

## Utilization of CO<sub>2</sub> as a Partial Substitute for Methane Feedstock in Chemical Looping Methane-Steam Redox Processes for Syngas Production

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### Supplemental Information

#### 1. Reactor Specifications

The reducer reactor is a moving bed reactor that takes in natural gas and partially oxidizes it to a mixture of CO and H<sub>2</sub> using a co-current solids stream of ITCMO. The ITCMO in the form of Fe<sub>2</sub>TiO<sub>5</sub> provides oxygen necessary to partially oxidize CH<sub>4</sub> to a mixture of CO and H<sub>2</sub>. In the reducer, the ITCMO is reduced to a mixture of Fe, FeTiO<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub> depending on the reactor design and contact mode. A co-current moving bed system ensures that, thermodynamic design conditions for a high syngas conversion can be obtained by controlling the reaction stoichiometric and ensuring that sufficient residence time are available for complete reactant conversion. If natural gas is represented by CH<sub>4</sub> and the oxidized and reduced ITCMO solids are represented by FeTi<sub>y</sub>O<sub>x</sub> and FeTi<sub>y</sub>O<sub>x-1</sub> respectively, the target reactions in the reducer reactor can be represented by Equation (1):



The design of the reducer reactor is based on an optimal oxygen carrier to fuel ratio, temperature and pressure of the reactor, and the weight ratio of active oxygen carrier to support material. The combustor reactor is a bubbling fluidized bed reactor which reoxidizes the reduced ITCMO particles from the reducer with air. The target reactions in the combustor reactor can be represented by Equation (2):



The combustor reaction is exothermic the heat can be transferred to the reducer reactor using the oxygen carrier to offset the energy requirements for the endothermic heat requirements of the reducer reactor.

## 2. Chemical Looping Reactor Heat Balance

In an auto-thermal design of the combustor reactor, the conditions are fixed at  $T_{out}$  and a pressure  $P_0$ . This  $T_{out}$  is initially set as the lowest feasible temperature at which the oxygen carrier re-oxidation has the reasonable reaction kinetics. This temperature can be varied in an iterative process to satisfy the system heat balance. If a set of manipulated variables is chosen such that  $\Delta H_{reducer} = 0$ ; it means that the reducer is maintained at a temperature such that no additional heat is required to supply to the system. If  $\Delta H_{reducer} < 0$ , it implies that the reducer requires to reject some heat to maintain the temperature ( $T_{out}$ ). If  $\Delta H_{reducer} > 0$ , it implies that the reducer requires some heat to maintain the temperature ( $T_{out}$ ). The overall methodology for satisfying an auto-thermal operation of the combustor is given in Equation (3):

$$(\Delta H_{combustor})_{T_{out}} \leq 0 \quad (3)$$

The reducer heat balance is conducted by specifying the heat duty of the reducer reactor to be equal to zero and calculating the reducer temperature swings. A set of reducer operating variables are defined and analyzed through Gibbs free energy minimization to obtain a temperature swing criterion for an auto-thermal operation. The approach requires the specification of a chemical looping system pressure ( $P$ ) and an inlet temperature ( $T_{in}$ ) of the solid oxygen carrier to the reducer reactor. The heat-duty of the system is set as zero. Equations (4), (5) and (6) are used to calculate the  $T_{out}$  of the reducer reactor.

$$(\Delta H)_{T_{out}, P} = \sum(\Delta H)_{IN} - \sum(\Delta H)_{OUT} = 0 \quad (4)$$

Assuming a reference temperature of 25 °C and a pressure of 1 atm,  $\sum H_{IN}$  can be given as:

$$\begin{aligned} \sum H_{in} &= \Delta H_{fsolids}(298K, 1 atm \rightarrow P) + \int_{25}^{T_{in}} C_{psolids} dT + \Delta H_{fst} \\ &+ \Delta H_{ffuel}(298K) + \int_{25}^{T_{fuel\ in}} C_{pfuel} dT \end{aligned} \quad (5)$$

Assuming a reference temperature of 25 °C and a pressure of 1 atm,  $\sum H_{out}$  may be written as:

$$\begin{aligned} \sum H_{out} &= \Delta H_{f solids} (298K, 1 atm \rightarrow P) + \int_{25}^{T_{in}} C_{p solids} dT + \Delta H_{f steel} \\ &+ \Delta H_{f fuel} (298K) + \int_{25}^{T_{fuel in}} C_{p fuel} dT \end{aligned} \quad (6)$$

Substituting Equations (5) and (6) into Equation (4) leads to an equation that expresses  $T_{out}$ .  $T_{out}$  for the reducer can thus be used to characterize a temperature swing of  $T_{in} - T_{out}$ .

