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Hydrogen Production with Integrated CO_2 Capture *via* Sorbent Enhanced Reforming

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Abstract

GTI Energy has been developing a novel process technology for hydrogen production from natural gas with inherent carbon capture. The GTI process, based on sorbent enhanced reforming (SER), has the advantage that it captures CO_2 inherently in the process via a pre-combustion technique instead of secondary capture from a flue gas stream. This approach is fundamentally different from conventional technologies such as steam methane reforming (SMR) and autothermal reforming (ATR) which require additional process steps to avoid CO_2 emissions. The inherent carbon capture capability results in step-out economics of the GTI process.

The GTI process is based on GTI's Hydrogen Generator (CHG) technology which converts natural gas and steam into H_2 and CO_2 in separate streams. The inherent carbon capture in the GTI process leads to its higher carbon capture potential, its substantially lower capital cost (by 40-60%) and substantially smaller footprint compared to the conventional approaches, resulting in overall lower levelized cost of hydrogen (by 10-30%). In its optimized configuration, carbon capture rates over 97.5%, with 10% lower levelized cost of hydrogen (LCOH) and ~50% reduction in CAPEX compared to conventional SMR with CO_2 capture are achievable. By relaxing the carbon capture rate to 96%, a LCOH ~20% lower than the SMR case can be achieved. LCOH and CAPEX advantages of the process compared to Autothermal Reforming (ATR) are even more pronounced.

Development of the process technology is currently supported by the U.S. Department of Energy (DOE) and by the U.K. Department for Business, Energy, and Industrial Strategy (BEIS). DOE has been supporting the development and operation of a 0.071 MW_{th} pilot plant at GTI's main test facility near Chicago, USA, to demonstrate the process chemistry and fluidized bed operation. Under BEIS funding, a team comprised of Cranfield University, GTI Energy, and Doosan Babcock has been developing a 1 MW_{th} pilot plant at a dedicated new test site at Cranfield University in the UK ("HyPER Project").

Keywords: hydrogen; CO_2 capture; pre-combustion capture; sorbent; sorbent enhanced reforming

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1. Introduction

Abundant natural gas can play a key role in transitioning the global energy system towards a sustainable future. Blue hydrogen, produced from natural gas while capturing carbon dioxide emissions, can become a new energy carrier for the power, industrial, commercial, and residential sectors. This requires development and deployment of process technologies that offer significant capital cost reductions over current technologies and can produce very low carbon intensity hydrogen efficiently.

According to IEA's Net Zero by 2050 study [1], hydrogen use, as a source of energy versus traditional uses as a chemical feedstock or in refining, will grow to as much as 6 times the current level of hydrogen production by 2050. Decarbonizing this amount of hydrogen requires a rapid deployment of large-scale electrolysis and carbon capture and sequestration (CCUS). IEA expects that, starting within the current decade, the fossil-based production of hydrogen with carbon capture and sequestration will grow rapidly because hydrogen from fossil fuels is currently by far the lowest cost option for hydrogen production. The levelized cost for fossil-based hydrogen is expected to increase over time as the economic penalty for unabated CO_2 emissions rises. In contrast, the costs for renewable electricity and electrolyzers need to and are expected to fall, shrinking that cost gap to fossil-based hydrogen. However, the projected costs of renewable hydrogen production beyond 2030 remain highly uncertain. Fossil-based clean hydrogen production with CCUS is expected to remain the lowest cost option in many parts of the world over the next decades. Due to that low-cost advantage and natural gas abundance, it can enable a rapid and affordable transition to a sustainable energy system.

GTI Energy, previously known as Gas Technology Institute (GTI), has been developing a novel process technology for hydrogen production from natural gas while avoiding CO_2 emissions. The GTI process, based on sorbent enhanced reforming (SER), has the advantage that it captures CO_2 inherently in the process via a pre-combustion technique instead of a secondary capture from a flue gas stream. The inherent carbon capture in the GTI process leads to its higher carbon capture potential, its substantially lower capital cost, and smaller footprint compared to the conventional approaches. The GTI process is distinctly different from conventional steam-methane reforming (SMR) or autothermal reforming (ATR) with carbon capture, in that it captures the CO_2 produced in the reforming reaction inherently in the process, and CO_2 capture is not an additional, capital-intensive process step. The result is a low-cost pathway to essentially clean hydrogen up to large scale.

2. Sorbent Enhanced Reforming: The Fundamentals

The production of H_2 from the conventional SMR process requires several steps [2]. The first step is the reforming reaction, shown in Equation 1. Steam and natural gas are mixed and preheated to the requisite temperature. This mixture passes down through a packed bed of catalyst, which is heated to ~855 °C from the outside to offset the endothermic nature of the reforming reaction. The resulting steam/H_2/CO/CO_2 and unreacted "slip" methane mixture is cooled to approximately 400 °C, where the remaining CO is converted to H_2 and CO_2 in the water-gas shift reaction, shown in Equation 2. The overall reaction is shown in Equation 3 and requires a net heat input of 168.2 kJ per mole of methane.

Unfortunately, the heat released from the water-gas shift reaction is not used for the reforming reaction, so external heating must provide most of the energy of 206 kJ per mole of methane. The final step is a purification process, where the impurities are separated from the hydrogen in a Pressure Swing Absorber (PSA) to a purity level of typically 99.99% purity.

