Report on CO₂ Abatement Opportunities at Existing Industrial Hydrogen and Ammonia Production Plants

Prepared for the Center for Applied Environmental Law and Policy under contract with

Hensley Energy Consulting LLC

October 4, 2023

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1. Introduction

Hensley Energy Consulting LLC was retained to investigate and evaluate the existing industrial hydrogen (H_2) production plants in the US, identify those existing plants that would be candidates for abatement of CO₂ emissions, and create a database of such plants listing owners, locations, type of plant, age, hydrogen or ammonia capacity, CO₂ emissions, and related H_2 pipeline systems.

For this study, we developed an inventory of all large H_2 and ammonia (NH₃) plants, and any associated H_2 pipelines and storage facilities. Only plants located in the US were investigated.

The report discusses the technical options for abating CO_2 emissions from the plants in the inventories, estimates of potential CO_2 reduction amounts, and indicative capital and operating costs for installing the abatement equipment. Costs for transporting and storing captured CO_2 were not included in the scope of work.

- 2. Hydrogen Plant Inventories
 - a. SMR Plants

All industrial H₂ plants produce H₂ from natural gas using a "steam methane reforming" process (SMR). The inventories are divided into "captive plants" (owned by the refinery) and "merchant" plants (owned by third party industrial gas companies).

Tables 1 and 2 contain lists of every SMR plant in the US exceeding 10 million standard cubic feet per day (MMSCFD) H_2 capacity. For this study, we eliminated smaller plants that were not deemed practical or economic for retrofitting for CO_2 capture. Most of these plants supply high quality H_2 to petroleum refineries that need H_2 to produce specification grade transportation fuels (gasoline, jet fuel, diesel, and other "clean" products). A few sell "syngas" or H_2 to petrochemical plants.

Table 1 lists 55 "merchant" plants. At the time "pressure swing adsorption" (PSA) became commercial, the independent industrial gas industry offered "over the fence" H_2 from SMR plants they built, owned, and operated. Some merchant plants serve several refineries from pipeline systems owned by the industrial gas company that constructed the SMR plants. The merchant H_2 producers provided lower costs and more reliable service. In recent years, some refining companies have sold their "captive" plants to the independent operators. Three companies dominate the merchant SMR business: Air Products, Air Liquide, and Linde. The solvent and PSA versions of SMR technology are discussed later in Section 4 of this report.

SMR technology has improved over many decades. Some older refineries use "solvent" systems to remove the "process" CO₂ contained in the reformer syngas. Circa 1980s, 90s, "pressure swing adsorption" (PSA) was invented and this system has replaced the older solvent systems. Using our judgment and information we identified the solvent plants in the Table 1 (see Notes column). These technologies are discussed in Section 4 of this report.

Table 2 identifies 31 "captive" plants. These plants are part of the refinery system that is owned by the refining company. None of the H_2 from captive plants is sold outside the refinery. Some of the older captive H_2 plants may use the solvent technology. The public data does not identify those units.

$Table \ 1. \ Inventory \ of \ Addressable \ SMR \ H_2 \ Plants \ - \ Market \ for \ CCS \ Retrofits \ - \ Merchant \ Hydrogen \ Plants$

	Industrial			IL Course /			Conosity	Conceitre	Conositry	Voor	
Merchant	Gas Company	City	State	Process	Customer	Industry	(Nm3/hr)	(MMSCFD	(kg/day)	Opened	Notes
Merchant	Linde	Saraland	AL	SMR	Shell	Oil Refining	11,163	10	24,098	2007	
Merchant	Air Products	Carson	CA	SMR	Marathon, others	Oil Refining	111,634	100	240,976	1999	
Merchant	Air Liquide	El Segundo	CA	SMR	Chevron	Oil Refining	96,005	86	207,240	2004	
Merchant	Air Products	Martinez	CA	SMR	Tesoro	Oil Refining	39,072	35	84,342	1989	solvent?
Merchant	Air Products	Martinez	CA	SMR	PBF formerly Shell	Oil Refining	98,238	88	212,059	1993	solvent?
Merchant	Air Products	Martinez	CA	SMR	PBF formerly Shell	Oil Refining	117,215	105	253,025		
Merchant	Air Products	TORRANCE	CA	SMR	PBF formerly Exxon Mobil	Oil Refining	162,985	146	351,826		
Merchant	Praxair	Richmond	CA	SMR	Chevron	Oil Refining	290,247	260	626,539	2015	
Merchant	Air Liquide	Rodeo	CA	SMR	ConocoPhillips	Oil Refining	133,960	120	289,172	2009	
Merchant	Air Products	Wilmington	CA	SMR	Marathon?	Oil Refining	178,614	160 -	385,562	1995	solvent?
Merchant	Air Products	Delaware City	DE	SMR	Delaware City Refining PBF	Oil Refining	106,052	95	228,928	2016	
Merchant	Air Products	Delaware City	DE	SMR	Delaware City Refining PBF	Oil Refining	106,052	95	228,928	2016	
Merchant	Air Products	Joliet	IL	SMR	ExxonMobil	Oil Refining	20,094	18	43,376	2006	
Merchant	Linde	Romeoville	IL	SMR	Litgo	Oil Refining	16,745	15	36,146	2003	
Merchant	Linde	Romeoville	IL	SMR	Litgo	Oil Refining	50,235	45	108,439	2010	
Merchant	Praxair	East Chicago	IN	SMR	BP	Oil Refining	22,327	20	48,195	2006	
Merchant	Praxair	East Chicago	IN	SMR	BP	Oil Refining	111,634	100	240,976	2011	
Merchant	Praxair Air Dro du ata	East Unicago		SMR	BP Marathan	Oil Refining	27.055	100	240,976	2011	
Merchant	Air Products	Cattettsburg	KI	SMK	Maration	On Kenning	37,955	- 34	81,932	2004	
Merchant	Air Products	Baton Rouge	LA	SMR	ExxonMobil	Oil Refining	133,960	120	289,172	2010	
Merchant	Air Products	Convent	LA	SMR	Motiva, others	Oil Refining	122,797	110	265,074	2006	
Merchant	Air Products	Garyville	LA	SMR	Marathon	Oil Refining	133,960	120	289,172	2009	
Merchant	Praxair	Geismar	LA	SMR	ExxonMobil, others	Oil Refining	100,470	90	216,879	1997	
Merchant	Air Products	Luling	LA	SMR	Monsanto, others	Chemicals	111,634	100	240,976	2012	
Merchant	Air Products	New Orleans	LA	SMR	Multiple	Multiple	66,980	60	144,586	1995	solvent?
Merchant	Air Products	New Orleans	LA	SMR	Murphy Oil	Oil Refining	44,653	40	96,391	2003	
Merchant	Praxair	Norco	LA	SMR	Valero	Oil Refining	150,705	135	325,318	2013	
Merchant	Air Products	St. Charles	LA	SMR	Valero	Oil Refining	167,450	150	361,465	2014	
Merchant	Praxair	Sulphur	LA	SMR	Citgo, Conoco	Oil Refining	140,658	126	303,630	1999	
Merchant	Air Products	Westlake	LA	SMR	Conoco Phillips	Oil Refining	122,797	- 110	265,074	2004	
Merchant	Air Products	Detroit	MI	SMR	Marathon	Oil Refining	66,980	60	144,586	2012	
Merchant	Linde	Lima	OH	SMR	International Specialty Products	Chemicals	14,177	13	30,604	2000	
Merchant	Linde	Lima	OH	SMR	Husky Energy	Oil Refining	24,559	22	53,015	2006	
Merchant	Linde	Lima	OH	SMR	Husky Energy	Oil Refining	28,243	25	60,967	2016	
Merchant	Linde	Oregon	ОН	SMR	BP, Sunoco	Oil Refining	133,960	120	289,172	2006	
Merchant	Air Products	Corpus Christi	TX	SMR	MarkWest	Oil Refining	33,490	30	72,293	2010	
Merchant	Markwest Jave	el Corpus Christi	TX	SMR	Citgo, Flint Hills	Oil Refining	39,072	35	84,342		
Merchant	Praxair	Freeport	TX	SMR	BASF, Yara	Ammonia	189,777	170	409,660	2017	
Merchant	Praxair	Houston	TX	SMR	Valero	Oil Refining	111,634	100	240,976	2006	
Merchant	Praxair	La Porte	TX	SMR	ExxonMobil	Oil Refining	27,908	25	60,244		
Merchant	Praxair	Mont Belvieu	TX	SMR	LCR	Oil Refining	32,374	29	69,883		
Merchant	Praxair	Old Ocean TX	TX	SMR	Phillips 66 Sweeny	Oil Refining	189,777	170	409,660	2021	
Merchant	Air Liquide	Pasadena	TX	SMR	Deer Park (Shell/Pemex)?	Oil Refining	111,634	100	240,976	2006	
Merchant	Praxair	Port Arthur	TX	SMR	Motiva	Oil Refining	111,634	100	240,976	2004	
Merchant	Praxair	Port Arthur	TX	SMR	Valero	Oil Refining	150,705	135	325,318	2013	
Merchant	Praxair	Texas City	TX	SMR	BP, Amoco	Oil Refining	184,195	165	397,611	2004	
Merchant	Praxair	Texas City		SMR	Valero	Oil Refining	111,634	100	240,976	2006	1 + 2
Morchant	Air Products	Baytown	1 A	SMK	EXXUII MODII EuropMobil	Oil Refining	13,396	12	28,917	1992	solvent?
Morchant	Air Froducts	Daytown	1 A TV	SMK	Valoro	Oil Refining	/8,144 55 017	/U E0	120,083	2006	
Morchant	Air Liquide	La Porto	1A TV	SMR	Valoro	Oil Refining	33,81/ 122.040	5U 120	120,488	2012	
Morchant	Air Droducto	Dasadona	1A TV	SMR	valet 0	Oil Refining	133,900	120	209,172	1007	coluent?
Merchant	Air Products	Port Arthur	TY	SMR	Premcor	Oil Refining	117 215	00 105	252 025	2000	sorvent (
Merchant	Air Products	Port Arthur	TX	SMR	Valero	Oil Refining	122,797	110	265,074	2000	
Merchant	Linde	Salt Lake City	UT	SMR	Chevron, Tesoro, others	Oil Refining	34,606	- 31	74,703	2006	

Total Merchant Plant Capacity

4,770 11,494,575

5,324,922

Notes: Original data if from H2Tools a database created by Pacific NW Labs under DOE Contract. Last update was 2016 Hensley Energy used published news to update and correct errors in the databases.