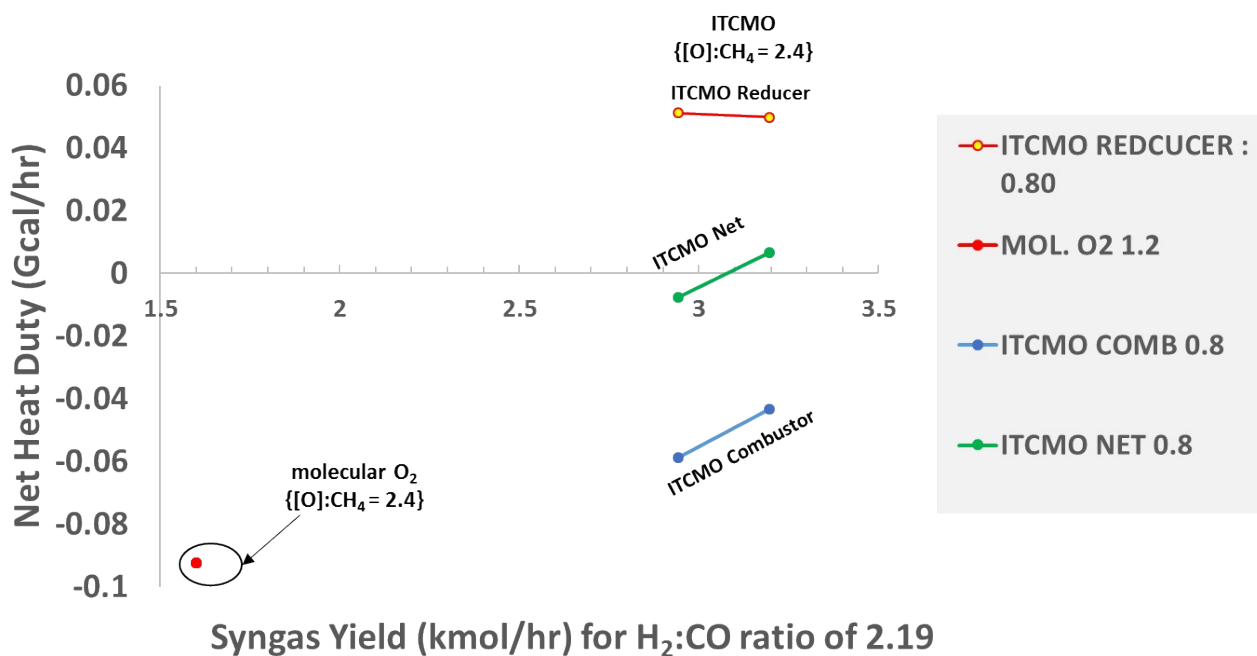
The solids exiting the reducer reactor at  $T_{out}$  are injected to the combustor. A set of combustor operating variables are defined and analyzed through Gibbs free energy minimization to obtain a temperature swing of  $T_{in} - T_{out}$  while the  $((\Delta H)_{T_{out}, P})_{combustor}$  is set as zero.

The overall criterion for an auto-thermal operation can be expressed by Equation (7).

$$(T_{in} - T_{out})_{reducer} = (T_{out} - T_{in})_{combustor} \quad (7)$$

The reducer heat balance calculation is more efficient than the combustor heat balance calculation in characterizing a chemical looping system. The reducer is the key reactor that dictates the chemical looping system performance and comprehension of its characteristics is essential prior to calculating its temperature swings. This study calculates the temperature swings for the reducer reactor and then examines the combustor heat balance by specifying a constant combustor outlet temperature.