The impurities are expelled from the absorber by reducing the pressure to near atmospheric levels and used as part of the heat source for the reforming reaction.

$$CH_4 + H_2O + 206\ kJ \rightarrow 3H_2 + CO \quad (1)$$

$$CO + H_2O \rightarrow H_2 + CO_2 + 37.8\ kJ \quad (2)$$

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2 \qquad \Delta H = 168.2\ kJ \quad (3)$$

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To improve the efficiency and cost of hydrogen production, researchers at GTI are developing the Compact Hydrogen Generator (CHG) technology, which is based on Sorption Enhanced Reforming (SER) as explained by Johnsen [3]. The process is protected by several patents. The CHG process uses calcium (in the form of CaO) as the sorbent to produce a high purity hydrogen stream by adsorbing the CO_2, as it is produced during the reforming reaction, to produce $CaCO_3$, combining Equations 4 and 5. This preferentially shifts the reaction via the well-known Le Chatelier's principle [4] converting the CO to CO_2 via the water-gas shift reaction, and methane conversion is increased to generate additional CO. These reaction shifts occur at the same location, taking advantage of the added heat liberated from the water-gas shift reaction. The shift proceeds until nearly all the CO is shifted to CO_2 and adsorbed in the sorbent, leaving essentially pure hydrogen as shown by the overall Equation 6. Lastly, after the sorbent has captured the available CO_2 in solid phase as $CaCO_3$, it is physically separated from the high purity hydrogen stream and calcined and regenerated back to CaO as shown in Equation 7. The advantage of the SER process is that the heat liberated during the carbonation reaction is equivalent to the heat required for the net reforming and water-gas shift reactions. In comparison, an SMR requires additional external heat input, multiple reactor steps, and further purification to produce a comparable hydrogen stream. Additionally, the operating temperature of the SMR is significantly higher (850 °C) compared to the CHG process (650-700 °C). This means the external heat input in an SMR must be at a high temperature, requiring significant heat recovery to achieve its efficiency.

$$CH_4 + 2H_2O + 168.2\ kJ \rightarrow 4H_2 + CO_2 \quad (4)$$

$$CaO + CO_2 \rightarrow CaCO_3 + 178\ kJ \quad (5)$$

$$CH_4 + 2H_2O + CaO \rightarrow 4H_2 + CaCO_3 \qquad \Delta H = -9.8\ kJ \quad (6)$$

$$CaCO_3 + 178\ kJ \rightarrow CaO + CO_2 \quad (7)$$

3. GTI Energy's Hydrogen Generator Process

GTI Energy's CHG process converts natural gas and water to hydrogen and CO_2 in separate streams. A simplified process schematic is shown in Figure 1. The CHG technology is a SER process which utilizes a sorbent to intensify the SMR reaction and capture the CO_2 generated, enabling simple separation from the hydrogen stream. The CHG employs a fluidized bed of reforming catalyst with a continuous throughflow of a calcium oxide (CaO) based sorbent for the in-situ removal of the by-product CO_2, producing high-purity hydrogen.

The process chemistry is segregated into two operations:

I. Natural gas and steam are fed to the reforming reactor (step 1 in Figure 1), the CaO selectively absorbs CO_2 in the reforming reactor, while being elutriated through the fluidized bed (steps 2, 3, 4), forming $CaCO_3$ as a fine solid. The remaining hydrogen-rich gas is separated from the sorbent (step 5) and is further purified.

II. In the calciner, heat is added indirectly to liberate the CO_2 from the sorbent (step 6). The regenerated sorbent, with its latent heat, is returned to the reforming reactor.

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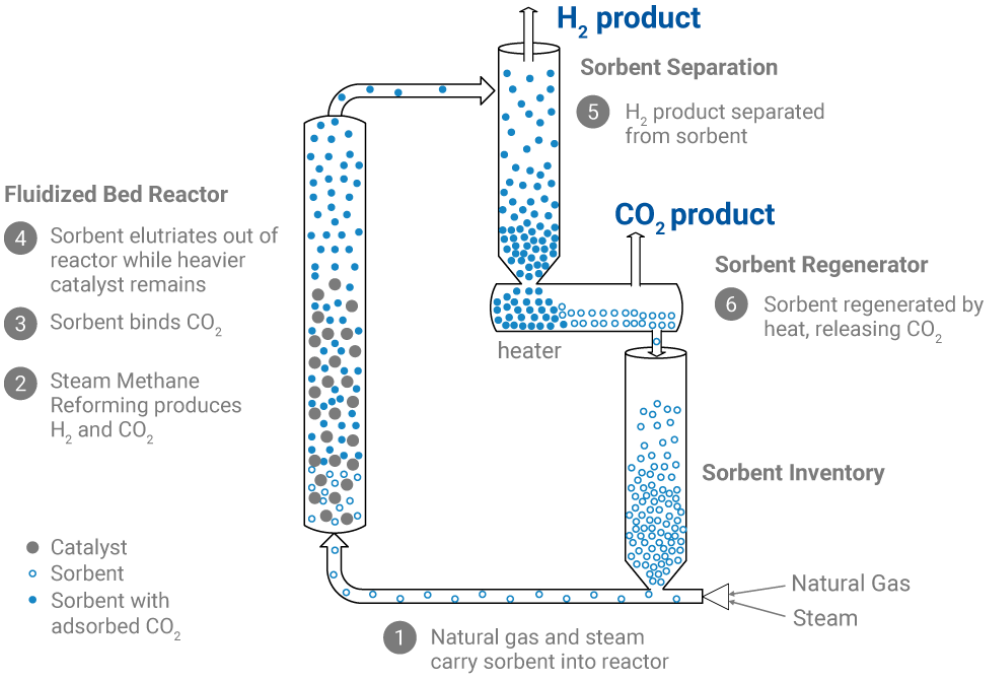

Figure 1: GTI Energy's sorbent enhanced reforming process schematic.

