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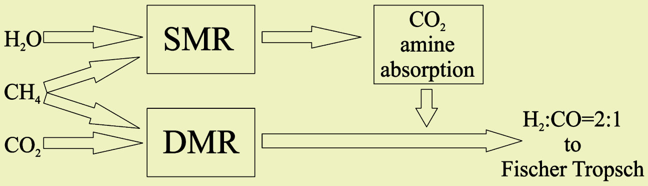
Methane Conversion to Syngas for Gas-to-Liquids (GTL): Is Sustainable CO_2 Reuse via Dry Methane Reforming (DMR) Cost Competitive with SMR and ATR Processes?

Jonas Baltrusaitis* and William L. Luyben

Department of Chemical and Biomolecular Engineering Lehigh University, Iacocca Hall, 111 Research Drive, Bethlehem, Pennsylvania 18015, United States

Supporting Information



ABSTRACT: Carbon dioxide is a greenhouse gas and is obtained as a waste via burning various forms of fuels. Syngas is an intermediate in large-scale long-chain hydrocarbon (C_{10}−C_{20} alkanes and alcohols) production processes via Fischer−Tropsch (FT) synthesis, typically to obtain high quality fuels. Thus, it is of particular interest to engineer syngas production processes for FT that can consume various combustion process waste CO_2 in the process and thus partially contribute to the sustainable carbon neutral fuel synthesis. In this work, a quantitative economic comparison of five alternative processes is presented for the production of synthesis gas with a hydrogen-to-carbon monoxide ratio of 2, which is suitable for feeding to the Fischer−Tropsch gas-to-liquid process. Combinations of steam methane reforming (SMR), dry methane reforming (DMR), autothermal reforming (ATR) and reverse water gas shift (RWGS) are explored. An amine absorber/stripper system is used for carbon dioxide removal. The effects of the cost of natural gas and of liquid oxygen and the magnitude of a potential carbon tax are demonstrated. With current prices of raw materials, the configuration with the lowest total annual cost (TAC) features a system composed of both SMR and DMR reactors.

KEYWORDS: *Syngas, Autothermal reforming, Reverse water gas shift, Partial oxidation, Steam reforming, Dry methane reforming*

INTRODUCTION

Sustainable generation of hydrocarbon fuels and commodity chemicals is a major challenge that is required to decrease accumulation of CO_2 in the atmosphere.[1] The utilization of CO_2 as a raw material itself offers a way to mitigate the increasing CO_2 amount. However, current CO_2 activation and reuse methods suffer from various drawbacks, including high energy input, low conversion, expensive catalyst material, to name a few.[2] The immediate need for liquid fuels and commodity chemicals dictates the pathway of a gradual incorporation of sustainable carbon feedstock, such as CO_2 or biomass, into the existing conventional fossil fuels, such as natural gas or oil.

Natural gas, with methane (CH_4) as its main constituent, is one of the most important fossil fuel resources to date, with new reserves constantly being discovered. With the advancements in extraction methods, large quantities became available from unconventional sources, such as shale gas coal bed methane and tight gas,[3] as well as via renewable sources, such as biogas generation.[4] The 56% increase in total natural gas production from 2012 to 2040 is projected in the U.S. with shale gas composing ∼50% of the total 38 Tcf supply by 2040.[5] Natural gas is currently primarily being used for heating and electricity generation via combustion due to its higher H/C ratio, as compared to coal, thus resulting in lower direct CO_2 emissions.[6] In a transition to the fully sustainable hydrocarbons, economically viable and easily controllable conversion of CH_4 into energy-dense liquid hydrocarbons is of tremendous importance for sustainable production of fuels and commodity chemicals worldwide.[7−11] In addition, onsite liquid hydrocarbon production could utilize currently flared methane and thus limit greenhouse gas emissions.[3,12]

Conversion of methane to easily transportable liquids is a challenging task due to the high H_3C−H bond dissociation energy (439.3 kJ/mol) and a symmetric tetrahedral structure of the CH_4 molecule.[13] Direct CH_4 conversion to liquids via one step process has been sought for decades, yet challenges persist. These methods can be divided into two broad groups:[14,15]

1. Direct endothermic dehydrogenation of CH_4 to $-CH_2-$ containing species and H_2 at high temperatures (500−1100 °C). Examples are CH_4 aromatization to yield benzene and H_2 over a Mo-ZSM-5 catalyst and pyrolysis to C_2H_4 and/or C_2H_2 and H_2.[16,17]
2. Oxidative (and exothermic) dehydrogenation (or partial oxidation) using O_2 as a cheap oxidant, as well as other less used oxidants, such as halogens or sulfur. Examples are partial oxidation of CH_4 to CH_3X (X = OH, Cl, Br or OSO_3H), oxidative coupling to C_2H_6/C_2H_4 and partial oxidation (POX) to syngas.[3,9,13,18] Nonoxygen containing reactants can drive the activation reaction via

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oxidative esterification at low temperatures but require recycling of the corrosive reactants and dehydration of the resulting acids. The use of oxygen to selectively yield higher hydrocarbons suffers from the overoxidation to form CO_2 because the activated products formed are much more reactive toward oxygen than their parent compound CH_4.[15,17] Indirect CH_4 activation, on the other hand, utilizes CH_4 reaction with H_2O vapor to yield a thermodynamically stable molecule pair of CO and H_2 (syngas). Syngas can then be processed into desired hydrocarbon products with very high selectivity.