The comparison of an ITCMO to molecular  $O_2$  at an [O]: $CH_4$  of 2.4 is shown in Figure S1 and illustrates the syngas generation advantages of a chemical looping system to traditional tri-reforming. The ITCMO shows a much larger operational range, with which it does not require additional heat input, while producing significantly greater syngas than molecular  $O_2$ .



**Figure S1:** Net Heat Duty (Gcal/hr) vs Syngas Yield for a [O]:CH<sub>4</sub> ratio of 2.4 at 1000 °C, 5 atm

### 3. Simulation Set-up

The MTS process analysis was conducted based on the process simulation methodology as given below. The chemical reactions of methane and ITCMO were simulated using the RGIBBS module in ASPEN which minimizes the free energy of the reactor products. The rationale for using a RGIBBS reactor to model a co-current moving bed reducer and its chemistry with ITCMO particles under isothermal conditions have been studied before<sup>1,2</sup>. The results under isothermal operation were obtained to validate previously obtained simulation results<sup>2</sup>, before

performing a detailed adiabatic simulation. The process simulations involving iron oxide-based chemical looping processes are completed using Aspen Plus v8.8 with a common base used for all simulations. Table 1 provides the component species defined for the process simulations, while Table 2 provided the modeling detail necessary.

**Table 1:** List of chemical components defined in the ASPEN simulations

<b>Type: Solid</b>	
Carbon-graphite (C)	Iron titanium oxide (FeTiO <sub>3</sub> )
Silicon carbide (SiC)	Di-iron titanium pentoxide (Fe <sub>2</sub> TiO <sub>5</sub> )
Titanium dioxide (TiO <sub>2</sub> )	Tri-iron carbide (Fe <sub>3</sub> C)
Iron (Fe)	Iron monosulfide (FeS)
Ferrous oxide (FeO)	Iron disulfide pyrite (FeS <sub>2</sub> )
Hematite (Fe <sub>2</sub> O <sub>3</sub> )	Magnetite (Fe <sub>3</sub> O <sub>4</sub> )
<b>Type: Conventional</b>	
Argon (Ar)	Ammonia (NH <sub>3</sub> )
Hydrogen (H <sub>2</sub> )	Hydrogen cyanide(HCN)
Oxygen (O <sub>2</sub> )	Propane (C <sub>3</sub> H <sub>8</sub> )
Water (H <sub>2</sub> O)	n-butane (C <sub>4</sub> H <sub>10</sub> )
Carbon monoxide (CO)	Nitrogen dioxide (NO <sub>2</sub> )
Carbon dioxide (CO <sub>2</sub> )	Methane (CH <sub>4</sub> )
Nitrogen (N <sub>2</sub> )	Ethane (C <sub>2</sub> H <sub>6</sub> )
Nitric oxide (NO)	