4. Process comparison of GTI's Hydrogen Generator with conventional SMR

The principal cost advantages of the CHG process compared to conventional SMR stem from the simplification of the reforming process and the elimination of the water-gas shift reactor. The two processes are compared in Figure 2. The SER chemistry enables the reforming process to be performed in a single reactor vessel instead of the myriad of small externally heated reactor pipes of an SMR surrounded by a furnace to externally supply the heat to the pipes. This difference and the elimination of the water-gas shift reactors enable 40-60% savings in capital costs. For the SMR, only 81% methane conversion is achievable, compared to well over 90% for the CHG process. This improvement is partially counteracted in the SMR by generating significant amounts of steam from heat recovery, and accounting for this in the overall efficiency. But this is only worthwhile where steam is needed for other processes. When CO_2 capture is needed, additional gas separation is required for the SMR process which requires a large steam demand. In the CHG process, CO_2 is captured inherently in the solid phase sorbent, and delivered as a pure co-product, requiring only compression and drying.

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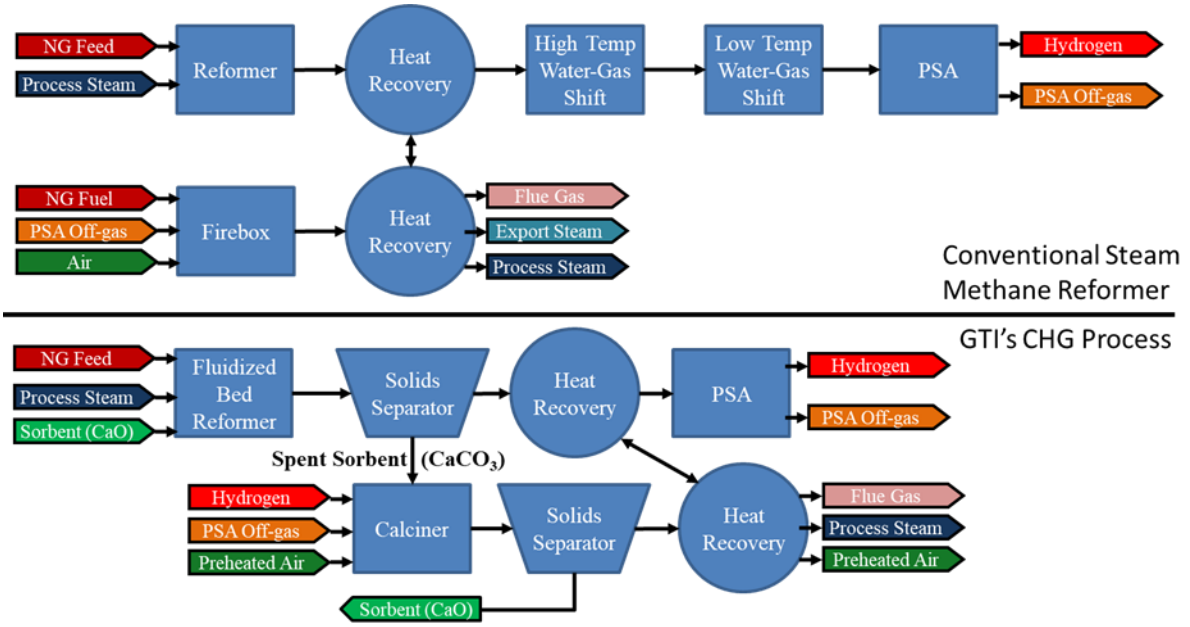

Figure 2: Process Flow Comparison, SMR vs. CHG process.

5. Close to Zero CO_2 Emissions

The CHG process can achieve 88-93% CO_2 capture in the low-cost, once-through configuration. However, greater CO_2 capture (up to 98%) is achievable by incorporating a recycle of the off-gas released from the PSA purification process. This captures all of the non-hydrogen impurities within the hydrogen product stream and delivers a 0.9999 pure hydrogen product. In the once-through process configuration, the off-gas is delivered to the calciner and used as fuel for the regeneration of the sorbent. The high-CO_2 capture process uses a compressor to raise the pressure of the off-gas and a hydrogen membrane to reduce the amount of hydrogen returning to the fluidized bed reactor to maximize carbon conversion (Figure 3).

The heat and mass balances are provided in Table 1. The recycling of the PSA off-gas is feasible since the impurities are controlled by the sorbent (CO_2), or blowdown (Nitrogen). Specific membranes tailored to permeate H_2 and N_2 could enable even greater CO_2 capture rates.