Small specialty plants and plants producing syngas for petrochemical plant feeds were deleted.

Shutdown plants deleted. Change of ownership noted. One new SMR merchant plant added

"Capacity" is the capability to produce H2. Actual output will be lower due outages, maintenance,

curtailment. "solvent" SMRs are older plants built before PSA was developed. Possible solvent plants are noted with a "?".

Table 2. Inventory of Addressable Market for CCS Retrofits - On-site Captive SMR Hydrogen Plants Owned by the Refining Company

				H ₂							
				Source/			Capacity	Capacity	Capacity		
Status	Company		State	Process	Product	Industry	(Nm3/hr)	(MMSCFD)	(kg/day)	Source	Year Opened
Captive	HUNT REFINING CO	TUSCALOOSA	ALABAMA	SMR	H ₂	Oil Refining	44,653	40	96,391	EIA	NA
Captive	CHEVRON USA INC	RICHMOND	CALIFORNIA	SMR	H ₂	Oil Refining	368,391	330	795,222	EIA	NA
Captive	CHEVRON USA INC	EL SEGUNDO	CALIFORNIA	SMR	H ₂	Oil Refining	82,609	74	178,323	EIA	NA
Captive	MARATHON PETROLEUM	CARSON	CALIFORNIA	SMR	H ₂	Oil Refining	133,960	120	289,172	EIA	NA
Captive	PHILLIPS 66 COMPANY	WILMINGTON	CALIFORNIA	SMR	H ₂	Oil Refining	117,215	105	253,025	EIA	NA
Captive	PHILLIPS 66 COMPANY (formerly Conoco Phillips	RODEO	CALIFORNIA	SMR	H ₂	Oil Refining	24,559	22	53,015	EIA	NA
Captive	VALERO REFINING CO CALIFORNIA	BENICIA	CALIFORNIA	SMR	H ₂	Oil Refining	150,705	135	325,318	EIA	NA
Captive	SUNCOR ENERGY (USA) INC	COMMERCE CITY	COLORADO	SMR	H_2	Oil Refining	24,559	22	53,015	EIA	NA
Captive	DELAWARE CITY REFINING CO LLC	DELAWARE CITY	DELAWARE	SMR	H ₂	Oil Refining	44,653	40	96,391	EIA	NA
Captive	WRB REFINING LP	WOOD RIVER	ILLINOIS	SMR	H ₂	Oil Refining	212,104	190	457,855	EIA	NA
Captive	BP	WHITING	INDIANA	SMR	H ₂	Oil Refining	111,634	100	240,976	EIA	NA
Captive	CHS MCPHERSON REFINERY INC	MCPHERSON	KANSAS	SMR	H ₂	Oil Refining	46,886	42	101,210	EIA	NA
Captive	COFFEYVILLE RESOURCES RFG & MKTG	COFFEYVILLE	KANSAS	SMR	H ₂	Oil Refining	24,559	22	53,015	EIA	NA
Captive	HOLLYFRONTIER EL DORADO REFINING LLC	EL DORADO	KANSAS	SMR	H ₂	Oil Refining	62,515	56	134,947	EIA	NA
Captive	VALERO REFINING NEW ORLEANS LLC	NORCO	LOUISIANA	SMR	H ₂	Oil Refining	111,634	100	240,976	EIA	NA
Captive	Flint Hills Resources LP	SAINT PAUL	MINNESOTA	SMR	H ₂	Oil Refining	222,151	199	479,543	EIA	NA
Captive	CHEVRON USA INC	PASCAGOULA	MISSISSIPPI	SMR	H ₂	Oil Refining	255,641	229	551,836	EIA	NA
Captive	CALUMET MONTANA REFINING LLC	GREAT FALLS	MONTANA	SMR	H ₂	Oil Refining	22,327	20	48,195	EIA	NA
Captive	Cenex Harvest States Coop	LAUREL	MONTANA	SMR	H ₂	Oil Refining	78,144	70	168,683	EIA	NA
Captive	EXXONMOBIL REFINING & SUPPLY CO	BILLINGS	MONTANA	SMR	H ₂	Oil Refining	25,676	23	55,425	EIA	NA
Captive	PHILLIPS 66 COMPANY (formerly Conoco Phillips	BILLINGS	MONTANA	SMR	H ₂	Oil Refining	39,072	35	84,342	EIA	NA
Captive	PHILLIPS 66 COMPANY (formerly Conoco Phillips)	LINDEN	NEW JERSEY	SMR	H ₂	Oil Refining	24,559	22	53,015	EIA	NA
Captive	HOLLYFRONTIER NAVAJO REFINING	ARTESIA	NEW MEXICO	SMR	H ₂	Oil Refining	42,421	38	91,571	EIA	NA
Captive	PHILLIPS 66 COMPANY (formerly Conoco Phillips	PONCA CITY	OKLAHOMA	SMR	H ₂	Oil Refining	39,072	35	84,342	EIA	NA
Captive	VALERO REFINING CO OKLAHOMA	ARDMORE	OKLAHOMA	SMR	H ₂	Oil Refining	30,141	27	65,064	EIA	NA
Captive	VALERO REF CO TENN LLC (formerly Premcorp)	MEMPHIS	TENNESSEE	SMR	H ₂	Oil Refining	33,490	30	72,293	EIA	NA
Captive	DIAMOND SHAMROCK REFINING CO LP (formerly Valero)	SUNRAY	TEXAS	SMR	H ₂	Oil Refining	33,490	30	72,293	EIA	NA
Captive	VALERO	CORPUS CHRISTI	TEXAS	SMR	H ₂	Oil Refining	178,614	160	385,562	EIA	NA
Captive	WRB REFINING	BORGER	TEXAS	SMR	H ₂	Oil Refining	101,587	91	219,289	EIA	NA
Captive	BP West Coast Products LLC	FERNDALE	WASHINGTON	SMR	H ₂	Oil Refining	207,638	186	448,216	EIA	NA
Captive	SINCLAIR WYOMING REFINING CO	SINCLAIR	WYOMING	SMR	H ₂	Oil Refining	58,049	52	125,308	EIA	NA
						2	2.952.708	2.645	6.373.826		

* EIA - is Energy Information Administration

EIA has capacity data on US refining operations, refinery unit capacities, including captive H_2 capacities.

Notes: Hensley Energy used published news to update and correct errors in the EIA databases. .

Shutdown plants deleted. Change of ownership noted.

No age data provided - many older small SMRs could be "solvent" plants that predate PSA technology. "Capacity" is

the capability to produce H₂. Actual output will be lower due outages, maintenance, curtailment, etc.

3. Ammonia Plant Inventory

Table 3 is a list of 32 ammonia plants in the USA.ⁱ Each plant capacity is reported as thousand metric tonnes per year of anhydrous ammonia. Most ammonia plants also produce urea and other nitrogen chemicals.

Ammonia plants include two SMR units in the front end of the processing train to provide the H_2 and N_2 needed to synthesize ammonia (NH₃).

Ammonia SMRs differ from the refinery H_2 SMR design, in that nitrogen is needed along with the H_2 to synthesize ammonia. This is accomplished by introducing air to one of the reformers. Ammonia SMRs must remove the "process" CO_2 from the reformer "syngas" (H_2/N_2) before feeding to the "NH₃ synthesis" section of the plant. Like refinery SMR's, the "process" CO_2 reject stream is a promising opportunity to capture CO2 from a concentrated stream. The fired reformer produces flue gas containing "fuel" CO_2 .

These technologies will be discussed in Section 4(b).

INVENTORY OF US ANHYDROUS AMMONIA PLANTS						
Source: USGS 2022 Databook	Hensley Energy Consulting LLC					
(Thousand met	tric tons per year of ammonia)					
Company	Location	Capacity				
AdvanSix Inc.	Hopewell, VA	530				
CF Industries Holdings, Inc.	Donaldsonville, LA (5 plants)	4,330				
Do.	Port Neal, IA	1,230				
Do.	Verdigris, OK (2 plants)	1,210				
Do.	Woodward, OK	480				
Do.	Yazoo City, MS	570				
Coffeyville Resources Nitrogen Fertilizers, LLC	Coffeyville, KS (coke feed, now CCS)	375				
Dakota Gasification Co.	Beulah, ND	355				
Dyno Nobel Inc.	Cheyenne, WY	178				
Do.	St. Helens, OR	100				
Dyno Nobel Louisiana Ammonia, LLC	Waggaman, LA	800				
East Dubuque Nitrogen Fertilizers, LLC	East Dubuque, IL	337				
Fortigen Geneva, LLC	Geneva, NE	31				
Green Valley Chemical Corp.	Creston, IA	32				
Iowa Fertilizer Co.	Wever, IA	770				
J.R. Simplot Co.	Rock Springs, WY	185				
Koch Fertilizer, LLC	Beatrice, NE	265				
Do.	Dodge City, KS	280				
Do.	Enid, OK	930				
Do.	Fort Dodge, IA	350				
LSB Industries, Inc.	Cherokee, AL	185				
Do.	El Dorado, AR	490				
Do.	Pryor, OK	240				
Mosaic Company, The	Faustina (Donaldsonville), LA	510				
Nutrien Ltd.	Augusta, GA	765				
Do.	Borger, TX	490				
Do.	Geismar, LA	535				
Do.	Kenai, AK3	280				
Do.	Kennewick, WA3	180				
Do.	Lima, OH	725				
OCI Partners LP	Beaumont, TX	332				
Yara Freeport LLC	Freeport, TX	750				
Total Locations - Annual Production	32	18,800				
Total Plants	38	tonnes/year				

Table 3 - Inventory of US Anhydrous Ammonia Plants

4. Discussion of Technical Options for CO_2 Capture

a. Refinery SMR Plants

Figure 1 is a simplified block flow diagram (BFD) for an old "solvent" SMR based upon widely known practice in the industry. This plant has two sources of CO_2 emissions: flue gas CO_2 and CO_2 captured in the amine CO_2 removal unit. The amine solvent captures most of the CO_2 since only small amounts are allowed in the H₂ product. In addition, the reformer furnace combusts natural gas with excess air and produces flue gas CO_2 that is released to the atmosphere. This flue gas contains CO_2 at lower concentration and pressure.

The solvent SMR provides a simple capture option in that the solvent stripper released CO_2 is in concentrated form. A simple compressor dryer system can be added for producing dry CO_2 at high pressure before feeding to a pipeline. Some plants do this now to sell "food grade" CO_2 . This option is not shown in Figure 1 due to its simplicity.



