Information Administration, 2014. Energy consumption by sector: 2.0 primary energy consumption by source and sector, 2011.
- [39] Energy Information Administration, 2014. Energy Overview: 1.3 Primary Energy Consumption Estimates by Source, 1949-2012.
- [40] Amos, W. A., 1998. Costs of storing and transporting hydrogen. Tech. Rep. NREL/TP-570-25106, National Renewable Energy Laboratory, Nov.
- [41] Zamfirescu, C., and Dincer, I., 2009. "Ammonia as a green fuel and hydrogen source for vehicular applications". *Fuel Processing Technology*, **90**(5), pp. 729–737.
- [42] Jenkins, D. R., 2000. Hypersonics before the shuttle: A concise history of the X-15 research airplane. Tech. Rep. NASA Publication SP-2000-4518, National Aeronautics and Space Administration, June.
- [43] Graves, C., Ebbesen, S. D., Mogensen, M., and Lackner, K. S., 2011. "Sustainable hydrocarbon fuels by recycling CO₂ and H₂O with renewable or nuclear energy". *Renewable and Sustainable Energy Reviews*, **15**(1), pp. 1–23.
- [44] Exponent Inc, Theis, T. L., and Hicks, A., 2012. Methanol use in wastewater denitrification. Tech. Rep. Report:

1105602.000 0101 0712 PT01, Exponent.

- [45] Stolaroff, J. K., Keith, D. W., and Lowry, G. V., 2008. “Carbon dioxide capture from atmospheric air using sodium hydroxide spray”. *Environmental Science & Technology*, **42**, pp. 2728–2735.
- [46] DiMascio, F., Willauer, H. D., Hardy, D. R., Lewis, M. K., and Williams, F. W., 2010. Extraction of carbon dioxide from seawater by an electrochemical acidification cell part I: Initial feasibility studies. Tech. Rep. NRL/MR/6180–10-9274, Office of Naval Research.
- [47] Wang, T., Lackner, K. S., and Wright, A., 2011. “Moisture swing sorbent for carbon dioxide capture from ambient air”. *Environmental Science & Technology*, **45**(15), pp. 6670–6675.
- [48] Kung, H. H., 1992. “Deactivation of methanol synthesis catalysts - a review”. *Catalysis Today*, **11**(4), pp. 443–453.
- [49] Morud, J. C., and Skogestad, S., 1998. “Analysis of instability in an industrial ammonia reactor”. *AIChE Journal*, **44**(4), pp. 888–895.