Steam methane reforming (SMR) and (catalytic) partial oxidation (POX) are two major CH_4 activation processes used in syngas generation for FT.[19] The SMR process is fed with methane and water. It is an endothermal process requiring the H_2O/CH_4 ratio of ∼3 to achieve high methane conversion. The reactor operates at 1073−1173 K and 15−30 atm on Ni based catalyst.[20] An upstream prereformer is typically used where higher hydrocarbons are converted to reduce the risk of carbon formation in the main reformer. This allows a decrease of the H_2O/CH_4 ratio. In addition, H_2 is produced by partial conversion of natural gas ensuring prereduced catalyst at the inlet of the main reformer. The POX process is fed with methane and oxygen. It generates H_2 lean ($H_2/CO = 1$ to 1.6) syngas at >1473 K if no catalyst is used. If catalyst is used, the temperature can be lowered to ∼1000 K.[21] An intuitive approach to achieve the desired H_2/CO ratio of 2 is to combine these two processes. This is called autothermal reforming (ATR). Autothermal reforming (ATR) is typically performed by dosing CH_4, O_2 and H_2O at 1200 K and 30 atm.[22] Steam is typically added in both POX and ATR with catalytic POX typically operating at low H_2O/CH_4 ratio from 0 to 1, whereas ATR operates at relatively higher steam loads ($H_2O/CH_4 > 1$).[23] The ideal H_2/CO ratio of 2 can be considered necessary for FT synthesis. Water gas shift reaction is typically used during the FT process to adjust for a desired H_2/CO ratio.[19] Fe based FT catalysts are also active in WGS and thus are commonly employed when coal or biomass (low H_2/CO ratio syngas of <1) is used.[19,24] Notably, SMR alone typically produces a high H_2/CO ratio of ∼3 syngas, which requires hydrogen removal.[15]

A very attractive process from a sustainable CO_2 use perspective is dry methane reforming (DMR), as it incorporates both methane and CO_2 as feed molecules. It generates syngas with a low H_2/CO ratio of ∼1 and can potentially be used to adjust the ratio of the syngas obtained after SMR to achieve that necessary for FT.[25] DMR and WGS reactions cannot be decoupled because the latter proceeds with the lower activation energy thus resulting in lower H_2 content at high (20 atm) pressures and 973 K.[26] Use of high temperature in DMR (∼1250 K) can potentially suppress WGS and operate in the reverse water gas shift (RWGS) regime, e.g., H_2/CO ratio adjustment can be decoupled from the FT reactor. Although technologically feasible, it has not been implemented at a scale needed to attain an appreciable amount of fuels or chemicals utilizing CO_2 as feedstock and comparative technological and economic assessment with the conventional methods of syngas generation is needed.

In this work, we explored several possible scenarios of adjusting the H_2/CO ratio for FT synthesis with particular emphasis on incorporating the DMR reaction because it results in a net CO_2 consuming process. Combinations explored included ATR with and without preceding SMR, as well as combined SMR/RWGS and SMR/DMR processes. Because DMR equilibrium shifts to the product side at low pressures, a low-pressure design with no CO_2 recycle, previously shown as the most economically sound,[27] is considered.

■ PROCESSES STUDIED

The production rate of synthesis gas used in this paper is based on the process considered by Panahi et al.[28] in which a flowsheet with SMR and ATR units in series was studied. The same amount of syngas (15 000 kmol/h H_2 and 7500 kmol/h CO) is produced in all the process configurations considered. The amounts of the raw materials (methane, oxygen, water and carbon dioxide) are different for each flowsheet.

The basic raw material is natural gas, which is relatively inexpensive, particularly compared to its cost a decade ago. Later in the paper we will show how the price of methane affects the economics of the alternative processes. In the autothermal reactor processes, oxygen is required, and we will show how its price affects the economics.

The SMR, DMR and ATR reactors are assumed to achieve chemical equilibrium. The Aspen *RGibbs* reactor model is used for these three reactors. This assumption is reasonable because of the very high temperatures at which these reactors are operated. The Choi and Stenger[29] powerlaw kinetics are used in the adiabatic RWGS reactor.

We begin with a brief description of each type of unit.

SMR. The steam methane reforming process is widely used in syngas generation as well as in hydrogen production via WGS. It is capable of producing high yields of hydrogen, which is consumed in very large quantities for sulfur removal in petroleum products or nitrogen fertilizer synthesis. The primary reaction is

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2$$

The resulting H_2/CO ratio is too large to feed to the Fischer−Tropsch (FT) process, which requires a ratio of approximately 2 to produce high molecular weight paraffin and olefin liquid transportation fuels. In applications where hydrogen is the desired product of SMR, the downstream use of a low temperature exothermal water gas shift reactor can produce addition hydrogen by the reaction of CO with water. The byproduct CO_2 must be removed via amine or pressure swing absorption to generate high-purity hydrogen

$$CO + H_2O \Leftrightarrow CO_2 + H_2$$

The steam methane reaction is very endothermic and requires large amounts of heat. Conversion is favored by high temperatures, so the reactor typically consists of a fired furnace with catalyst inside the furnace tubes. Conversion is also favored by low pressure, but the produced syngas must be at high pressure to feed to FT, which operates at 30 bar. Methane conversion can be increased by increasing temperature or increasing the water-to-methane feed ratio. Steam-to-methane ratios (S/C) of 3 are typically used in SMR.