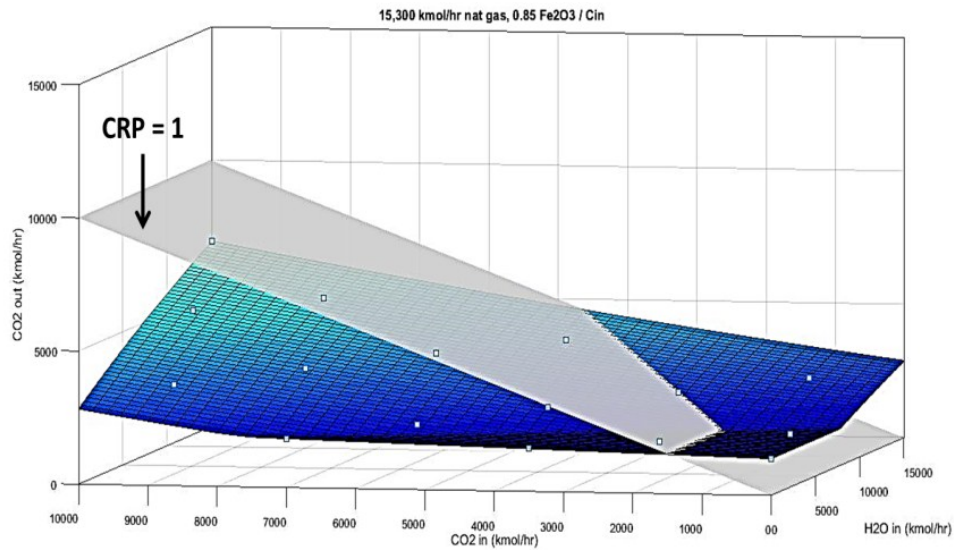
**Table 2:** Reactor model set-up

Parameter	Setting
Reactor module type (Gibbs Free Energy Minimization Module)	RGIBBS
Stream Class	MIXCINC
Thermodynamic and Physical data bank (in order)	Combust, Inorganic, Solids, Aqueous, Pure 22
Base Method	PR-BM (Peng-Robinson Base method)
Free Water method	Steam Tables (Steam-TA)

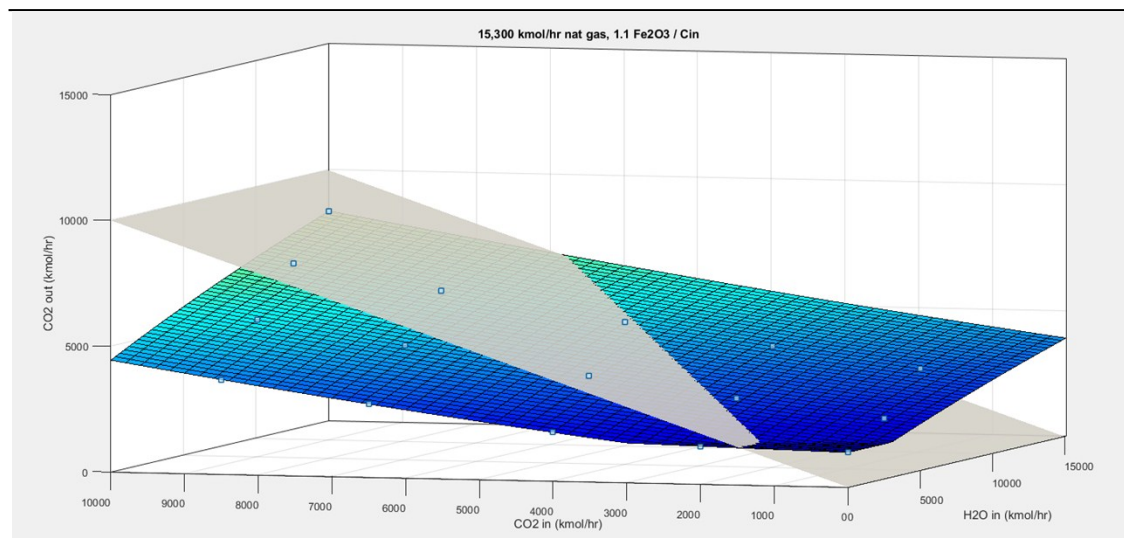
#### 4. CO<sub>2</sub> negative chemical looping reducer system (CRP > 1)

In addition to the natural gas savings resulting from CO<sub>2</sub> recycle, discussed in the communication, CO<sub>2</sub> is also able to be consumed using the MTS process in a CO<sub>2</sub> neutral and CO<sub>2</sub> negative process. Figure S2 shows the CO<sub>2</sub> produced from the chemical looping reducer system for T = 900 °C, P = 1 atm and an Fe<sub>2</sub>O<sub>3</sub>:C molar ratio of 0.85. The plane corresponding to CRP = 1 is depicted. This plane shows the set of points where the CO<sub>2</sub> input to the reducer is equal to the CO<sub>2</sub> in the syngas output from the reducer. As the Fe<sub>2</sub>O<sub>3</sub>:C molar ratio is increased from 0.85 to 1.1 and then to 1.3 the portion of the surface that resides above the CRP=1 plane increases. From a pure thermodynamic standpoint, increasing the Fe<sub>2</sub>O<sub>3</sub>:C molar ratio increases the CO<sub>2</sub> formation at a given CO<sub>2</sub> input and H<sub>2</sub>O input. This is shown in Figures S3 and S4. The design from Figures S3 and S4 shows that for a higher CRP and correspondingly a higher CO<sub>2</sub> utilization value, a lower Fe<sub>2</sub>O<sub>3</sub>:C molar ratio is preferred. In other words, the system should be operated at the lowest Fe<sub>2</sub>O<sub>3</sub>:C molar ratio for which the auto-thermal heat balance can be satisfied.