Figure 1. Simplified Block Flow Diagram for Pre PSA "Solvent" Steam Methane Reformer

Figure 2 is a simplified BFD for a modern "PSA" SMR based upon widely known practice in the industry. The PSA rejects all the CO_2 along with unconverted methane and carbon monoxide and sends this "tail gas" to the reformer furnace for fuel along with natural gas fuel.

Figure 2. Simplified Block Flow Diagram for Modern PSA Steam Reformer



There are many options and combinations available to capture CO_2 from a modern PSA SMR plant. Covering all of those is beyond the scope of this study. Figures 3 and 4 show two of the more common options for capturing CO_2 from a modern PSA SMR plant. As SMR plants follow

the same flow sheet, these options are available to all SMR plants. These options are discussed in more detail in the literature.ⁱⁱ

- a. Adding an amine solvent system upstream of the PSA unit will capture about 99% of the CO_2 contained in this stream. This may require modifying the PSA unit and the reformer burners. (Figure 3)
- b. Adding a post combustion solvent system to the reformer flue gas will capture about 90% of the CO₂ contained in the flue gas. Since all the process CO₂ remains in the tail gas, which is then combusted at the reformer, this CO₂ will be captured in a post combustion capture system (Figure 4).
- c. A third option is to add both capture units shown in Figures 3, 4. This option is not shown in the figures. The combination would result in capturing about 96% of the carbon in the feed and fuel system.

Figure 3. Simplified Block Flow Diagram for Modern PSA Steam Methane Reformer with Process CO₂ Capture



Figure 4. Simplified Block Flow Diagram for Modern PSA Steam Methane Reformer with Flue Gas CO₂ Capture



b. Ammonia Plants

Figure 5 is a simple BFD of a typical ammonia plant as widely practiced in the industry. The CO_2 capture options shown in green.

Figure 5. Ammonia Plant Block Flow Diagram with Carbon Capture Options



Like refinery SMR H_2 plants, ammonia plants have two major sources of CO_2 emissions: the fired reformer flue gas and the amine CO_2 removal unit which is inside the reformer section that produces the H_2 for NH_3 synthesis.

The flue gas contains oxygen and nitrogen from the combustion air and produces flue gas with low CO_2 concentration. A specialized version of a post combustion capture unit can be added to capture about 90% of the CO_2 .

About 99%+ of the CO_2 in process stream must be removed to enable the NH_3 synthesis process. That CO_2 stream is concentrated and can be dried and compressed for pipeline transport and storage or used as feedstock for urea production. In most large ammonia plants, a portion of the process CO_2 is used for urea production.

Figure 5 shows the captured CO_2 that is fed to the urea synthesis section. The remaining CO_2 is released to the atmosphere.

5. Hydrogen Pipelines and Storage Inventories

Many existing SMR H_2 plants are interconnected to customer sites via H_2 pipelines and storage "domes". Table 4 is an inventory list of H_2 pipelines in the USA.

Table 4 - Inventory of USA HydrogenPipelines

Hensley Energy Consulting LLC

	USA	Texas	Louisiana
Operator Name	Total Miles	Total Miles	Total Miles
AIR PRODUCTS & CHEMICALS INC	559.8	202.5	329.0
LINDE	458.5	298.0	127.3
AIR LIQUIDE LARGE INDUSTRIES U.S. LP	369.3	368.0	1.3
subtotal majors	1,387.6	868.5	457.6
EQUISTAR CHEMICALS, L.P.	24.4		
FLINT HILLS RESOURCES, LC	22.6		
INEOS USA LLC	21.3		
US AMINES	20.1		
PHILLIPS 66 COMPANY - SWEENY REFINERY	14.8		
MATHESON TRI-GAS, INC	11.8		
CITGO REFINING & CHEMICAL CO. L.P.	8.0		
PIONEER AMERICAS LLC DOING BUSINESS AS OLIN CHLOR ALKALI PRODUCTS	6.0		
LAFITTE GAS PIPELINE	5.9		
BLUE CUBE OPERATIONS, LLC.	5.1		
HOLLY REFINING & MARKETING COMPANY	4.3		
THE DOW CHEMICAL COMPANY	3.6		
VALERO REFINING-TEXAS, L.P.	3.2		
EXXONMOBIL OIL CORPORATION	3.1		
HEP JAVELINA COMPANY, LLC	2.7		
HEP GAS SERVICES, LLC	2.6		
AIRGAS MERCHANT GAS KALAMA	2.4		
BUCKEYE DEVELOPMENT & LOGISTICS, LLC	2.3		
INDORAMA VENTURES OXIDES LLC	2.1		
OCCIDENTAL CHEMICAL CORP	1.9		
PHILLIPS 66 PIPELINE LLC	1.7		
VALERO REFINING-NEW ORLEANS, L.L.C.	1.6		
HOLLY ENERGY PARTNERS - OPERATING, L.P.	1.5		
CITGO PETROLEUM CORPORATION (REFINERY)	1.4		
WESTLAKE PETROCHEMICALS LLC	1.2		
TPC GROUP, LLC	0.9		
SASOL CHEMICALS USA LLC	0.8		
NOURYON PULP AND PERFORMANCE CHEMICALS LLC	0.5		
EVONIK	0.4		
EXXONMOBIL PIPELINE COMPANY LLC	0.4		
SOLVAY CHEMICALS, INC.	0.1		
subtotal others	178.7	128.9	18.6
Grand Total H ₂ Pipelines	1.566.3	997.4	476.2

Data Source: US DOT Pipeline and Hazardous Materials Safety Administration (2021)

These pipelines provide high purity, high pressure H_2 essentially "on demand" to customers that rely on reliable supplies of critically needed H_2 . There are 1,566 miles of H_2 pipelines in the US. 1,388 miles of these pipelines are owned by the 3 major industrial gas companies. Most of this capacity is in Louisiana and Texas where the pipelines serve the hydrocarbon processing industry.

Figure 6 shows a map of the 3 largest H₂ pipeline systems and 3 storage domes.

Louisiana Lake Charles H, pipeline continues Conroe to Baton Rouge Liberty and New Orleans Houston Beaumont Baytown **Texas City** Galveston H₂ pipeline H₂ production unit Freeport H₂ storage caverns

Figure 6. Map of Gulf Coast Hydrogen Plants, Pipelines and Storage Caverns

Table 5 contains data on the existing H_2 storage salt domes in the US, all in Texas. Some of the data in the table were calculated by the author using the data from the original sources.⁽¹⁾ ^v ^v</sup> These domes have been in operation for many years and provide backup to the pipeline

system and customers of the industrial gas companies. We have added data on the proposed Delta hydrogen storage dome under development in Utah.

Location	Clemens Dome TX	Moss Bluff TX	Spindletop TX	NA	Delta Utah
Source	Southern Companies Presentation (1)	Southern Companies Presentation	Southern Companies Presentation	SMR Inventory (CAELP)	Recent Press Releases
Geology	Salt dome	Salt dome	Salt dome	None	Salt dome
Operator	ConocoPhillins	Linde ev Pravair	Air Liquide	Air Products	ACES Delta
Vear	1083	2007	All Equide	An Troducts	2022
Volume (m3)	580,000	566,000	906.000		2022
Mean depth (m)	1,000	1,200	1,340		
Pressure range (bar)	1.015-1.986	797-2,204	986-2.929		
H2 capacity (GWh)	81	123	274		300
H2 storage (tonnes)	2,400	3,690	8,230		7,621
Days of Storage for 1 GW H2CC					
(50% eff.)	2	3	6		5

Table 5. Summary of Hydrogen Salt Dome Storage in the U.S.

Source:	Texas Railroad Commission	Texas Railroad Commission	Texas Railroad Commission	SMR Inventory	Recent Press Releases
Operator	Phillips 66 Pipeline	and the second	Air Liqude Large		11000000000000
	Co	Linde Inc.	Ind US	Air Products	ACES Delta
Permitted Fluids	Gas	Hydrogen	Gas	none	Hydrogen
max inject Pressure psi	2198	2100	2955	none	NA
Gas inject rate, MCF/day	130000	7500000	150000	none	NA
max to min depth range, ft	2200	1000	1000		
	2200	1900	1900	none	NA
Permit Year	2014	2004 -2015	2008	none	2022
County	Brazoria	Liberty	Jefferson	none	Millard
Green H2 production, tonnes/day	NA	NA	NA	none	100
Green H2 production, MMSCFD	NA	NA	NA	none	NA
H2 Storage in MMSCF	1.002	1,540	3,436	NA	3.187
Texas SMR Capacity, MMSCFD	customers not	2.5.1.20.00			
	identified	994	270	407	NA
Utah H2 Capacity, MMSCFD	NA	NA	NA	NA	166.98
Days H2 storage vs TX Fleet	NA	1.55	12.72	NA	76.35
Days H2 Storage for 100 MMSCFD SMR	10.0	15.4	34.4	NA	NA

(1) H2@Scale Workshop, Southern Company Services, R&D, Hydrogen and Energy Storage Noah D. Meeks, Ph.D. Nov 5, 2019

6. Estimates of CO₂ Emissions and Capture Potential from SMR H₂ plants.

Table 6 summarizes the potential CO_2 capture potential from SMR H_2 plants in the US. The capture ratio factors for the capture options were derived from the detailed published papers.^{vi} Since SMR plants all follow very similar process line ups, these factors can be applied to a wide range of plants. The total capture potentials in Table 6 assume every plant in the inventories is retrofitted with one or more of the technologies described above.