The operating cost of an SMR unit is the cost of the fuel consumed in the fired furnace/reactor. The hot stack gas is used to preheat the fresh feeds and generate steam. The capital cost of the reactor/furnace depends on the size of the equipment, which is set by a maximum heat-flux limitation and the cost of catalyst.[30]

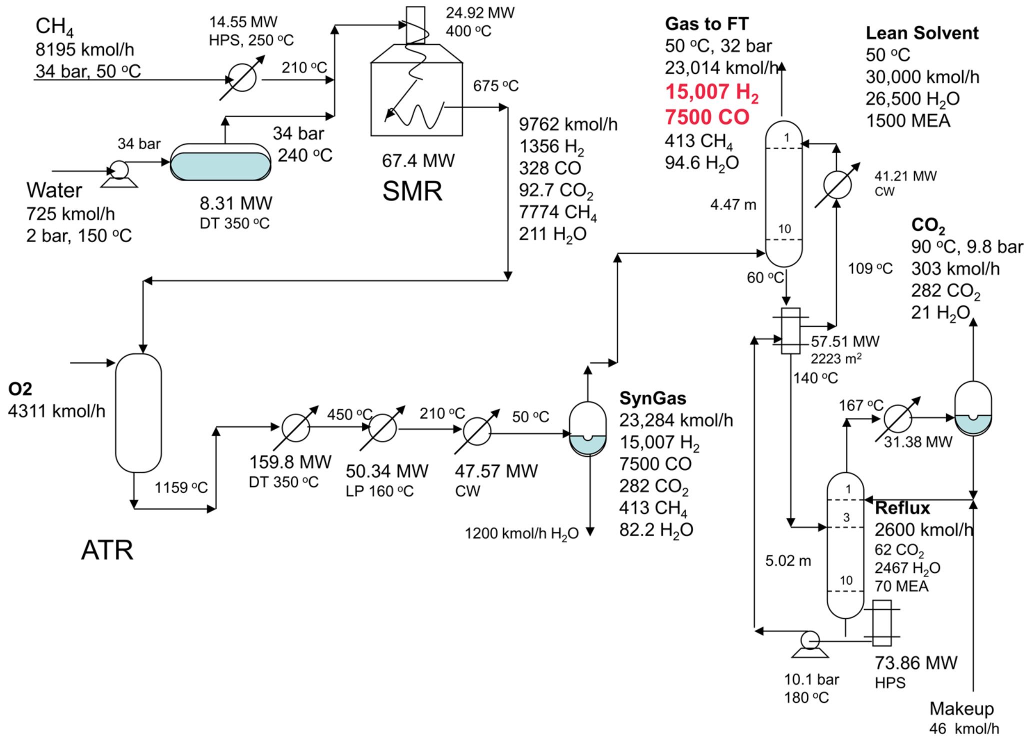

Figure 1. Process flow diagram of SMR/ATR process to produce 15 000 kmol/h H_2 and 7500 kmol/h CO. Tabulated information on equipment sizing, capital and fuel costs, carbon tax as well as the total annual cost (TAC) is provided in Supporting Information Table S1.

DMR. In the dry methane reforming process, methane reacts with carbon dioxide to form CO and hydrogen in a one-to-one ratio.

$$CH_4 + CO_2 \Leftrightarrow 2CO + 2H_2$$

Because it consumes the greenhouse gas carbon dioxide, it is attractive from an sustainability and environmental protection perspective.[25,26] It is also attractive because it generates syngas with a H_2/CO ratio of about 1, which can be used as a low-hydrogen syngas source in the feed to the FT process to adjust for a large H_2/CO feedstocks or processes, such as SMR.

The reaction is highly endothermic and requires large amounts of heat. Conversion is favored by high temperatures, so the reactor typically consists of a fired furnace with catalyst inside the furnace tubes. High temperatures favor conversion and have the additional benefit of reducing coking.[31]

The DMR reaction is highly sensitive to pressure, so the reactor pressure must be kept much lower (4 bar)[27] than that required to feed to the FT process (30 bar). Therefore, a multistage compression system on the product syngas is required, which entails significant capital and energy costs.

Because the H_2/CO ratio of the syngas from DMR is ∼1 and the H_2/CO ratio of the syngas from SMR is 3, a process that is a combination of the two reactors is intuitively attractive.

ATR. The autothermal reforming reactor is fed with oxygen and uses the exothermic heat of partial oxidation of methane to provide the required endothermic heat of the reforming reaction. The main advantages of this process are generation of favorable H_2/CO ratio (1.6 to 2.6), reduction of CO_2 emissions due to internal heat supply within the reactor and high methane conversion. There is no large energy cost for fuel, but fairly expensive oxygen is required from an upstream air separation unit. High temperatures can be attained by the use of refractory-lined high-pressure vessels, which means that methane conversion can be kept high without requiring a large amount of water to drive the reaction to the product side. The low steam-to-methane ratio reduces energy costs in the water vaporizer.