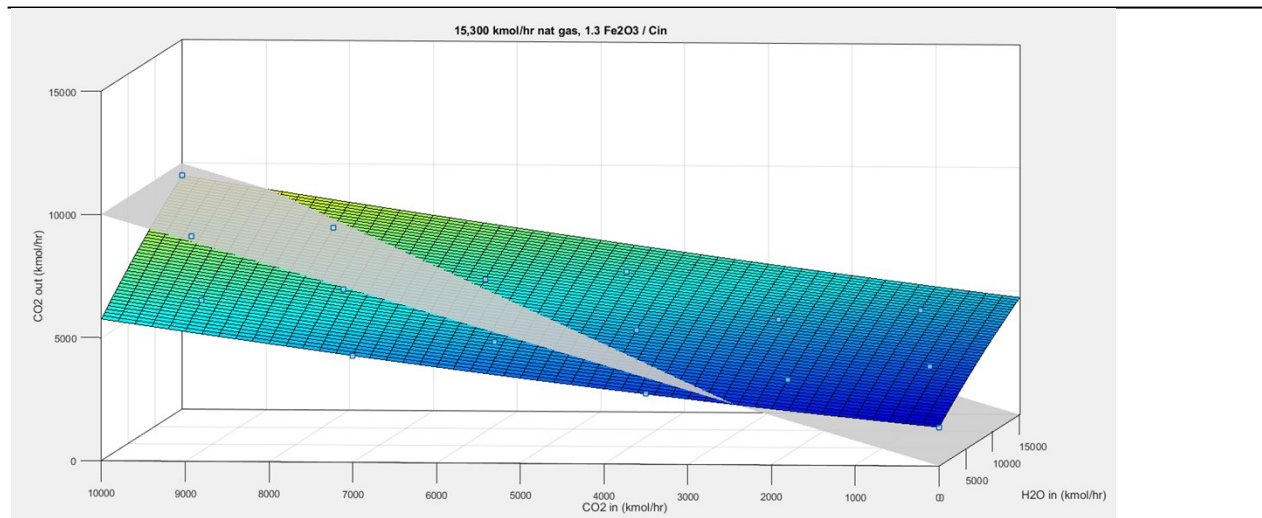
Analysis of data in Table 3 shows that for a natural gas flow condition specified by 15,300 kmol/hr a CRP value equal to 1.1 can be achieved when the CO<sub>2</sub> input is greater than or equal to 2000 kmol/hr and less than or equal to 5000 kmol/hr and the steam flow increases from 7,050 kmol/hr to 14,150 kmol/hr in conjunction with the increasing CO<sub>2</sub> injection. However, at these conditions the ideal H<sub>2</sub>:CO molar ratio of 2.19 and 100% baseline H<sub>2</sub> production are sacrificed to compensate for the additional CO<sub>2</sub> usage.



**Figure S2:** H<sub>2</sub>:CO molar ratio variation as a function of steam molar input and CO<sub>2</sub> molar input at a natural gas flow of 15,300 kmol/hr, Fe<sub>2</sub>O<sub>3</sub>:C molar ratio of 0.85, P = 1 atm and T = 900 °C



**Figure S3:** H<sub>2</sub>:CO molar ratio variation as a function of steam molar input and CO<sub>2</sub> molar input at a natural gas flow of 15,300 kmol/hr, Fe<sub>2</sub>O<sub>3</sub>:C molar ratio of 1.1, P = 1 atm and T = 900 °C



**Figure S4:** H<sub>2</sub>:CO molar ratio variation as a function of steam molar input and CO<sub>2</sub> molar input at a natural gas flow of 15,300 kmol/hr, Fe<sub>2</sub>O<sub>3</sub>:C molar ratio of 1.3, P = 1 atm and T = 900 °C