Captive SMR PSA Plants		Capture Potential				
	Existing Plants CO2	Process CO2	Flue Gas CO2	Process+Flue Gas CO2		
% capture	0%	50%	90%	96%		
CO2 emissions sT/day	70,093	<mark>35,04</mark> 6	7,009	2,804		
CO2 captured sT/day		35,046	<mark>63,083</mark>	67,289		
CO2 emissions MMsT/year	24.3	12.2	2.4	1.0		
CO2 captured MMsT/year	0	12.2	21.9	23.3		
Merchant Solvent SMR			Capture Potentia	1		
	Existing Plants CO2	Process CO2	Flue Gas CO2	Process+Flue Gas CO2		
% capture	0%	60%	NA	96%		
CO2 emissions sT/day	11,528	4,611	NA	461		
CO2 captured sT/day		6,917	NA	11,066		
CO2 emissions MMsT/year	4.0	1.6	NA	0.2		
CO2 captured MMsT/year	-	2.4	NA	3.8		
Merchant SMR PSA Plants		Capture Potential				
	Existing Plants CO2	Process CO2	Flue Gas CO2	Process+Flue Gas CO2		
% capture	0%	50%	90%	96%		
CO2 emissions sT/day	107,988	53,994	10,799	4,319		
CO2 captured sT/day		53 <i>,</i> 994	<mark>97,1</mark> 89	103,668		
CO2 emissions MMsT/year	37.4	18.7	3.7	1.5		
CO2 captured MMsT/year	-	18.7	33.7	35.9		
Summary			Capture Potentia			
All USA SMR H2 Plants	Existing Plants CO2	Process CO2	Flue Gas CO2	Process+Flue Gas CO2		
CO2 emissions MMsT/year	65.7	32.5	6.2	2.6		
CO2 captured MMsT/year	-	33.3	55.6	63.1		

Table 6. Estimates of USA Hydrogen Plant Inventory CO₂ Capture Potential

The summary for all SMR plants states that total CO_2 emissions from all SMR plants is about 65.7 mm tons per year of CO_2 . If all technologies were applied, about 63 mm tons per year could be removed and prevented from entering the atmosphere. SMR plants typically have a carbon intensity of about 10 kg CO_2/kg H₂. If an SMR plant is retrofitted with process capture equipment, the carbon intensity would fall to about 4-5 kg CO_2/kg H₂. If the post-combustion capture is retrofitted, the carbon intensity would fall to about 0.4-0.5 kg CO_2/kg H₂. Actual performance would depend on local site conditions and the specific licensed technologies selected.

These estimates are the addressable market. Even with financial incentives, there are other constraints that will limit emissions abatement. These are discussed in Section 9.

7. Estimates of CO₂ Emissions and Capture Potential from Ammonia Plants

Table 7 contains our estimate of the CO₂ emissions from, and abatement potential for, US ammonia plants.

As described earlier, there are two sources of CO_2 emissions in a typical NH_3 plant: the process CO_2 from the reformer syngas and the flue gas CO_2 from the fired reformer furnace. The inventory of US ammonia plants is from the USGS databases as well as the author's own calculations. ^{vii}

A portion of the process CO_2 is used to produce urea in some plants and the balance is vented to the atmosphere. For our estimates, we looked at the urea produced in the US and used that data to estimate the process CO_2 required and computed the balance that is vented. We do not have the data to make this calculation on a plant-by-plant basis. Table 7 shows the nationwide net process CO_2 available for abatement. All flue gas CO_2 is currently vented to the atmosphere.

Table 7 - US Ammonia Plants CO2 Potential	Process CO2 after Urea draw	Flue Gas CO2	Total CO2 Fuel and Feed		
	mm	tonnes/yr	mm tonnes/yr	mm tonnes/yr	mm tonnes/yr
Total US Ammonia Capacity		18.4	13.9	9.7	23.5
Average Plant Capcity Factor	92%	17.0	12.7	8.9	21.6
CO2 Capture Rate			99.0%	90.0%	95.3%
CO2 Captured (metric tonnes)	CO2 Captured (metric tonnes) Total Potential		12.6	8.0	20.6
			mm sTon/yr	mm sTon/yr	mm sTon/yr
CO2 Captured (short tons) Total Potential			13.9	8.8	22.7

Table 7. US Ammonia Plants CO₂ Emissions and Capture Potential

Assuming a typical annual capacity utilization of 92%, we estimated the masses of CO_2 that is emitted from these plants. Process CO_2 is already captured, so it needs to be dried and compressed before pipelining to storage. Flue gas CO_2 needs a solvent capture plant designed for oxygen bearing flue gas. As 90% capture has been demonstrated, we assume 90% capture in this report.

Table 7 shows that the technical potential CO_2 capture from all the ammonia plants is about 22.7 million short tons per year. Other factors may limit the number of CCS plants that could be constructed and some of those constraints are discussed in Section 9 of this report.

8. Range of Cost Estimates for Retrofitting CCS to SMR H₂ and Ammonia Plants

Table 8 summarizes our preliminary estimates of the capital and total annual costs (including recovery of capital costs) for capturing CO_2 using the technology options described above to retrofit all the addressable industrial SMR H_2 and ammonia plants in the US.

We developed these costs from published studies and reports cited above and internal confidential data. At this time, the Shell Quest project in Canada is the only large refinery SMR H₂ complex that has been retrofitted to capture and store CO₂. This project has been operating successfully demonstrating, on a commercial scale, the capture of process CO₂ and

underground storage nearby. Post-combustion capture was not included in the Shell Quest project. Process CO_2 is being captured upstream of the PSA units. Also, the project is fed in part by H_2 rich refinery fuel gas. This complicates the interpretation of the data for application to other locations. The Shell project is "first of a kind" (FOAK) project. Such projects typically cost much more than "2nd Generation" or "Nth of a Kind" projects. For these reasons, we did not use the reported capital costs for the Shell Quest project.

To develop capital and operating costs for retrofitting capture technologies to existing plants, we relied upon detailed studies of new plants using the available technologies.^{viii} These studies present costs for both new uncontrolled plants and costs for new controlled plants (with CCS features). We analyzed those differences to determine the incremental costs for retrofitting the uncontrolled plants. We adjusted for differing timeframes, fuel prices and utility costs to arrive at more consistent results Our estimates apply best to current Gulf Coast location economics. All costs are in overnight 2021 dollars. We would judge the accuracy of these costs for Nth of a kind projects to be plus or minus 30-40%.

We used a fixed cost recovery factor of 8%. This includes the cost of equity, debt, and corporate income taxes. This factor is used by the DOE in its studies. ^{ix} This factor can vary with market rates for equity and debt.

We did not endeavor to account for individual plant size in estimating costs as a study of each individual site was not within the scope of this study. DOE and EIA reports were based on 100 MMSCFD facilities.

Table 8 - Preliminary Estimates of Capital and Annual Costs for Addressable SMR $\rm H_2$ and Ammonia CCS Markets in USA

Hensley Energy Consulting LLC

Captive SMR Plar	nts					
					Post Comb	
Total Capital and O	perating Costs ref ST data	Dry/C	ompress	PSA only	Capture Only	PSA + PCC
Capital Costs	\$ Million	1	NA	1,701	7,000	8,400
Annual Cost	\$ MM/yr	1	NA	425	1,203	1,517
	mm sT/yr captured		-	12.15	21.87	23.33
Merchant Solven	t SMR	-				
Total Capital and O	perating Costs ref ST data	Dry/C	ompress	PSA only	Post Comb Capture Only	Dry/Comp + PCC
Capital Costs	\$ Million	\$	168	NA	\$ 1,151	\$ 1,381
Annual Cost	\$ MM/yr	\$	56	NA	\$ 198	\$ 249
	mm sT/yr captured		2.40	0	3.60	3.84
Merchant PSA SM	/IR					
					Post Comb	
Total Capital and O	perating Costs ref ST data	Dry/C	ompress	PSA only	Capture Only	PSA + PCC
Capital Costs	\$ Million	1	NA	\$ 2,621	\$ 10,784	\$ 12,941
Annual Cost	\$ MM/yr	1	NA	\$ 655	\$ 1,854	\$ 2,337
	mm sT/yr captured		0.00	18.72	33.70	35.95
Ammonia Plants						
					Flue Gas	Dry/Comp
Total Capital and O	perating Costs ref tonne data	Dry/C	ompress	NA	Capture	+ PCC
Capital Costs	\$ Million	\$	1,069	NA	\$ 3,405	\$ 4,474
Annual Cost	\$ MM/yr	\$	214	NA	\$ 585	\$ 799
	mm sT/yr captured		15.27	-	10.64	25.91
Total SMR + Amn	nonia					
Capital Costs	\$ Million	\$	1,237	\$ 4,322	\$ 22,340	\$ 27,196
Annual Cost	\$ MM/yr	\$	270	\$ 1,081	\$ 3,840	\$ 4,902
	mm sT/yr captured		17.67	30.87	69.81	89.02
All Sectors						
Annual Cost	\$/sT CO ₂	\$	15.27	\$ 35.00	\$ 55.00	\$ 55.06
Transport Storage	\$/sT CO ₂	\$	20.00	\$ 20.00	\$ 20.00	\$ 20.00

These estimates show that costs can vary from \$15 to \$55 per short ton of captured CO₂. Plants that release process CO₂ (no capture required) are the lowest cost opportunity. If all retrofits were implemented to capture process CO₂, we estimate this would remove about 18 million short tons per year (mm sT/yr) CO₂. If all technologies were applied to all addressable CO₂ emissions at plants, including flue gas and process CO₂, the costs would be about \$55/short ton CO₂, and about 89 mm sT/yr of CO₂ could be abated. If all addressable plants were retrofitted, we estimate the overnight capital costs would be about \$89 billion (\$2022) +/- 30-40%.

The cost of transporting compressed CO_2 to storage sites is not included in the above costs. Table 8 shows \$20/short ton as a typical T&S cost. Such costs will vary greatly from site to site.

Note that these retrofit projects are "Nth of Kind". The early movers could be "2nd Generation" projects and encounter higher costs. For this study, we assume the CCS technology is widely practiced and the learning curve is behind us.

9. Discussion of Constraints to SMR and NG Retrofit Projects

Recently Congress enacted the "Inflation Reduction Act of 2022" which includes specific financial incentives for CCS projects and low carbon H_2 production. This report does not include an analysis of this new law. Nonetheless it appears to be a major step forward in providing the government financial support the CCS and green hydrogen industries needed to move toward large scale applications. Some of constraints facing the CCS and SMR and NH_3 retrofits and new build industry that need to be addressed are:

- 1. Economics The primary constraint to SMR retrofits in the US is the economic challenge. Other than the enhanced oil recovery market, the CO₂ abated has no significant market value and no revenue stream is available to recover the invested capital. The IRA law includes improvements to the 45Q CCS production credits that are expected to address this problem. Several projects have been announced that will test the effectiveness of these credits and incentives.
- 2. Access to CO_2 Pipeline Corridors and Storage Sites the US DOE has an active program to identify and characterize underground CO_2 storage reservoirs.[×] Projects can be screened to determine (in principle) if the plant site may be within economic distance to a storage site. The engineering, design and testing of a storage site takes time and money. Significant operating CO_2 pipeline systems exist today. Most of these serve EOR customers and access to these pipelines for anthropogenic CO_2 may be limited. All of this can change over time as several CO_2 "hubs" are being developed now.
- 3. Disruption to Existing Operations. Refiners can be profitable only if they operate continuously 365 days per year, 24 hours per day. The existing retrofit SMRs in the US, Canada, France, and Japan prove retrofits can be done. When the refinery is down for maintenance, the interconnections can be made. However, there will be some delays, disruptions, and startup costs. If the refinery is connected to one of the H₂ pipelines, the disruptions would be minimized.