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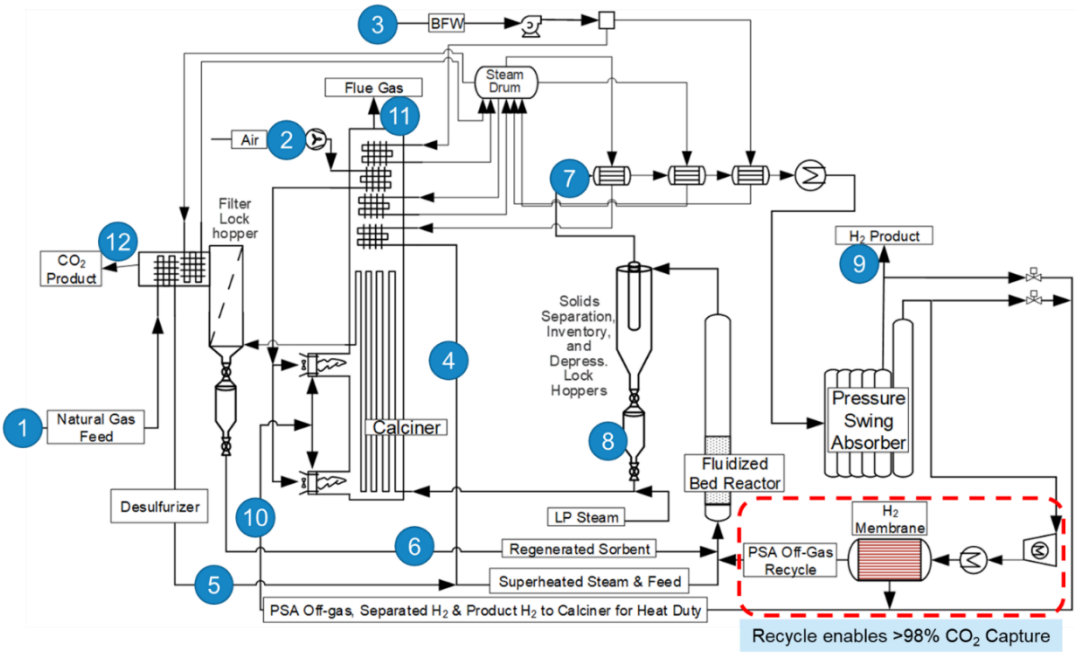

Figure 3: GTI Energy's CHG process with off-gas recycle enables high CO_2 capture (>98%).

Table 1: Operating conditions for high CO_2 capture case.

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Heat & Material Balance

Case 4- 300 MWth CHG with PSA/Recycle-H2 membrane. CO_2 98.2% capture

Date: 28-Feb-22

Stream		1	2	3	4	5	6	7	8	9	10	11	12
Description	Units	Natural Gas from B.L.	Air	Boiler Feed Water Makeup	Steam to Reactor	Feed to Reactor	Sorbent to Reactor	Hydrogen - Out of Reactor	Calciner Sorbent - IN	Hydrogen to B.L	Calciner Fuel	Flue Gas to B.L.	CO2 to B.L.
Temperature	°C	25	21	41	777	371	892	709	709	27	55	75	38
Pressure	MPa	2.76	0.10	2.76	2.76	0.02	2.48	0.40	0.10	2.47	0.12	0.12	29.98
Molar Flow	kmol/h	1699.4	7298.6	3595.7	7256.2	1699.4	3875.0	10932.1	3841.4	4464.1	2592.9	8641.3	1812.8
Mass Flow	kg/h	30645	211406	64778	130722	30645	216074	87074	295196	8999	6863	218269	79782
Composition													
CO2	mol/mol	0.0200	0.0003	--	--	0.0200	0.0004	0.0014	--	--	0.0009	0.0040	1.0000
CO	mol/mol	--	--	--	--	--	0.0005	0.0019	--	--	0.0012	0.0000	--
Hydrogen	mol/mol	--	--	--	--	--	0.0007	0.6341	--	1.0000	0.9642	0.0000	--
H2O	mol/mol	--	--	1.0000	1.0000	--	0.0001	0.3354	--	--	0.0167	0.3014	--
Methane	mol/mol	0.8900	--	--	--	0.8900	0.0042	0.0164	--	--	0.0103	0.0000	--
Ethane	mol/mol	0.0700	--	--	--	0.0700	--	--	--	--	--	--	--
Propane	mol/mol	0.0100	--	--	--	0.0100	--	--	--	--	--	--	--
N-Butane	mol/mol	0.0011	--	--	--	0.0011	--	--	--	--	--	--	--
Nitrogen	mol/mol	0.0089	0.7808	--	--	0.0089	0.0019	0.0075	--	--	0.0047	0.6612	--
Oxygen	mol/mol	--	0.2095	--	--	--	--	--	--	--	--	0.0255	--
Argon	mol/mol	--	0.0094	--	--	--	--	--	--	--	--	0.0079	--
Solids													
CaCO3	mol/mol	--	--	--	--	--	--	--	0.4719	--	--	--	--
CaO	mol/mol	--	--	--	--	--	0.9913	--	0.5281	--	--	--	--

Notes: 1.) Feedstock purification to <50 ppbv of H2S has been assumed in NG to Hydrogen Plant
2.) NOx is not assessed
3.) CO2 Purity is assumed to be >99% vol

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6. Current Status: Pilot Plant Design and Operation

Development of the process technology to incorporate the indirect-fired, atmospheric calciner for carbon capture is currently supported by the U.S. Department of Energy (DOE) under the Advanced Manufacturing Office (AMO) for a small-scale pilot at GTI's main test facility in Des Plaines near Chicago, USA, and by the U.K. Department for Business, Energy, and Industrial Strategy (BEIS) for a larger pilot system at Cranfield University in the UK, both of which will be operational in 2022.