**Table 3:** Flow rates that satisfy the H<sub>2</sub>:CO molar ratio requirement natural gas flow of 15,300 kmol/hr with a fuel gas recycle split of 99% and a CRP = 1.1

CO <sub>2</sub> in	CO <sub>2</sub> out	CRP	H <sub>2</sub> O	%H <sub>2</sub>	H <sub>2</sub> :CO
2000	1814.086	1.102484	7050	98.59595	2.112439
2500	2266.564	1.102991	8250	98.55191	2.105848
3000	2721.667	1.102266	9450	98.49337	2.099544
3500	3178.949	1.100993	10650	98.4279	2.093512
4000	3626.893	1.102872	11800	98.3339	2.086105
4500	4087.989	1.100786	13000	98.26467	2.080602
5000	4539.771	1.101377	14150	98.17106	2.073759

Analysis of data in Table 4 shows that for a natural gas flow condition specified by 15,300 kmol/hr a CRP value equal to 2.0 can be achieved when the CO<sub>2</sub> input is greater than or

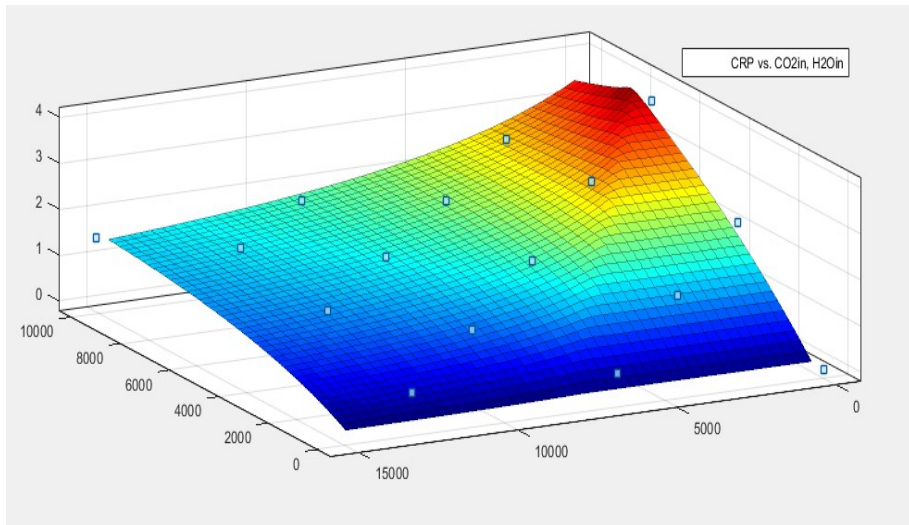


equal to 3,500 kmol/hr and the steam flow increases from 4,800 kmol/hr in conjunction with the increasing CO<sub>2</sub> injection. However, similarly to the conditions at a CRP value of 1.1, the ideal H<sub>2</sub>:CO molar ratio and % H<sub>2</sub> produced are sacrificed even further for the higher CRP. Figure S5 shows an alternative visualization of the Figure S4, where in intersection of various CRP values with the constant CRP planes are observed. It can be seen that under certain conditions, a CRP greater than 3 is thermodynamically obtainable. It should be noted that the choice of downstream technology is crucial for maximizing CO<sub>2</sub> substitution for carbonaceous feedstocks

**Table 4:** Flow rates that satisfy the H<sub>2</sub>:CO molar ratio requirement natural gas flow of 15,300 kmol/hr with a fuel gas recycle split of 99% and a CRP = 2

CO <sub>2</sub> in	CO <sub>2</sub> out	CRP	H <sub>2</sub> O	%H <sub>2</sub>	H <sub>2</sub> :CO
3500	1747.923	2.002377	4800	95.10253	1.897492
4000	1998.409	2.001592	5100	94.59167	1.866288
4500	2241.023	2.008012	5350	94.05344	1.834735
5000	2488.626	2.009141	5600	93.52088	1.804441
5500	2741.05	2.00653	5850	92.9949	1.775333
6000	2998.144	2.001238	6100	92.47609	1.747344
6500	3246.457	2.002183	6300	91.93451	1.718909
7000	3499.113	2.000507	6500	91.40075	1.691528
7500	3742.605	2.003952	6650	90.8446	1.663693
8000	3990.151	2.004937	6800	90.29633	1.636853
8500	4241.662	2.003931	6950	89.7559	1.610954
9000	4497.052	2.001311	7100	89.22324	1.585951
9500	4742.663	2.003094	7200	88.66786	1.560442
10000	4991.908	2.003242	7300	88.11998	1.535784