The combustion of methane produces CO_2, so there is more to remove (higher costs in the absorber/stripper unit and higher carbon tax). More importantly, more methane must be fed to achieve the same syngas production rate. Therefore, the ATR process requires more methane feed and consumes expensive oxygen. However, the capital cost of the single vessel ATR design is less expensive than that of the large fired furnace/reactor in the SMR process.

RWGS. Because the H_2/CO ratio from the SMR reactor is too large to feed to the FT process, the ratio can be reduced by running the syngas into a water gas shift reactor that is fed with fresh CO_2 from an external source. The high CO_2 concentration drives the reaction back toward CO and water. Of course the excess CO_2 occurring due to the equilibrium limitations must be removed, which increases the cost of the downstream CO_2 removal process. There is a small net consumption of CO_2, so there is a carbon tax credit. Because some of the required CO in the product comes from the CO_2 fresh feed, the flow rate of the fresh methane is somewhat smaller than in the other processes. The fresh CO_2 is supplied at 1 bar, so a compression system is required to increase its pressure to 33 bar so that it can be fed to the RWGS reactor. For RWGS, the reaction equilibrium is not significantly affected by the pressure so the pressure necessary for FT can be maintained.

The RWGS reaction is mildly endothermic, so a simple inexpensive adiabatic reactor can be selected. The inlet temperature to the reactor is obtained by the use of a fired furnace and is adjusted to give the desired amount of CO leaving the RWGS reactor. This temperature depends on the

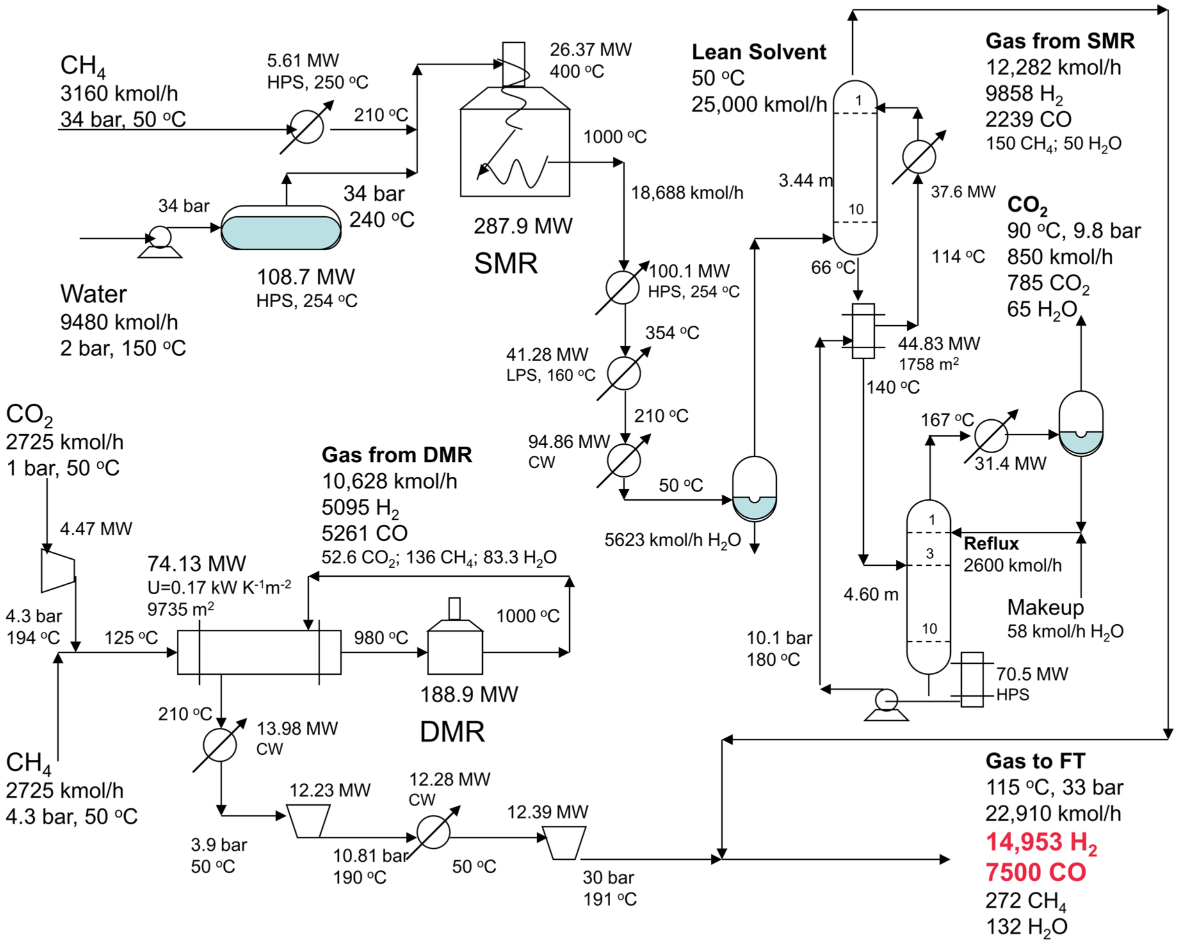

Figure 2. Process flow diagram of SMR/DMR process to produce 15 000 kmol/h H_2 and 7500 kmol/h CO. Tabulated information on equipment sizing, capital and fuel costs, carbon tax as well as the total annual cost (TAC) is provided in Table 1.

amount of fresh CO_2 fed. The more fed, the lower the temperature. So, there is a trade-off between furnace energy cost and CO_2 recovery costs.