DOE has been supporting the development and operation of a 0.071 MW_{th} pilot plant, shown in Figure 4, to demonstrate the process chemistry and fluidized bed operation. De-risking of major process aspects has been accomplished.

Under the current DOE contract, the project evaluated the benefits of incorporating an indirect-fired, atmospheric calciner to produce a high purity CO_2 co-product. Additional risk mitigation testing of the calciner and necessary solids handling components (pressurization and depressurization lock hoppers) were successfully completed to pass a stage gate for constructing the upgraded pilot. Figure 5 shows the overall pilot plant layout within the test bay at GTI's Des Plaines facility, this plant has incorporated a rotary kiln style calciner. Figure 6 shows installation of various component that were identified in Figure 5.

Figure 4: Original CHG pilot plant (0.071 MWth).

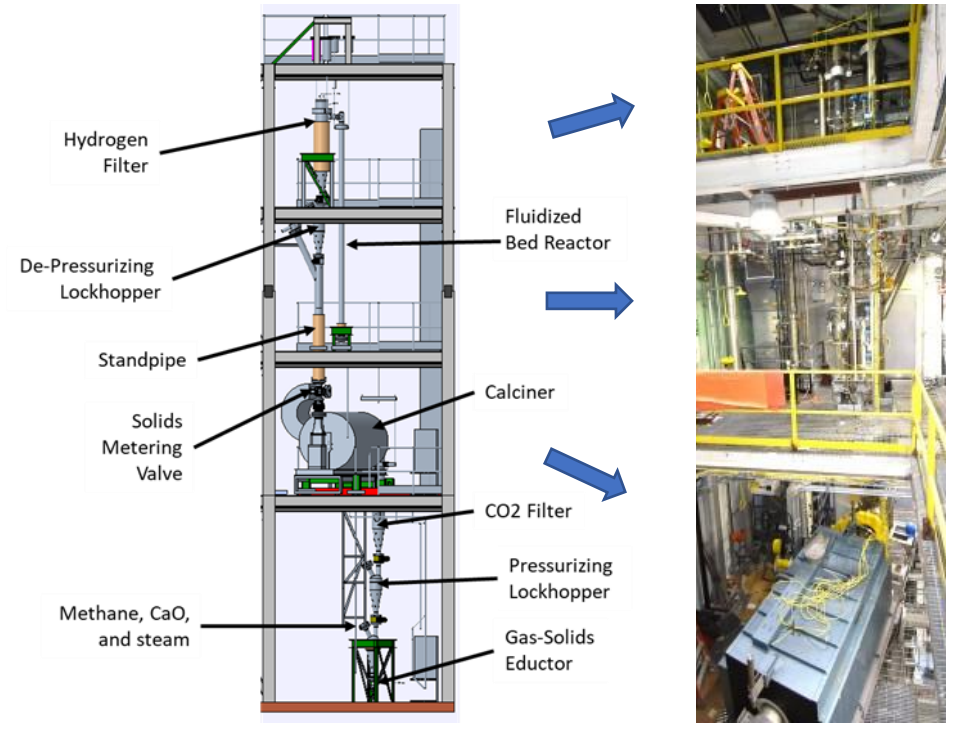

Figure 5: GTI Energy's CHG pilot, upgraded with atmospheric calciner for CO_2 capture, located at GTI Energy's test facility near Chicago, USA.

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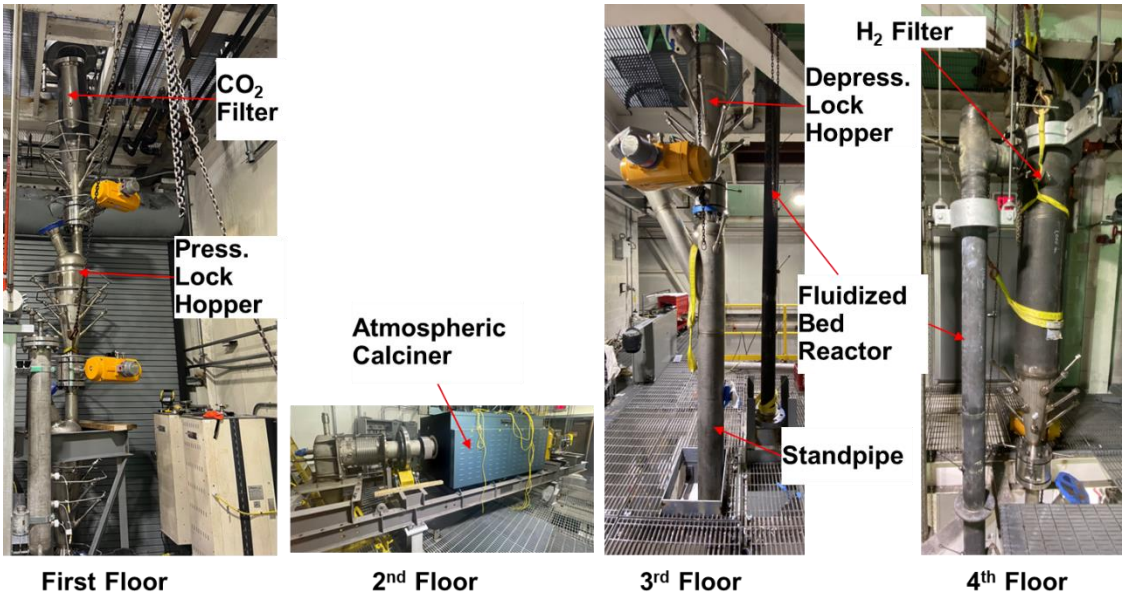