- 4. CO_2 markets If the transportation and storage of CO_2 is delayed or disrupted then the CCS plant would have to reject the CO_2 to the atmosphere until operations are restored. Recent experience suggests this is not a major risk. Nonetheless, significant expansion of the CO_2 transportation and storage infrastructure will be needed to fully abate existing industrial sources of CO_2 .
- 5. New CO_2 markets Commercial development of new uses for CO_2 would increase the optionality for recycling or permanent storage of captured CO_2 . Many new uses for CO_2 are under development now. This market is expected to become a viable option for recycling or conversion of CO_2 to useful products.
- 6. Permitting. Retrofitting an SMR or NH_3 plant may require modifying air quality permits. New CO_2 pipelines and sequestration sites will also need to be permitted. New ROWs for pipelines and utilities will be needed. These permits take time to complete and often attract public opposition which can delay construction of CCS facilities. Accelerating these permitting processes may be needed to meet climate goals.
- 7. Loss of Steam Export and Sources of Thermal Energy If the SMR has contracted for steam sales, then the loss of steam must be addressed. The refinery may have other sources of make up steam. But those sources may produce CO₂. Finding low cost, low carbon sources of thermal energy to run carbon capture plants is an important issue.
- 8. Land Cost and Availability– The land required for the additional equipment could amount to an additional 50 to 100% of the current land occupied by the SMR. In most cases, refineries have additional land that could be used. Adjacent vacant land could be purchased. In some refining areas land is scarce or costly and could be a major impediment.
- 9. Gas and Electric Utilities SMR retrofits and new H₂ plants will require more reliable power and natural gas. The power needs to be low carbon or projected to fall in carbon intensity. Additional NG production, processing and transportation with low carbon intensity will be needed. The life cycle carbon footprint will need to be addressed.
- 10. Storage Infrastructure To ensure reliable supply and operations, expanded storage facilities for renewable power, NG, and H₂ will be needed.
- 11. Age of existing SMR plant (deferred maintenance, inefficient design, obsolete technology, etc.) may harm the business case for adding expensive new equipment to a plant with limited remaining useful life. Life extension of most modern SMR plants is generally feasible. But in other cases, the plant is too old to justify retrofitting it. One alternative is to build new, more efficient, better CO₂-controlled, "fit for purpose" plants.

Technical Appendix

Discussion of CO₂ Emissions Abatement Options for New and Existing Hydrogen Production Facilities in US

Prepared under contract with Hensley Energy Consulting LLC

Introduction

This technical appendix addresses the history of syngas technology development, and current and prospective technologies for producing hydrogen from natural gas with CO_2 abatement options resulting in very low CO2 emissions.

<u>A Brief History of Natural Gas Syngas Technology.</u>

Synthesis gas ("syngas") is a manufactured gas produced from hydrocarbon feed stocks. It consists mostly of H_2 , CO, CO₂ and small amounts of methane. Syngas can be converted to a wide range of synthetic fuels and chemicals, including hydrogen. For this report, we are focused on hydrogen production and pathways to reduce CO_2 emissions.

The conversion of fossil hydrocarbons (coal, oil, natural gas) to syngas is commonly referred to as "gasification", "partial oxidation" or "reforming." Syngas technology dates to before World War II in Europe when oil was in short supply and conversion of coal to syngas and liquids was considered a solution to the shortage in domestic supplies of crude oil. Development of syngas technology accelerated during World War II in Germany when aircraft and other liquid fuels were needed. Lurgi developed coal gasification technology and "Fischer Tropsch" processes were developed to produce synthetic liquids such as gasoline, diesel, and aviation fuels from syngas.

<u>Gasification</u>. The term "gasification" generally refers to conversion of coal and heavy (residual) oils to clean syngas. Texaco (US), Shell (Netherlands), Lurgi (Germany) and others led the post-World War II effort to commercialize gasification technology. During this period, there was general belief that "Synfuels" were needed to address the expected decline in production of crude oil and natural gas. The goal was to make synthetic liquid fuels from all types of coal and refinery residual oils. With the creation of the Environmental Protection Agency in 1970, gasification was also seen as a method to reduce the environmental impact of burning coal and residual oils. This trend was accelerated after the passage of the Clean Air Act amendments in 1990.

Gasification normally refers to a process where oxygen and heavy oil or coal are injected into a high pressure, high temperature non-catalytic reactor to produce raw syngas. Modern coal gasification reactors are "entrained flow" systems at temperatures high enough to melt and remove the ash contained in the raw coal. These reactors are designed to melt and remove ash as molten product and convert other impurities such as sulfur to gases that can be easily separated and controlled. At high temperatures (typically 2500 F), "chemical equilibrium" is attained and nearly 100% of the feed material is converted to "raw syngas."

<u>Partial Oxidation (POX).</u> <u>A</u> POX reactor is similar to a coal or heavy oil gasification reactor but designed for natural gas and liquids such as naphtha and lighter paraffinic hydrocarbons.

POX feeds do not contain ash. Similar to coal gasification reactors, POX reactors are refractory lined to withstand the high temperatures needed to convert the feed materials to nearly 100% syngas without the use catalysts.

POX has been used primarily to produce syngas where a mix of CO and H₂ content is needed for downstream petrochemicals production. The primary disadvantage is low thermal efficiency as the heat to drive the reactions at high temperature is provided by burning part of the feedstock inside the reactor. POX efficiency was later improved by developing special heat recovery steam generators. Steam is needed to drive the POX reactions and shift the syngas to the required mix of H₂ and CO. Today, there is renewed interest in POX for H₂ production since the raw gas contains almost no methane and high capture rates for CO₂ removal are more easily achieved. (Note: the legacy Texaco coal and POX technologies are now owned by Air Products. Air Products also acquired Shell coal gasification technology. Shell retains ownership of its gas POX technology. Air Liquide acquired Lurgi gasification technology.)

For a detailed review of the gasification and POX technologies, see the textbook "Gasification" by Chris Higman.^{xi} Since its publication in 2007, there have been substantial progress and many improvements driven by the growing interest in applying these technologies to abate CO_2 emissions.

<u>Steam Methane Reforming (SMR).</u> Starting in the 1930s, SMR was developed when commercial catalysts became available to drive the endothermic (heat required) reforming reaction ($CH_4 + H_2O > CO + H_2$) at much lower temperatures than POX. The catalyst accelerates the reactions at lower temperatures, thus increasing the thermal efficiency of the process. Unlike POX, the heat to drive the reforming reaction is provided by burning fuel gas (typically purchased natural gas and byproduct gas) in an externally heated furnace containing proprietary solid catalyst. Steam produced in the furnace becomes a "chemical feedstock," and contributes to the high H₂yields and overall thermal efficiency

To maximize H_2 production and minimize the cost of H_2 production, the syngas is reacted with additional steam to "shift" CO to CO_2 and H_2 (the "water gas shift reaction," or WGS). Note that about half the H_2 in the final product comes from steam and the other half from natural gas feedstock.

WGS is an "exothermic" reaction and generates heat. That excess heat is recovered by generating more steam. H₂ is separated and the recovered "process" CO₂ is released to the atmosphere. SMR with its associated CO shift reactors, and gas purification technologies, became the "gold standard" for high purity H₂ production in the refining industry. The use of SMR technology grew rapidly after World War II. In the US, there are over 80 large SMR H₂ operating plants. In the US, there are over 35 ammonia plants that use SMR H₂ technology. SMR technology is licensed by several global companies, such as Technip, Linde, Johnson Matthey, Air Liquide, KBR, Haldor Topsoe, Uhde and others. Each licensor offers a proprietary process and equipment license.

<u>Auto-Thermal Reforming (ATR)</u>. ATR is a catalytic reforming process which uses pure O_2 (from an air separation plant) inside the catalytic reactor to provide the heat that drives the steam methane reforming reactions. The combustion of natural gas with O_2 provides the heat to drive the reactions. The internal combustion produces CO_2 that remains in the high-pressure

syngas product stream. ATR plants typically include a "pre-reformer" SMR reactor to partially reform the natural gas feed upstream of the ATR reactor. ATR was first developed in the 1950s and is widely used outside the US to produce ammonia and methanol in large scale plants. For ammonia plants, ATR uses air as the oxidant to provide the nitrogen needed to manufacture ammonia downstream. More recently, ATR has been proposed to produce H₂ as low carbon fuel to combat climate change. Large scale ATR H₂ projects have been proposed in Europe, US and Canada.^{xii} xiii</sup> These proposed projects utilize a modified ATR design that reduces or eliminates the fuel burned in the pre-reformer along with associated CO₂ emissions. This is accomplished by integrating the heat recovery from the primary ATR reactor and replacing the pre-reformer with a "gas heated" reformer. The primary advantages of ATR systems are higher efficiency and lower cost of capturing process CO₂. The primary disadvantage is the high cost of oxygen and the power consumption associated with cryogenic separation of oxygen from air.

Descriptions of Existing Steam Methane Reforming Plants in US

The analysis in this paper focuses on the existing SMR plants in the US and the potential for capturing CO_2 from these plants. The inventory of SMRs provided previously indicates that there are 31 captive SMRs and 55 merchant SMRs in the US (over 10 MMSCFD H₂ capacity). All these plants are providing high purity H₂ to petroleum refining plants.^{xiv})

- a. Captive Plants these SMR plants are owned by the refining company and integrated into the refining system. At the time they were constructed they were designed to optimize overall refinery performance and profit margins. They typically use refinery byproduct gas and purchased NG as feed and fuel to operate the SMR unit. SMR plants produce significant amounts of byproduct steam that helps meet refinery steam requirements. In some cases, hydrogen rich refinery streams are fed to the SMR to extract high purity hydrogen for refinery use.
- b. Merchant Plants for decades now, many refinery operators have preferred to contract "over the fence" for hydrogen produced by industrial gas companies who specialize in providing reliable, lower cost, high purity hydrogen. For most of these SMRs, the only other product crossing the fence is byproduct steam which is sold to the refinery. In major refining centers in Texas, Louisiana, and California, merchant hydrogen plant operators have connected their plants and refining customers with merchant hydrogen pipelines and underground storage caverns. This allows the merchant companies to increase reliability, automate operations, and reduce costs.