Two different process configurations with the RWGS reactor are considered. In the first, the gas from the SMR is cooled and the condensed water is removed before sending it to the RWGS reactor. This would appear to be a reasonable approach because the excess water pushes the reaction in the wrong direction. Removing it means less CO_2 needs to be added (with a portion of it removed later) to produce the desired amount of CO. However, cooling and then reheating the stream requires capital investment in heat-exchanger area.

The second alternative is to simply send the gas produced in the SMR reactor directly into the RWGS reactor. More fresh CO_2 is required to shift the equilibrium, which increases the costs of the fresh CO_2 compression and the costs of the amine absorber/stripper CO_2 removal unit. However, a number of other factors change, so the net effect is not intuitively obvious. A quantitative economic comparison is presented later in this paper.

■ PROCESS DESIGN FLOWSHEET EVALUATION

Flowsheets for the five alternative processes, including SMR, DMR, ATR and combinations thereof are given in Figures 1–5. Each process is described in detail in this section. Economic comparisons are presented in the next section.

SMR/ATR. Figure 1 provides a flowsheet for syngas production using a combination of SMR/ATR reactors. Information on equipment sizing, fuel consumed and carbon tax is provided in Table S1. The process configuration is similar to that studied by Panahi et al.[26] A small SMR prereactor at 34 bar is fed with 8195 kmo/h of methane and a small amount of steam (725 kmol/h). The methane is heated to 210 °C by high-pressure steam.

The steam is generated by feeding high-pressure liquid water into a vaporizer. Because the temperature of saturated steam at 34 bar is 240 °C, high-pressure steam (42 bar and 254 °C) does not provide enough temperature differential driving force to give a reasonable vaporizer heat-transfer area. Therefore, Dowtherm vapor at 350 °C is used as the heat source in the vaporizer. This Dowtherm is generated later in the process in a heat-recovery section.

The two fresh feed streams are combined and heated to 400 °C in the convection section of the SMR furnace/reactor by the hot stack gas. The reaction occurs in the catalyst-filled tubes in the SMR reactor, which is heated by burning fuel with air. The heat duty to provide the endothermic heat of reaction is 67.4 MW when the exit temperature is set at only 675 °C. The conversion of methane in this prereactor SMR is only 5% because the temperature is low and there is only a small amount of water fed to drive the reaction to the product side.

The stream is then fed to an adiabatic ATR into which oxygen is fed. The oxygen feed is set at 4311 kmol/h to achieve

Table 1. SMR/DMR Process: Equipment and Economics[a]

	Q (MW)	area (m^2)	capital (10^6 \$)	fuel (kmol/h CH_4)	utility
preheater	5.61	192	0.2225	33.67	HP steam
vaporizer	108.7	1746	0.9343	652.3	Dowtherm
SMR	287.9		10.39	1728	fuel
SMR catalyst			4.595		
DMR	188.9		6.790	1134	fuel
DMR catalyst			2.942		
FEHE DMR	74.13	9735	2.854		
HX2	100.1	1217	0.7387	(600.7)	Dowtherm credit
HX3	41.28	1080	0.6835	(247.7)	HPS credit
SMR cooler	94.86	7091	2.323		CW
absorber			0.3248		
stripper			0.4427		
reboiler	70.50	1121	0.7005	423.1	HP steam
FEHE stripper	44.83	1758	0.9383		
condenser	31.40	1805	0.9554		CW
compressors	29.09		10.52	174.6	electricity
DMR cooler	13.98	1045	0.6692		CW
DMR cooler	12.28	999.6	0.6501		CW
stripper cooler	37.60	1708	0.9209		CW

[a] Total capital = \$49,690,000. Cost of methane (fuel + fresh feed) = \$329,500,000 per year. Carbon tax (fuel + process) = \$13,500,000 per year. Total annual cost = \$359,200,000 per year.

an exit temperature of 1159 °C, which gives the required flow rate of H_2 (15 000 kmol/h) and CO (7500 kmol/h) in the exit gas from the ATR. The gas also contains 282 kmol/h of CO_2 (which must be removed) and 413 kmol/h of CH_4 (95% conversion).

The hot gas from the ATR is cooled in a series of heat exchangers. Dowtherm at 350 °C is generated in the first (159.8 MW), cooling the gas stream from 1159 to 450 °C. Low-pressure steam at 160 °C is generated in the second (50.34 MW), cooling the gas stream to 210 °C. The final heat exchanger uses cooling water (32 °C inlet and 43 °C exit) to cool the gas to 50 °C (47.57 MW). Liquid water (1200 kmol/h) is removed in a separator drum and the gas is fed to the CO_2 removal system.

A conventional amine system is used in the CO_2 removal system. The absorber operates at 32 bar with the off-gas fed to the FT process. The lean solvent flow rate to the top of the 11-stage absorber is 30 000 kmol/h of 5 mol % MEA and 95 mol % water at 50 °C. All of the CO_2 in the absorber feed gas leaves in the fat solvent at 60 °C. This stream is heated to 140 °C in a FEHE by the hot bottoms from the stripper at 180 °C. The heat exchanger area is 2223 m^2 and duty is 57.51 MW. The heated stream is fed to Stage 3 of the 11-stage stripper.