Figure 6: The pictures show the process components from the bottom to the top of the 4-story facility.

The objectives of the 0.071 MW_{th} pilot are to demonstrate the CHG process with the atmospheric calciner and the pressurizing and depressurizing lock hoppers. Planned testing includes extended operation to confirm prior results and determine the impact of increased sorbent flow.

Under BEIS funding, a team comprised of Cranfield University, GTI, and Doosan Babcock has been developing a 1 MW_{th} pilot plant at a dedicated new test site at Cranfield University in the UK, under the BEIS "HyPER" project. Commissioning of this plant is to begin in the fourth quarter of 2022, and first operation is scheduled to commence in by end of 2022 and into 2023. Figure 7 shows the completion of the civil construction of the test site and a rendering of the pilot system. The objective of the pilot operation is to demonstrate a first scale-up step and the industrial readiness of system components, while achieving sufficient operating hours of the integrated process to support a next scale (7-20 MW_{th}) demonstration.

Facility construction is in its final stages. The HyPER pilot uses a transport calciner which is indirectly fired (shown in Figure 8) and is the vision for the commercial scale design. Transport calcination offers numerous advantages over rotary kilns and is feasible for this application due to the small particle size of the sorbent used in the CHG process. The advantages of the transport calciner in this application are drastically reduced particle residence time (increasing sorbent life), enables articulation of the unit (minimizing hot-gas pipes and ducting), eliminates potential for air in-leakage or CO_2 out-leakage, and the ability to scale to ~300 MW_{th} (kilns are limited to ~15 MW_{th}). These technical attributes result in lower costs compared to rotary kilns for this application. Detailed views of the transport calciner under construction at Cranfield University are shown in Figure 8.

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Figure 7: Test site at Cranfield University with rendering of 1 MW_{th} CHG pilot plant to start operation in 2022 (BEIS "HyPER" project).

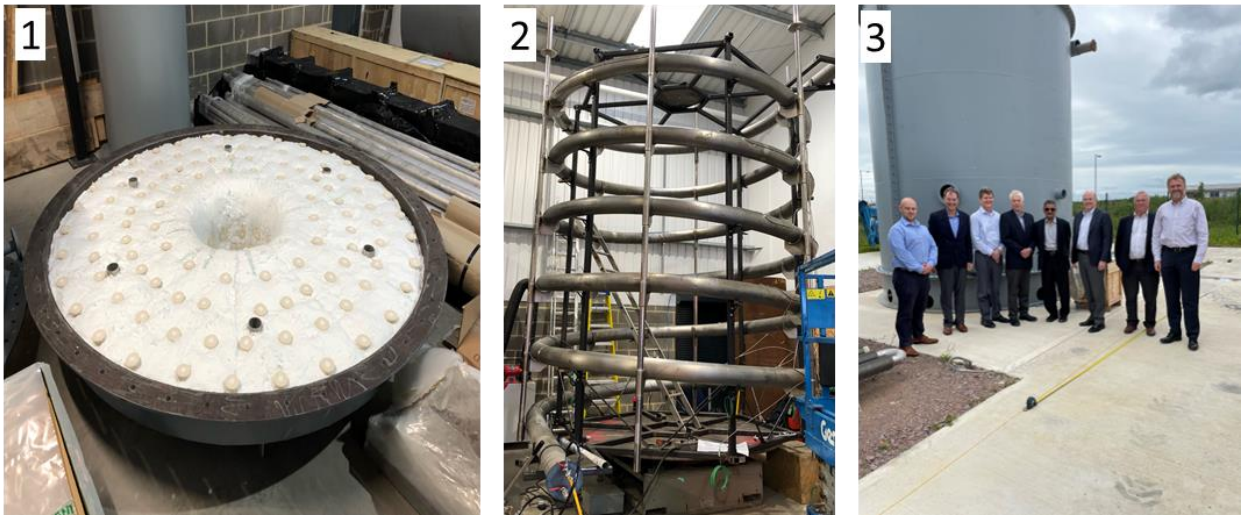

Figure 8: Transport calciner for the HyPER pilot plant. (1) calciner base, (2) calciner coil before installation, (3) outside view. The design enables lower cost and greater benefits than rotary kiln calciners for this application.