Following the passage of local and federal air pollution laws in the 1970s regulating transportation and fixed plant emissions, the demand for hydrogen grew rapidly.^{xv} This increase in demand occurred because hydrogen is needed to hydrocrack and hydrotreat residual oil streams and thereby reduce the sulfur content of diesel fuel. Nitrogen content of finished products was also reduced by hydrotreating of refinery streams. As demand for H₂ rose, the need to reject carbon from the refinery also grew. This led to increased use of vacuum residue coking. The liquids and gases from coking are deficient in hydrogen. This increased the need for H₂ to upgrade these coker "distillates." As hydrogen demand grew and new SMRs were built, this led to continuous improvements in SMR technology as industrial gas companies competed on price and reliability for their share of the business.

Each SMR is custom designed and constructed to serve the local market and customers. Although no two SMRs are identical, modern SMRs all follow a similar process line up and equipment designs often using a "reference" design. The merchant industry leaders are Linde, Air Products and Air Liquide (note Linde acquired the US -based Praxair company). Each company has its own portfolio of proprietary technologies they claim is superior to their competition. Each company builds both SMR for ownership by a refinery or merchant gas companies.

As described above, central to all SMRs is the reforming reactor / furnace that converts methane (and other paraffins) to syngas by reacting the hydrocarbon feed gas with high pressure steam ($CH_4 + H_2O + heat > CO + H_2$). The reforming furnace contains a (proprietary) catalyst that accelerates the reactions at lower temperature. This reaction is endothermic, i.e. requiring heat input. The reactor must be heated by firing gas at the base of the furnace. The heat generated must be controlled and removed from the furnace. This is accomplished by generating steam that is needed to drive the reforming reactions. Integration of the heat recovery systems is complicated but critical to achieving a high overall plant efficiency and minimizing the cost of hydrogen production.

Although the catalyst is very effective, the reactions are "equilibrium limited" at the peak temperature. That peak temperature is limited to preserve catalyst life and control carbon deposition. Chemical reaction equilibrium means that all the methane cannot be completely converted to syngas. Thus, methane "bleed" (aka "slip") to the raw syngas of 2-4% cannot be avoided. The unconverted methane ends up in the "tail gas," burned in the furnace along with additional natural gas and the flue gas containing the CO₂ is released to the atmosphere. In a typical SMR plant, this flue gas accounts for 50-60% of the CO₂ emissions. Also common to all SMRs is the "water gas shift" (WGS) reaction. This reaction is required to convert the CO in raw syngas to H_2 and CO_2 by shifting the CO reaction with steam (CO + $H_2O > CO_2 + H_2$). The shift reaction is typically a "high temperature shift reactor" to convert most of the CO to CO₂. However, a "low temperature shift" reactor can be added to further reduce CO and increase H₂ production. Shift reactions are exothermic and excess heat is recovered by generating more steam. Shift is also equilibrium limited so not all the CO is converted to H_2 and CO_2 . A few percent by volume CO can remain in the syngas following the water-gas shift stage, depending on the outlet temperature. In a solvent plant, that residual CO is converted back to methane which becomes part of the H_2 product stream. In pressure swing adsorption (PSA) SMRs, it ends up in the tail gas fuel system. The "process CO_2 " is removed and released to the atmosphere. This accounts for the remaining 40-50% of the total CO₂ emissions.





Figure A-2. Simplified Block Flow Diagram for Modern PSA Steam Methane Reformer



Simplified block flow diagrams (BFDs) for the two types of SMR operating today are shown in Figures A-1 and A-2.

a. Solvent SMRs – Prior to the development of "pressure swing adsorption" (PSA), refinery hydrogen was produced mostly in captive plants, using the "solvent" process. This process utilized "open art" technology that was provided by engineering contractors. They were constructed as part of the original design of the refining system. Several common solvents have been used, including chemical and physical solvents. Chemical amine solvents have been the most popular solvent. Following the water gas shift reaction, amines react with the CO₂ to capture the CO₂ which is then stripped from the "rich solution" using steam to break the chemical bonds.

The solvent process relies entirely upon the CO_2 capture process to purify the hydrogen product stream. Residual unconverted CO is "methanated". The resultant methane stays in the H₂ that goes to the refinery. The amine process can be designed for very high CO_2 capture rates. In solvent SMRs this is done to produce a 95-97% pure H₂ product stream.

Note that in a solvent SMR plant there are two sources of CO_2 emissions: The process CO_2 from the solvent stripper and the flue gas from the reformer furnace.

b. PSA SMRs- circa 1990s. PSA technology was developed to provide highly selective separation of mixed gas streams containing CO₂ and H₂. PSA uses proprietary molecular sieves. This allows SMR plants to produce a cleaner separation of H₂ gas from the mix of other gases (CO, CO₂, CH₄, argon) contained in the shifted gas stream. A major advantage is the very high purity H₂ (99.9+%) which is valued by the refinery. As PSA technology gained acceptance, the solvent SMR was no longer competitive and was mostly retired. However, a few are still operating. Figure A-2 shows the simplified BFD for a typical modern SMR using PSA gas separation. The PSA is a physical separation process that cycles between adsorption and desorption. Unlike the amine capture process, PSA requires little or no steam and produces very high H₂ purity of 99.9+%. As a result, this SMR design produces more excess steam that is valuable to the refiner or for cogeneration of power onsite.

In a PSA SMR plant the syngas from which hydrogen has been removed becomes "tail gas" composed primarily of CO_2 , residual H_2 , and small amounts of methane and CO, which is used as supplemental fuel for the reformer furnace burners, converting essentially all carbon to CO_2 in the furnace exhaust. Note that in a PSA SMR, all the shifted "process CO_2 " is concentrated in the tail gas. Therefore, there is only one source of CO_2 emissions: the reformer flue gas.

c. Fuel Balance, Design Criteria and CO₂ management.

Existing SMRs were designed following specific "design criteria." The design criteria are set by the merchant gas company or the refiner if a captive plant. The refiner contracts with the merchant plant owner for the H₂ product which must meet the composition and pressure agreed to by contract. Plant reliability is also often a contract requirement. Design criteria typically includes minimizing the use of purchased NG for feed and fuel to fire the reformer furnace. This typically drives the design to implement some of the following:

- Allow higher methane bleed in the reformer to provide "tail gas" to the burners thus reducing NG fuel costs.
- Allow higher CO bleed in the shift units to provide more "tail gas" fuel to the burners.
- Maximize heat recovery to produce steam for sale or power generation.
- Control burner flame temperatures and other furnace conditions to meet or exceed permit emission requirements.

Note that the reformer stack in a PSA SMR is the only place CO_2 created in the process can leave the system and enter the atmosphere. For existing units, minimizing CO_2 or other GHGs was not part of the design criteria since environmental laws did not require such controls. Criteria pollutants are regulated and NOx, CO, VOCs and particulates are subject to emissions rules. Except for very large SMRs, most

SMRs operating today did not emit enough criteria pollutants to require EPA PSD permits. However, local and state regulations may require permits that impose more stringent air quality standards.

Descriptions of CO2 Abatement Options for Existing SMR Plants in US

1. Solvent SMR plants

Solvent plants produce a concentrated stream of CO₂ from the amine stripper. This stream contains mostly CO₂ along with small amounts of hydrocarbon gases dissolved in the solvent. The CO₂ vented gas is saturated with moisture. Typically, this stream would be vented to the atmosphere. However, this stream can be cooled, dried, and compressed to over its critical pressure (1070 psi). At this pressure, "dense phase" CO₂ can be transported by pipeline to a geological sequestration location. The compression train is not shown in Figure 1. It can be easily added to an existing solvent SMR provided space is available. Drying is needed to avoid pipeline corrosion.

The number of solvent SMR plants operating today could not be determined within the scope of this study. However, the number is likely small. Solvent plants are over 30 years old and considered obsolete technology. However, if needed for the refinery, they continue to be maintained and operated.

In 2009, Hensley Energy Consulting was part of a team proposing to collect and geologically sequester the CO₂ process gas from a solvent SMR at the Shell Martinez CA refinery plant in response to a DOE Funding Opportunity Announcement (FOA). The proposal was accepted by DOE, but Shell declined to proceed due the low value of captured CO₂ at that time. The project also relied upon CO₂ from other SMRs in the area to achieve economy of scale. Those SMRs were modern PSA SMRs and the owners of those plants supported Shell's proposal.

Solvent SMR plants also produce flue gas that contains CO_2 (though at low partial pressure). A CO_2 capture plant could be installed at an existing plant provided space and utilities are available. A flue gas capture plant would require steam to strip CO_2 from the solvent. Generally, the SMR reformer and shift units produce enough steam to strip out the CO_2 .

2. Modern PSA SMR Plants

There are several options for capturing CO_2 from an existing PSA SMR plant. The two most studied are shown in Figures A-3 and A-4.

 Add CO₂ Capture Upstream of the PSA unit (as shown in Figure A-3). In this case, an amine (typically methyl diethanolamine or MDEA) scrubber is inserted upstream of the PSA unit to capture process CO₂. This stream is at elevated pressure and contains CO₂ at a higher partial pressure than the flue gas from the reformer or the low-pressure tail gas that leaves the PSA unit. The process stream leaving the CO₂ capture unit is returned to the PSA unit to recover high purity H₂. The captured CO_2 is then dried and compressed to dense phase pressures and delivered to the pipeline. (Not shown in Figure A-3.) In most cases, the dense phase CO_2 is "pumped" at up to 1800 to 2000 psi so the CO_2 can travel long distances without intermediate recompression. Most studies report that this is lowest cost option per ton of abated CO_2 .

There are constraints that might limit the level of CO_2 capture in this case. First, the reformer was designed for a high concentration of CO_2 since this moderates the "flame temperature" in the reformer combustion zone to limit NOx production. The temperature profile in the reformer reaction zone is also affected by CO_2 content in the fuel to the reformer. Capture and removal of CO_2 upstream of the PSA reduces the CO_2 concentration in the reformer fuel gas and could impact reformer function and increase NOx emissions. As discussed below, there are measures that owners and operators could take to address these issues, including installing selective catalytic reduction (SCR) to control NOx emissions and flue gas recirculation.