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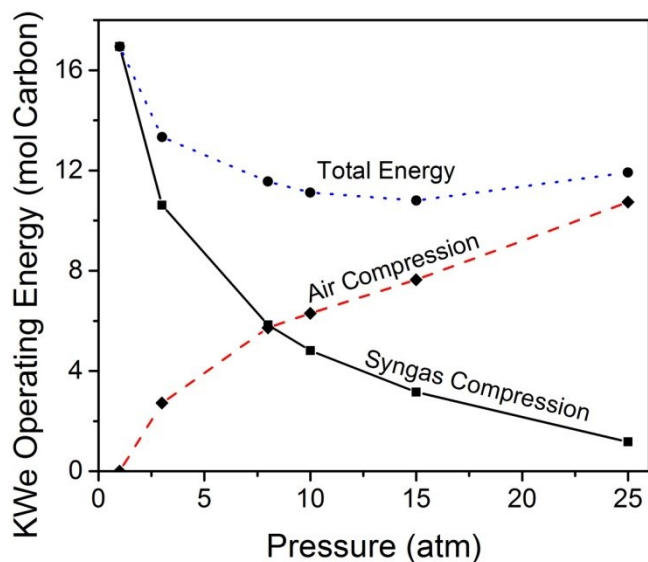
**Figure S5:** CRP variation as a function of steam molar input and CO<sub>2</sub> molar input at a natural gas flow of 15,300 kmol/hr, Fe<sub>2</sub>O<sub>3</sub>:C molar ratio of 0.85, P = 1 atm and T = 900 °C

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## 5. Energy Optimizaton

Figure S6 shows the results for the net operating energy requirement as a function of operating pressure for a downstream syngas pressure of 30 atm. A sensitivity analysis is conducted which further considers competing factors characterized by an increase in the operating pressure which results in enhancement of reaction kinetics, increase in air compression operating energy, decrease in syngas compression operating energy, and decrease in syngas thermodynamic equilibrium composition. An operating pressure of 5 atm is chosen from the sensitivity analysis for integrating the MTS process into a 50,000 bpd liquid fuel production scheme.

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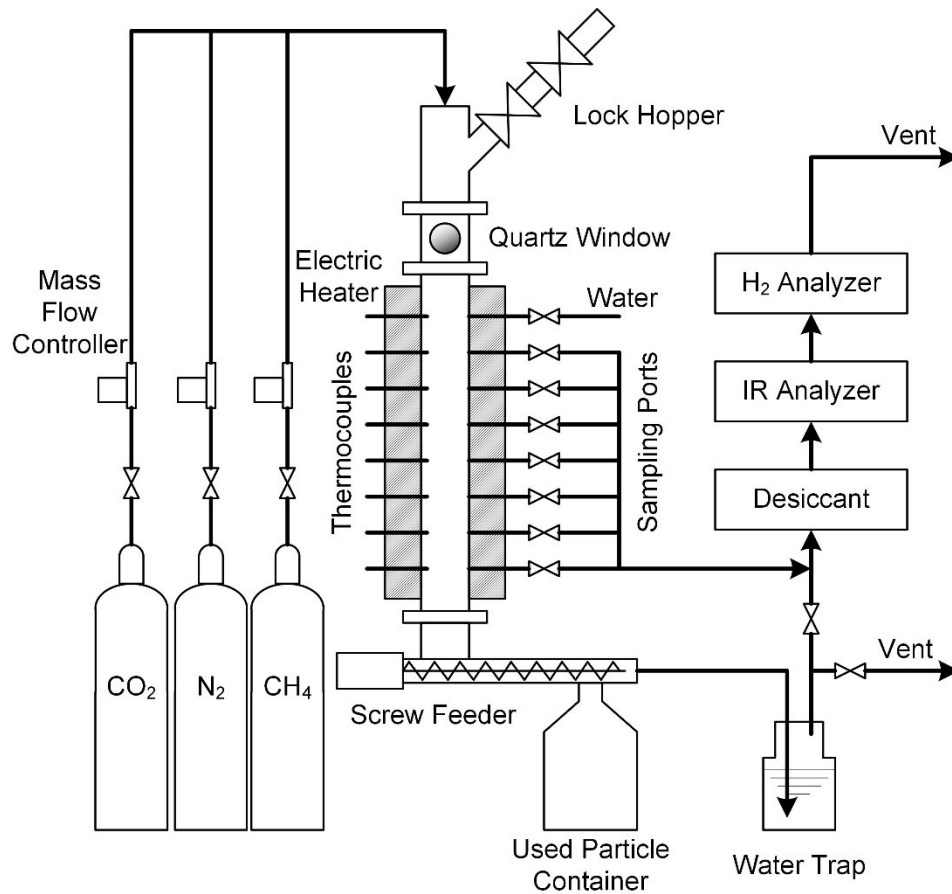
**Figure S6:** Net compression energy requirements for the CTS compressors and expanders