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7. Scale-up of CHG Process Technology

Together with its partners, GTI Energy has developed a process scale-up approach that will allow for the construction of modular intermediate commercial (50-150 MW_{th}) to large, utility scale CHG systems (300 MW_{th}, 600 MW_{th} and 900 MW_{th} or larger). Figure 9 shows the envisioned scale-up approach. A key scaling issue is the solids handling loop. It is envisioned that a scaleup from the demonstration scale of ~7-10 MW_{th} will be performed to achieve a 50 MW_{th} system with one solids handling loop (solids separation, depressurization, calcination, CO_2-side solids separation and pressurization). This loop can then be replicated with a single fluidized bed reactor up to 150-200MWth (3-4 solids loops), thus enabling fast commercial scale-up. Further scaleup would be required to achieve larger 300 MW_{th} solids handling loops and would subsequently replicate additional loops to achieve 600-1200 MW_{th}. Current limitations on scale are perceived to be near the 300 MW_{th} scale and limited by the equipment in the solids handling loop.

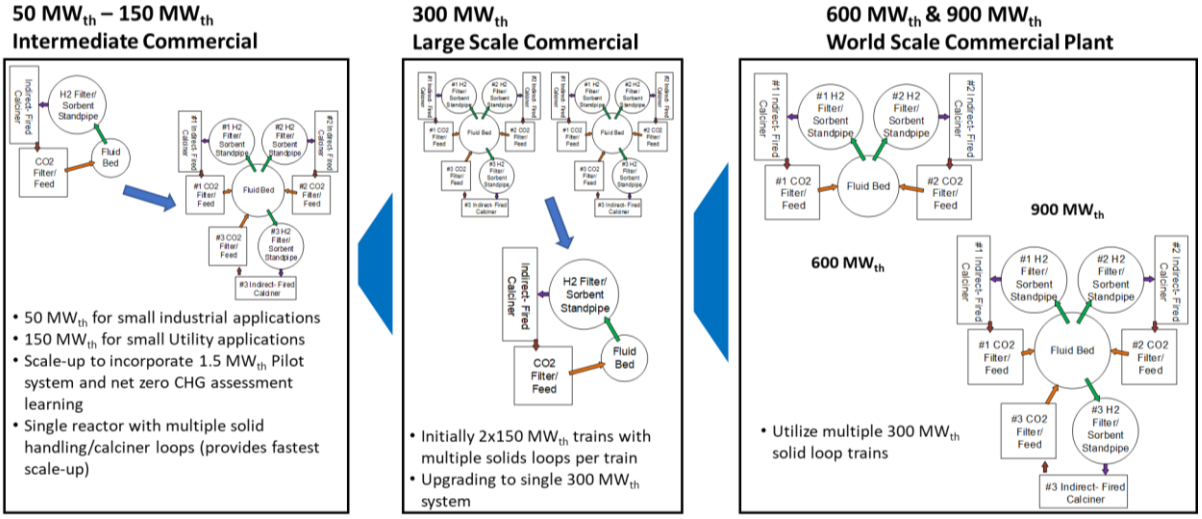

Figure 9: Scale up approach for GTI Energy's CHG technology from industrial scale to large utility scale systems.

8. Techno-Economic Analysis of the CHG Process with Integrated CO_2 Capture

The process intensification, increased efficiency, and the inherent, in-situ carbon capture help to drive lower cost of hydrogen from the CHG process. As part of the stage gate for the DOE project, a technoeconomic comparison was performed against a benchmark of a comparable SMR both with and without capture [5] under DOE contract DE-EE0008637. The basis for the TEA is 300 MW_{th} (214 metric tons/day), 0.9999 purity hydrogen and 90% CO_2 capture. SMR costs and the Levelized Cost of Hydrogen (LCOH) cost model used the IEAGHG 2017-2 report [6]. CHG costs were based on equipment costs and estimates obtained from a third-party EPC contractor. The process intensification realizes drastic reductions in the overall equipment costs as shown in Table 2.

The modularity and relative compactness also enable reductions in installation costs; however, these were not included to ensure equivalent basis for the analysis. As shown in Table 2, the reduced CAPEX produces lower cost of hydrogen without CO_2 capture and even greater savings with CO_2 capture since CO_2 capture is inherent to the CHG process. Upon review and validation of this assessment with DOE AMO IPA (Introspective Performance Assessment) group, the economics stage gate was passed.

A second economic assessment was performed to compare the different technologies (CHG, SMR, and ATR) for a high CO_2 capture application. The basis is similar to the DOE assessment in size and hydrogen purity, but the

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Table 2: Cost Comparison between SMR and CHG, with and without CO_2 capture.

	Total Installed Cost ($MM)	% lower than baseline	Total Capital Requirements ($MM)	% lower than baseline	Levelized Cost of Hydrogen $/kg	% lower than baseline
SMR w/o CO_2 Capture	$178		$277		$1.03	
CHG w/o CO_2 Capture	$102	42.9%	$159	42.6%	$0.84	19.2%
SMR with 90% Capture	$318		$497		$1.68	
CHG with 90% Capture	$156	50.8%	$244	50.9%	$1.21	27.9%

economic model is the BEIS LCOH calculator with significant differences in operating costs compared to the DOE cases. As shown in Figure 10 the CHG process has the lowest cost of hydrogen due to its lower CAPEX. Additionally, the comparison identifies that the CO_2 capture rate is the largest driver for reduced carbon footprint, with power consumption having a smaller but still significant impact.