The absorber operates at the full pressure of 30 bar, so that the gas can feed the FT process. If the CO_2 gas leaving the stripper reflux drum is to be sequestered, the optimum pressure in the stripper is a trade-off between the CO_2 compression costs and the stripper reboiler duty. Sustainable underground injection pressures of 250 bar are typically required.[32] The stripper pressure is set at 10 bar in this paper as a reasonable compromise for purposes of comparison of the alternative flowsheets. The stripper reboiler duty is 73.86 MW using high-pressure steam (254 °C) with the stripper base temperature of 180 °C. Stripper bottoms are pumped up to the absorber pressure and cooled in the FEHE and a water-cooled heat exchanger (41.21 MW) before entering the top of the absorber as a lean solvent.

The overhead vapor from the stripper is cooled to 90 °C that permits the 282 kmol/h of CO_2 in the syngas from the ATR to leave in the vapor stream from the top of the reflux drum. Condenser heat duty is 31.38 MW. The liquid that condenses is fed to the top of the stripper along with 46 kmol/h of makeup water to account for the net loss of water in the gas streams leaving the process (absorber off-gas and stripper CO_2 gas). Losses of MEA are negligible.

3.2. SMR/DMR.

Figure 2 gives the flowsheet that features two parallel reaction systems. The upper is a conventional SMR. The lower is a conventional DMR and methane is fed to both. Equipment sizing, fuel consumed and carbon tax information is provided in Table 1. Water is fed to the SMR and CO_2 is fed to the DMR. The gas streams leaving each system are combined to make the feed stream to the FT process with a H_2/CO ratio of 1.99. Note that the H_2/CO ratio from the SMR section is 4.4 whereas that from the DMR section is 0.97.

The methane fed to the SMR is 3160 kmol/h and that fed to the DMR is 2725 kmol/h. A conventional steam-to-methane ratio (S/C) of 3 is used in the SMR. The 9480 kmol/h of water require a large vaporizer duty (108.7 MW). The preheated methane and steam are fed to the large SMR furnace/reactor, which has a very large duty of 287.9 MW. The reactor exit temperature is set at 1000 °C, which gives a methane conversion of 95% with the S/C ratio of 3.

The energy recovery system for the hot gas leaving the SMR is the same as that described in the previous process. Heat duties and heat exchanger areas are smaller than in the SMR/ATR process because the gas flow rate is smaller. The absorber/stripper CO_2 removal unit must remove the 785 kmol/h of CO_2 formed in the SMR. The flow rate of the gas fed to the absorber is smaller than in SMR/ATR case (13 065 vs 23 284 kmol/h), so the lean solvent flow rate is smaller (25 000 vs 30 000 kmol/h) and the columns have smaller diameters. However, the amount of CO_2 that must be removed is larger (785 vs 282 kmol/h).