These constraints may limit the CO_2 capture level in the capture unit to minimize costly changes to the reformer furnace. At the Shell Quest Project in Canada, recirculation of flue gas to the reformer burners was used to control NOx emissions and flame temperatures. This partially mitigated the problem. The Shell Quest project has been capturing about 50% of the SMR plant's total CO_2 emissions. This project is discussed later in this report.

Based on published studies referenced in the companion report, about 50% of total SMR plant CO_2 emissions can be abated by adding the process CO_2 capture device as shown in Figure A-3.

Note 1: a variation in this approach is to substitute the amine capture unit with a "vacuum swing adsorption" (VSA) unit. In 2011-13, Air Products installed VSA technology at two SMRs at its Port Arthur TX location. These SMRs are unique in that the reformers are heated using exhaust gas from a gas turbine cogeneration plant. Three other SMRs in the US use this integrated cogen/SMR configuration. In the companion report, we did not list the VSA as an alternative CO2 abatement option, since it appears to be best applied to a small number of SMRs with integrated cogen power plants.

Note 2: another variation of this approach is to install the amine capture unit downstream of the PSA unit where the rejected gas has a higher concentration of CO₂. This option would apply to any modern PSA SMR plant. Since the abatement potential for this option is similar to installing the amine capture unit upstream of the PSA unit, we have not described it in a separate Figure. The Tomakomai CCS Demonstration Project in Japan has demonstrated this concept at a 300 tons per day (tpd) capacity. (See discussion below).

Process CO_2 capture has been practiced on a commercial basis for decades to produce large volumes of CO_2 needed for urea production. Also, natural gas processing plants, LNG plants and solvent SMR plants use amine solvent-based CO_2 capture units.



Figure A-3. Simplified Block Flow Diagram for Modern PSA Steam Methane Reformer with Process CO₂ Capture

b. Add CO₂ Capture to Reformer Flue Gas (as shown Figure A-4).

This approach has the advantage that the SMR can continue to operate as designed and the capture unit treats all the CO_2 that exits the reformer furnace. The carbon capture levels for the retrofitted SMR would depend on the performance of this "post combustion" capture unit.

Currently, there is limited commercial experience with post combustion capture on flue gas from gas burning plants. Fluor constructed a small "first of a kind" CO₂ capture unit operating on gas turbine combined cycle flue gas in 1990s in Bellingham MA.^{xvi} This capture plant produced 365 tons per day (tpd) of food grade CO₂ until it was shut down in 2005. Post-combustion CO₂ capture technology is available from several licensors: MHI, Cansolv (Shell), Fluor, Aker, and others. Two commercial scale post combustion plants have been constructed at coal fired power plants: Petra Nova (Texas, MHI technology) and Boundary Dam (Saskatchewan, Canada, Cansolv).^{xvii}

Post-combustion CO₂ capture requires proprietary solvent formulations that can withstand oxygen-bearing flue gases. In an oxidizing atmosphere, amine solution degenerates more quickly and can be more corrosive. The licensors of flue gas capture technology have addressed these issues and the commercial scale Petra Nova and Boundary Dam "first of a kind" coal flue gas units have reported successful operations after addressing early operating issues. Those technical issues related to heat exchangers, CO₂ compressors, gas fired cogen plant, etc.

A key factor that drives the cost of amine capture plants is the low partial pressure of CO_2 in the gas stream. For example, reformer flue gas with 15% CO_2 has a partial pressure of about 15 psi x 15% or 2.25 psi. By contrast, shifted syngas fed to a PSA unit has a CO_2 partial pressure of 400 psi x 15% or

60 psi. Due to the low partial pressure of CO_2 in gas fired flue gas, the absorber equipment must be much larger.

The design criteria for the Petra Nova and Boundary Dam coal projects included 90% CO₂ capture. The target capture rate of 90% was achieved over long periods of time. Petra Nova was temporarily shut down due primarily to poor oil production economics and the cost of making needed improvements to improve reliability. Recently that plant has changed ownership and a restart completed in September 2023. Boundary Dam continues to operate successfully and reports frequently on their operations. There are reports that two new coal CCS plants are under development, one in North Dakota and one in New Mexico.^{xviii}

Figure A-4. Simplified Block Flow Diagram for Modern PSA Steam Methane Reformer with Flue Gas CO₂ Capture



c. Add Both Flue Gas and Process Gas CO₂ Capture.

We did not provide a BFD for this case. It would include both the capture units as shown in Figures A-3 and A-4.

This alternative would achieve an overall capture rate of about 95%. Although technically feasible, it may not be the most economically attractive option. When the capture unit is installed upstream or downstream of the PSA, it removes 50% of the overall plant CO_2 emissions at relatively low cost. That CO_2 is no

longer in the PSA tail gas and is not fed to the reformer burners. This lowers the CO_2 content in the flue gas. A post-combustion capture unit will be more expensive per ton of CO_2 removed because of the much lower flue gas pressure and CO_2 partial pressure.

Recent Experience with Retrofitting Existing SMR Hydrogen Production Facilities

As discussed above, retrofitting existing SMRs (mostly modern ones with PSA H₂ purification) requires addressing constraints inherent to the original design. The last new SMR in the US was built by Praxair (now Linde) in 2020 at the Phillips refinery in Sweeney, TX. This is a world class 170 MMSCFD plant (single train) that uses state of the art technology. The plant was designed for highest efficiency and lowest cost of H₂. The CO₂ emissions from this plant are not regulated and reducing these emissions was not considered in the design.

This plant and many other existing SMRs could be retrofitted with Figure A-3 and or Figure A-4 technology to capture 50 to 95% of the CO₂.

Currently, we are aware of only four SMRs retrofitted with CO_2 reduction technology, one in each of the US, Canada, Japan, and France.

a. Air Products Port Arthur TX

As discussed above, this project (completed in 2021) was funded in part with a DOE grant.^{xix} The two SMRs serving the Valero Refinery are owned by Air Products. The SMRs are using an integrated gas turbine cogeneration unit to provide combustion turbine exhaust heat to the reformer furnace. This shifts some of the CO₂ emissions to the gas turbine exhaust stack and obviates changes to the reformer that could be needed with higher CO₂ capture upstream of the PSA unit. For this unique configuration, Air Products recommended a carbon capture system upstream of the PSA unit. This system is based on Air Products' "vacuum pressure swing adsorption" (VPSA or VSA) technology. The VSA unit captures 90% of the inlet CO₂ in the reformer syngas stream. The plant is operating today. The public reports on this project do not disclose the overall carbon capture performance. Our assumption would be that CO₂ captured in the VSA unit represents about half the total plant CO₂ emissions. (Note: a similar project using VSA was proposed by Praxair at the BP Texas City Refinery in 2009. DOE funded detailed studies. Praxair elected not to proceed with the Texas City project.)

b. Shell Quest Port Saskatchewan, Alberta

Another large scale SMR retrofit project is located at the Shell "Scotford" heavy oil upgrading complex in Port Saskatchewan, Alberta.^{xx} Three existing "captive" SMRs (with PSA) have been retrofitted with amine capture units. This project has been operating for about 7 years and detailed reports have been published. Since the SMRs are captive to the refinery operations, the design, construction, and operation of the capture components had to be managed to allow continuing reliable operations.

The design of Quest was constrained by the following:

- The amine capture system was designed for about 80% capture, even though much higher design capture rates could be achieved. A higher capture percentage is possible in this project only with changes to the reformer furnaces, as noted below.
- The feed to the SMR includes H_2 rich streams from the refinery so that this H_2 can be recovered and purified.
- The uncaptured CO₂ that remains in the PSA tail gas is needed to insure smooth operations of reformer furnace. Controlling combustion temperatures and NOx emissions was required.
- Recirculating flue gas was included to assist in maintaining reformer operating conditions and reduce NOx formation within the original design parameters.

The Quest SMR CCS project has been operating successfully for several years.

c. Tomakomai CCS Demo Project

The Japan Ministry of International Trade and Industry sponsored a commercial scale CCS project in Japan. The project included capturing CO_2 from an SMR PSA tail gas stream and injecting and sequestering it offshore. During 2016-19, the plant successfully captured and sequestered 300,000 tonnes of CO_2 or about 1,600 tpd. The capture plant used an amine solvent system. Unlike Quest, the capture plant used a two- stage absorption and flash system that reduced the steam requirements about 50%. Capture rates were over 99.9%. The reports do not discuss the use of the CO_2 depleted tail gas in the SMR plant or refinery.^{xxi}

d. Port-Jérôme CRYOCAP™ Plant Project

Air Liquide retrofitted an SMR plant in France with a cryogenic CO_2 capture plant. The feed to the proprietary "Cryocap" unit is PSA tail gas containing CO_2 . The plant captured about 300 tonnes per day of CO_2 that was sold as food grade CO_2 . The CO_2 depleted stream is recycled to the SMR PSA unit where additional H₂ is recovered for sale. Air Liquide states that this technology is commercial and can be scaled up to 1600 tpd.^{xxii}

<u>Review of Improvements under Development for Retrofitting Existing and New SMR</u> <u>Hydrogen Plants</u>

Currently, there is a great deal of research and development in SMR and other "blue" hydrogen technologies in response to the climate change crisis. A complete discussion of these improvements is not within the scope of this report. Some of the more significant technologies that we are aware of are discussed below. Most apply to retrofits of existing SMRs, and others apply to newly built "blue" hydrogen plants.

The suppliers of SMR technology are working on ways to address these constraints discussed above. For example, some improvements that have been announced but not yet commercially demonstrated include:

- Universal Oil Products (now Honeywell UOP) has announced a combustor for new or existing reforming furnaces that can accept up to 100% H₂ in the flue gas.^{xxiii} We are not aware of this being demonstrated in a commercial SMR plant. If successful, it would sharply reduce the CO₂ emissions from a conventional SMR plant.
- UOP, Air Liquide (CryoCap) and others have announced cryogenic CO₂ separation processes that will use less energy than amine solvent systems.
- Johnson Matthey has reported they can retrofit SMRs with larger pre-reformers that would reform more methane using primary reformer waste heat and without using combustion heat. This would reduce the fuel needed in the primary reformer burners and reduce CO₂ emissions.^{xxiv}
- There have been reports of indirect electric heated amine reboilers that would replace the current steam heated units. Acid gas recovery units in LNG export plants use heated oil in the amine reboilers.xxv If the heat transfer oil is heated electrically with renewable energy, then the CO₂ associated with steam production would decline or be eliminated.