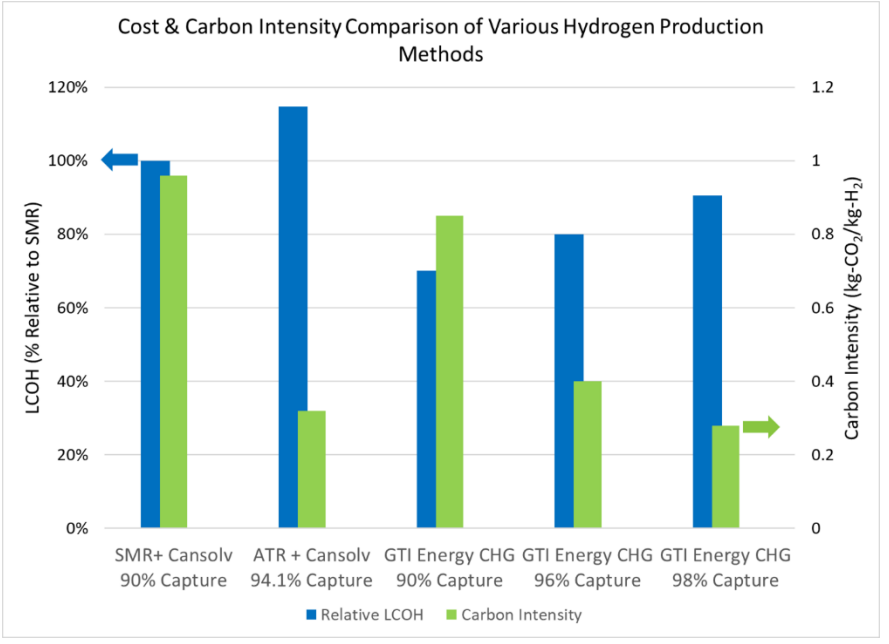

Figure 10: Hydrogen production cost comparison between CHG and conventional blue hydrogen production.

One additional attractive feature to GTI Energy's SER process advantages described above is the compactness of the system. This can reduce the plant footprint by nearly 75%. Figure 11 shows a comparison of a 335 MW_{th} (238 metric tons/day) conventional SMR with CO_2 capture plant versus a notional 300 MWth (214 metric tons/day) SER process plant. Both include 90% CO_2 capture. The SMR-based plant requires nearly 2 acres while the SER plant requires 0.5 acres.

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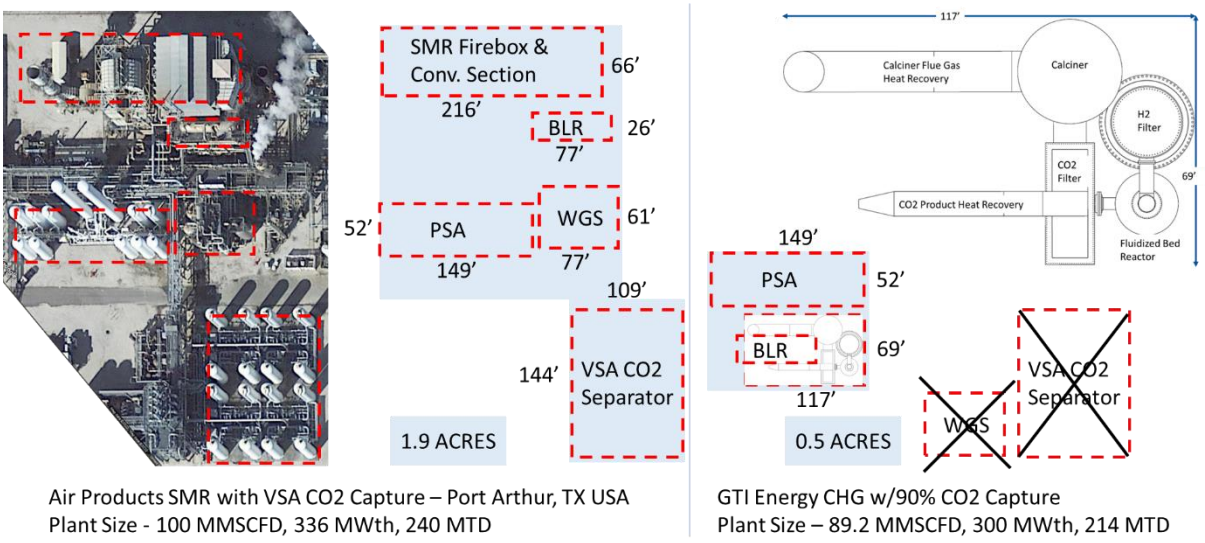

Figure 11. Footprint reduction of GTI Energy's SER process.

9. Summary

In summary, GTI has developed a novel approach to large scale sustainable hydrogen production from natural gas at substantially lower cost compared to conventional technologies such as SMR and ATR. High carbon capture rates approaching 100% are achievable, with a ~50% reduction in CAPEX compared to conventional SMR with CO_2 capture, and with 10-30% lower levelized cost of hydrogen produced, depending on carbon capture rate. Two pilot plants, one in the USA and one in the UK, are in their final stages of construction and will be operational in 2022.

Acknowledgements

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