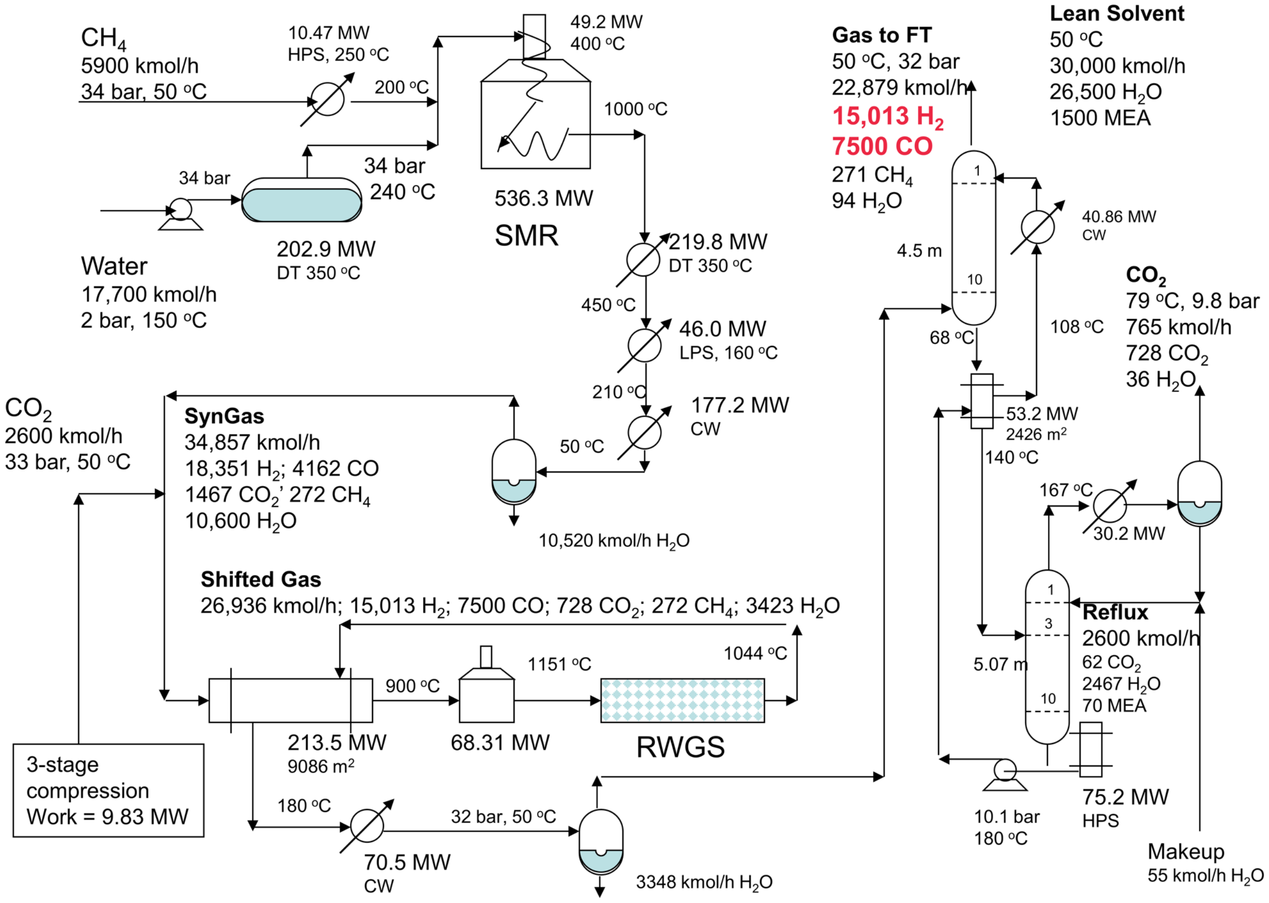

Figure 3. Process flow diagram of SMR/RWGS process to produce 15 000 kmol/h H_2 and 7500 kmol/h CO. Tabulated information on equipment sizing, capital and fuel costs, carbon tax as well as the total annual cost (TAC) is provided in Table 2.

Table 2. SMR/RWGS Process: Equipment and Economics[a]

	Q (MW)	area (m^2)	capital (10^6 \$)	fuel (kmol/h CH_4)	utility
preheater	10.47	331	0.3171	62.8	HP steam
vaporizer	202.9	2178	1.079	1218	Dowtherm
SMR	536.6		20.61	3218	fuel
SMR catalyst			8.355		
furnace	121.2		4.027		fuel
RWGS			0.1118		
RWGS catalyst			0.1414		
HX2	219.8	2672	1.232	(1319)	Dowtherm credit
HX3	46.00	1203	0.7334	(276)	HPS credit
SMR cooler	177.2	13,250	3.487		CW
absorber			0.4324		
stripper			0.4941		
reboiler	75.20	1196	0.7303	451	HP steam
FEHE stripper	53.20	2426	1.157		
condenser	30.20	1902	0.9877		CW
compressors	9.83		5.780	134	electricity
intercoolers	10.76	990	0.9495		CW
stripper cooler	40.86	1958	1.006		CW

[a] Total capital = \$56,170,000. Cost of methane (fuel + fresh feed) = \$338,700,000 per year. Carbon tax (fuel + process) = \$15,620,000 per year. Total annual cost = \$373,000,000 per year.

The two fresh feed streams fed to the DMR are 2725 kmol/h of methane and 2725 kmol/h of carbon dioxide. Because the reactor operates at 4.2 bar, the fresh CO_2 feed must be compressed to 4.3 bar from its 1 bar supply pressure. A large FEHE preheats the feed to the reactor to 980 °C by using the hot reactor effluent at 1000 °C. This heat exchanger transfers 74.13 MW with 9735 m^2 of heat-transfer area assuming an overall gas/gas heat-transfer coefficient of 0.17 kW K^{-1} m^{-2}.

The DMR furnace/reactor heat duty is 188.9 MW. The cooled gas from the FEHE is cooled further to 50 °C and sent