## 6. Experimental Apparatus

The moving bed reactor shown in Figure S7 consists of a 2 inch (5 cm) ID steel tube heated externally by electric heaters along with a screw feeder installed at the bottom of the reactor. To investigate the performance of CO<sub>2</sub> injection in the reducer reactor, the moving bed experiments were conducted on a bench scale unit. The reactor system consists of a gas mixing panel, a moving bed reactor and a gas analysis system. Figure S7 shows the experiment setup. The reactor is operated under ambient pressure. The gas mixing panel enables inert and reactive gases such as N<sub>2</sub> and CH<sub>4</sub> to be mixed prior to their injection into the reactor. N<sub>2</sub> is used as a balance gas to maintain the total gas flow rate, thus resulting in steady residence time for the methane flow in the reactor. All the gaseous and/or solid feedstocks are injected from the top of the reactor, flowing downward along with metal oxides in a co-current moving bed mode. Particles are removed from the reactor by the screw feeder at the bottom of the reactor. Oxidized ITCMO particles are introduced in batch mode. A quartz window is located below the solid feeding pipe to monitor the solid inventory. Thermocouples are installed along the reactor to measure the temperature profile. Opposite to the thermocouples, eight gas sampling ports are set to enable the sampling of solid and gas from different parts of the reactor. The bench scale of the reactor setup renders it unfeasible for an adiabatic operation mode. The isothermal operating temperature is based on the previously determined average temperature at which the system exhibits good

kinetics and feasible thermodynamics.<sup>2</sup> Gaseous products are sampled from the bottom of the reactor. The gas analysis system consists of an infrared gas analyzer (Siemens ULTRAMAT 23) and a thermal conductivity gas analyzer (Siemens CALOMAT 6), quantifying the concentration of CO, CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>. After the experiment, a sample of the reduced ITCMO particles is collected from the bottom of the reactor for carbon content characterization. A carbon analyzer (CO<sub>2</sub> Coulometer, UIC, Inc.) is used to determine the carbon content in the reduced ITCMO particle sample.

It should be noted that the system performance improves markedly with increasing temperature and hence the eventual commercial reactor will be designed so that the current isothermal temperature is the minimum in the adiabatic temperature profile in the reactor ensuring similar or even better reactor performance. Further the various iso-thermal operation enable to determine the effect of the temperature on reactor performance.



**Figure S7.** Bench-scale moving bed reactor system

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**References**

1. Fan L.-S., Zeng L, Luo S. Chemical-looping technology platform. *AIChE J.* 2015;61(1):2-22.
2. Luo S, Zeng L, Xu D, et al. Shale gas-to-syngas chemical looping process for stable shale gas conversion to high purity syngas with a H<sub>2</sub> : CO ratio of 2 : 1. *Energy Environ Sci.* 2014;7(12):4104-4117.