It is not known at this time if, or when, any of these improvements will be commercially available for retrofitting existing SMRs. However, many promising technology improvements are under development that will lead to reduction in GHGs from existing and new SMR H₂ plants. This report highlights only a few of the many now under development.

Discussion of Hydrogen Production Technology for New SMR/ATR Plants

Currently, there is growing interest in building new "blue" hydrogen plants using existing "off the shelf" technologies. These plants will be designed as a greenfield plant and with the goal of achieving maximum abatement of CO₂ emissions. Aside from the mature petroleum refining and ammonia markets, there appears to be a new market for H₂ as a fuel for transportation, power, chemical, steel, cement, commercial and residential applications. The recently enacted Inflation Reduction Act (IRA) includes significant financial incentives to encourage development of new "clean H₂ plants" and reduce CO₂ emissions from exiting industrial and power plants. Here is a brief discussion of some these future hydrogen technologies that use NG as a feedstock or fuel.

a. SMR Technology

In the sections above we discussed the constraints posed by existing SMR plants serving the refining industry. Although forecasts differ, the long-term growth of the refining industry appears to be declining in the US and developed countries although it may be growing in lesser developed countries. In the US and Canada, we are not aware of any new uncontrolled SMR plant announcements.

Any new "fit for purpose" SMR H₂ plant would be designed for a wide range of fuel markets as well as "feedstock" refining and petrochemical markets.

With today's "off the shelf" technology, a "blue" SMR plant could be designed to capture about 50 to 60% or more of the carbon fed to the plant as feed or fuel without added post-combustion flue gas capture, "pre-reformer heat exchange" or substituting H_2 rich fuel gas for NG to the reformer furnace.

The primary barriers to high capture performance in an SMR are:

- Unconverted methane in the reformer;
- Unconverted CO in the shift unit;
- High carbon content in tail gas fuel to the reformer burners.

The methane "bleed" could be reduced by using reformer heat exchange in the prereformer as discussed above. This has been done in ATR plants but would have to be demonstrated in SMR applications. It would need to compete with ATR with reformer heat exchange.

The unconverted CO can be reduced by adding a low temperature shift reactor. This is proven technology. It would reduce the CO burned in the reformer furnace increase carbon capture rate.

A new SMR could be constructed using only post-combustion CO_2 capture. Licensors claim this technology is commercially available at 95% capture.

The high content of carbon in the reformer fuels could be reduced by substituting H_2 rich gas for the purchased NG reformer fuel. This would divert hydrogen from the final product stream and increase the price of H_2 . It would require development of H_2 rich reformer furnace with control of NOx emissions. Currently, there is no commercial scale demonstration of this technology.

Licensors of reformer heat exchange pre-reformer technology like that used in NH_3 and methanol plants claim this approach will sharply reduce CO_2 emissions. However, details have not been published.

b. Auto Thermal Technology (ATR)

ATR technology is a NG reforming technology that has been widely applied in the ammonia and methanol industry. No ATR plants have been built in the US. These are typically very large plants located in the Middle East where NG price is low and large petrochemical export plants can be sited. If H_2 fuel demand grows in the US, ATR plants could be constructed with very high CO_2 capture rates.

Unlike SMR where fuels are burned in a radiant heated catalytic reactor, the ATR reformer heat is added by injecting oxygen (or air in the ammonia case) into the catalytic reactor. This results in all the CO_2 from oxidation of the fuel remaining in the process stream at high pressure. The unreacted CO is shifted in high and low temperature shift reactors. The resultant CO_2 can be captured in a traditional amine solvent system. Process CO_2 capture rates up to 99% have been discussed by ATR technology providers.

ATR plants typically include a fired "pre-reformer". This creates flue gas with CO₂ that is expensive to abate. This problem has been addressed by Johnson Matthey, Haldor Topsoe, and others replacing the fired pre-reformer with a gas-to-gas exchanger, called a "reformer heat exchanger". This is accomplished by integrating the hot gases exiting the primary reformer with the un-fired pre reformer. This concept has been proven in two commercial plants producing ammonia and methanol.

ATR technology with a "reformer heat exchange" can be applied directly to largescale hydrogen production. The HyNet^{xxvi} project in the UK will use this technology. It is in the final detailed stages of design and site development. It has not yet been sanctioned for construction. Recently, Air Products has announced an ATR with heat exchange reformer project in Canada. (See above references.) These ATR H₂ projects claim the overall CO_2 capture rate of 97% or more.

The primary disadvantage of "unfired" ATR technology for H_2 production is the need for oxygen. An air separation unit (ASU) is used to provide the oxygen. The ASU requires large amounts of electricity. If the power comes from renewable or nuclear sources, then there will be no CO_2 emissions. If the power is supplied from utility grid with a fossil fueled power component, that CO_2 would need to be accounted for in the carbon balance of a non-fired ATR hydrogen plant. As the utility grid becomes more green, or new advanced nuclear power is deployed, then CO_2 emissions from the electric grid become less of an issue.

c. Partial Oxidation (POX)

POX is a mature technology that is discussed above. More recently, this old technology has been considered as a means for producing H_2 with high levels of carbon capture.^{xxvii}

Shell has recently announced a POX based system called Shell Blue H₂ Process.^{xxviii} Shell is claiming this new version of POX with CCS can compete with SMR and ATR technologies with CCS. Since POX requires oxygen, the issue of grid carbon intensity and electricity consumption by an ASU must be considered.

Air Products has announced the Louisiana Clean Energy Project which appears to use their POX technology.^{xxix}

d. Long Term Prospects for Reforming Technologies

This topic is beyond the scope of this report as the literature on research into reforming technologies is very active worldwide and impossible to forecast. However, it is worth mentioning that some NG based technologies are being developed that would be a radical departure from current or near-term technologies. For example:

i. Electric Heated Reformers. Haldor Topsoe has reported they have a pilot plant testing an electrically heated SMR.^{xxx} Presumably, the power would be zero carbon renewable power. If successful, this would eliminate the combustion CO₂ from the

hydrogen plant. The syngas would need to be shifted and separated from the process CO_2 . Some tail gas might be produced. But the capture ratio could be 99% or more.

- ii. Methane Pyrolysis. There have been recent announcements of large pilot plants designed to carbonize or pyrolyze methane, leaving only carbon solids and pure H₂. Monolith Corporation appears to be in the advanced stages of building a commercial scale methane pyrolysis plant in Nebraska.^{XXXi} The technology has been tested in a pilot plant and a permit application has been filed to construct a full-scale plant in Nebraska. The Monolith technology uses a plasma reactor to decompose methane. If heated with electrical energy this power will need to come from low carbon sources. If successful, the plant would have little or no CO₂ emissions. The byproduct carbon black would need to be sold or landfilled to achieve a low carbon footprint. There are several other methane pyrolysis technologies under development.
- iii. Membrane Reformers, and other "Disruptive Technology". Membrane reformers carry out the methane reforming reactions in a single reactor with membranes that concurrently separate the H₂, CO and CO₂ product streams.^{xxxii} This is an active area of laboratory research since it promises to carry out the SMR reactors in one device and possibly reduce capital and operating costs. This is just one example where a revolutionary idea could radically change the industry.
- iv. "Electrification" of industrial, commercial, and domestic energy sectors is advocated by many climate change policy groups. If widespread large-scale development of "zero carbon" power (i.e., renewable, nuclear) is feasible, then that same "green" power would be available to electrify major components of NG based hydrogen, ammonia, refining, petrochemical, and other energy intensive industrial facilities. These "hard to abate" industries would benefit from plentiful, affordable green power. Even with green power, new NG based H₂ would still need to address some of the constraints discussed below. Some suppliers of heat exchanger and fired heater equipment are promoting direct electric heat models. It is not clear if any of these have been tested in large scale applications. However, if commercialized they could be applied to blue hydrogen plants where solvent reboilers using carbon intensive steam is used.
- v. BioGas Feeds to SMR Plants

SMRs or ATRs that are retrofitted with carbon capture equipment can achieve 50 to 97% carbon capture. Bio-methane from renewable biomass resources could be used as feed or fuel to an existing SMR plant. Feeding bio-methane would increase the "carbon capture" to net zero or negative carbon emissions. Such use of bio-methane would require large volumes of renewable methane gas. Since bio-methane and natural gas are the same chemically, it could be used today if the cost of bio-methane is competitive with NG with available credits and incentives.

Statement on Cost Estimates for Capture Retrofits

The purpose of this paper is to survey the available carbon capture technologies for existing SMR and ammonia facilities, and to provide illustrative estimates for carbon abatement potential, technology costs, and abatement costs. The cost estimates appearing in the tables are derived from the two data sources listed below, a range of assumptions and author input. As described above, these estimates required simplifying assumptions for financing and economic terms as defined in the report, including capital recovery factor, currency exchange rates, inflation rates, natural gas and power prices, and other assumptions to produce capital and operating costs in current overnight 2021 US dollars generally expressed in the cost per short ton of CO₂ captured and abated. Cost estimates provided in this analysis do not account for the extension of the 45Q tax credit applying to carbon capture technologies passed by Congress as part of the Inflation Reduction Act of 2022. For purposes of estimating the cost of CO_2 abatement (Scope 1 abatement only), the author relied on cost and performance data from the following studies: "Comparison of Commercial, State-of-the-Art, Fossil-Based Hydrogen Production Technologies," dated April 12, 2022 by the Department of Energy (DOE) and the National Energy Technology Laboratory (NETL); and IEA Greenhouse Gas R&D Programme,"Techno-Economic Evaluation of SMR Based Standalone (Merchant) Plant with CCS, February 2017. It is important to note that the technology and abatement cost estimates in this analysis can be refined as projects continue to be financed and constructed and more data becomes available.

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END NOTES

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xii BEIS Hydrogen Supply Programme, HyNet Low Carbon Hydrogen Plant, Phase 1 Report for BEIS hynet.co.uk, Progressive Energy Ltd

xⁱⁱⁱ <u>Air Products to Receive Approximately \$475 Million (CAD) in Funding for Alberta, Canada Net-Zero Hydrogen Energy Complex from</u> <u>Government Energy Transition Programs</u>

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^{xv} The regulations limited the sulfur content of fuel oil (for power generation and ships' bunker fuels), and diesel and jet fuel products. Gasoline composition was regulated in California. As auto mileage was increased, auto manufacturers increased octane and other requirements. The emission limits of SOx, NOx, particulates from refineries were reduced. These and other environmental standards for transportation and stationary facilities all led to the increased demand for H2 in fuel-production processes.

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