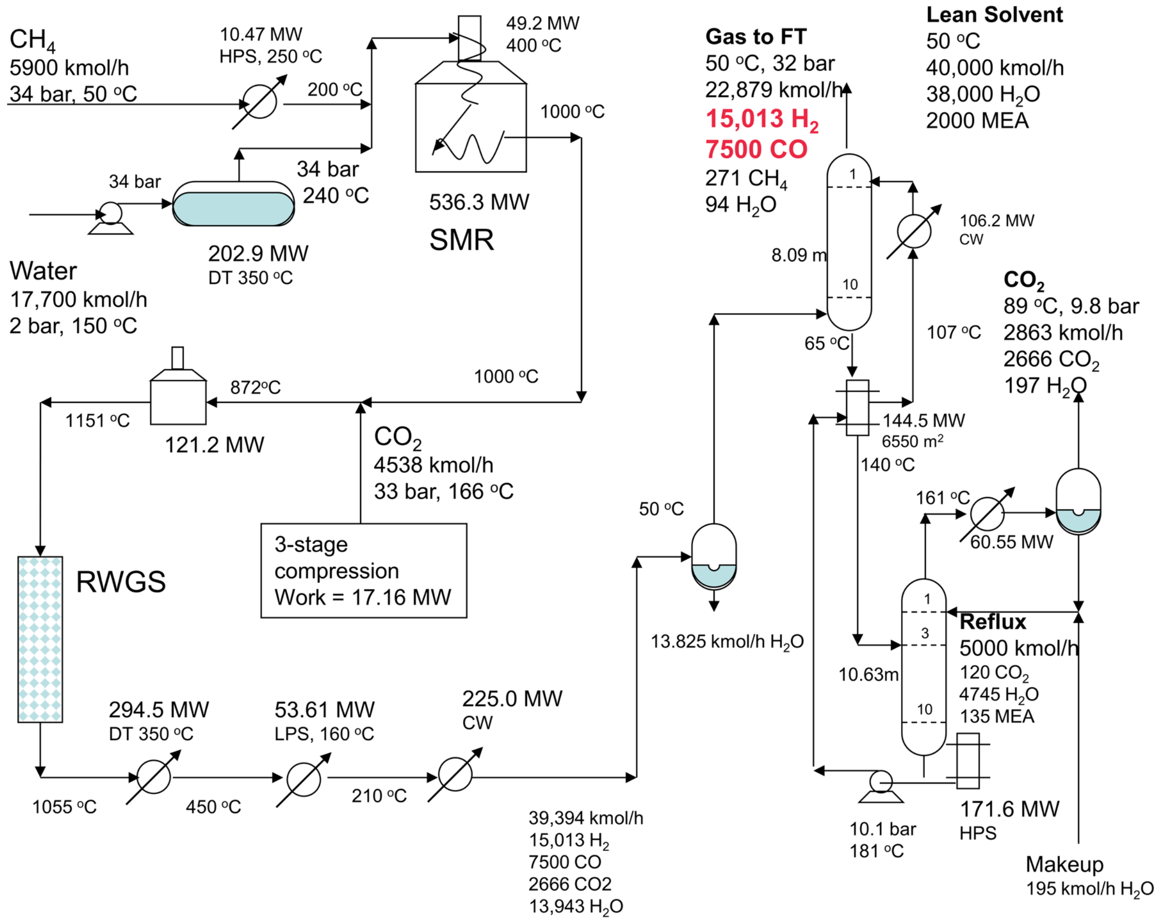

Figure 4. Process flow diagram of modified SMR/RWGS process to produce 15 000 kmol/h H_2 and 7500 kmol/h CO. Tabulated information on equipment sizing, capital and fuel costs, carbon tax as well as the total annual cost (TAC) is provided in Supporting Information Table S2.

to a two-stage compression system with intercooling to raise pressure to 30 bar. The compression ratios in the two compressors are the same. Total compressor power is 24.62 MW. The results obtained in this work agree well with the very recent work by Noureldin et al.[33] who found combined DMR and SMR as an optimal situation for CO_2 fixation.

SMR/RWGS. Figure 3 gives the flowsheet of the process with SMR and RWGS reactors in series with CO_2 addition before the RWGS reactor. Equipment sizing, fuel consumed and carbon tax is provided in Table 2. The SMR is operated with the conventional steam-to-methane ratio of 3, so the duties of both the vaporizer (202.9 MW) and the SMR furnace/reactor (536.3 MW) are very large.

The hot gas leaving the SMR is cooled from 1000 to 50 °C in a series of energy-recovery heat exchangers in which Dowtherm, LP steam and cooling water are used. The condensed water is removed in a separator drum (10 520 kmol/h), and 2600 kmol/h of fresh CO_2 are added after being compressed up to 33 bar in a 3-stage compression system with interstage cooling. Total compressor power is 9.83 MW.

A large FEHE is used to heat the stream back up to 900 °C using the hot RWGS reactor effluent at 1044 °C. The heat duty is 213.5 MW and heat-transfer area is 9086 m^2. A fired furnace (68.31 MW) heats the stream to 1151 °C before entering the RWGS reactor. The reaction is mildly endothermic and the reactor is adiabatic, so the reactor exit temperature is 1044 °C. At this temperature and with the 2600 kmol/h of fresh CO_2, there are the required amounts of CO (7500 kmol/h) and hydrogen (15 013 kmol/h) leaving the reactor. Note that there are 728 kmol/h of CO_2 in this stream that must be removed. The stream from the FEHE is cooled to 50 °C, water is removed and the gas is fed to a conventional CO_2 removal unit in which the 728 kmol/h of CO_2 are removed.

Figure 4 gives an alternative SMR/RWGS flowsheet in which the syngas from the SMR reactor is not cooled to remove water but sent directly to the RWGS section. It is combined with 4538 kmol/h of fresh CO_2 and the stream is heated to 1151 °C in a furnace (121.2 MW). Equipment sizing, fuel consumed and carbon tax is provided in Table S2. The larger flow rate of CO_2 is required to push the reaction to the CO product side because of the higher concentration of water. The compression system work increases from 9.83 to 17.16 MW because of the larger fresh CO_2 feed flow rate.

Importantly, the amount of CO_2 in the RWGS effluent increases from 728 to 2666 kmol/h. The larger load on the absorber/stripper unit increases column diameters, stripper reboiler duty (171.6 vs 75.2 MW) and other heat-exchanger duties and sizes.

More energy is recovered in the Dowtherm and LP steam heat exchangers because of the larger flow rate. The economic effects of all these changes are presented in the next section.

ATR. The final process considered is shown in Figure 5 with the equipment sizing, fuel consumed and carbon tax is provided in Table S3. There is a single vessel into which methane, water and oxygen are fed. The exothermic oxidation of some of the methane provides the heat required for the endothermic SMR

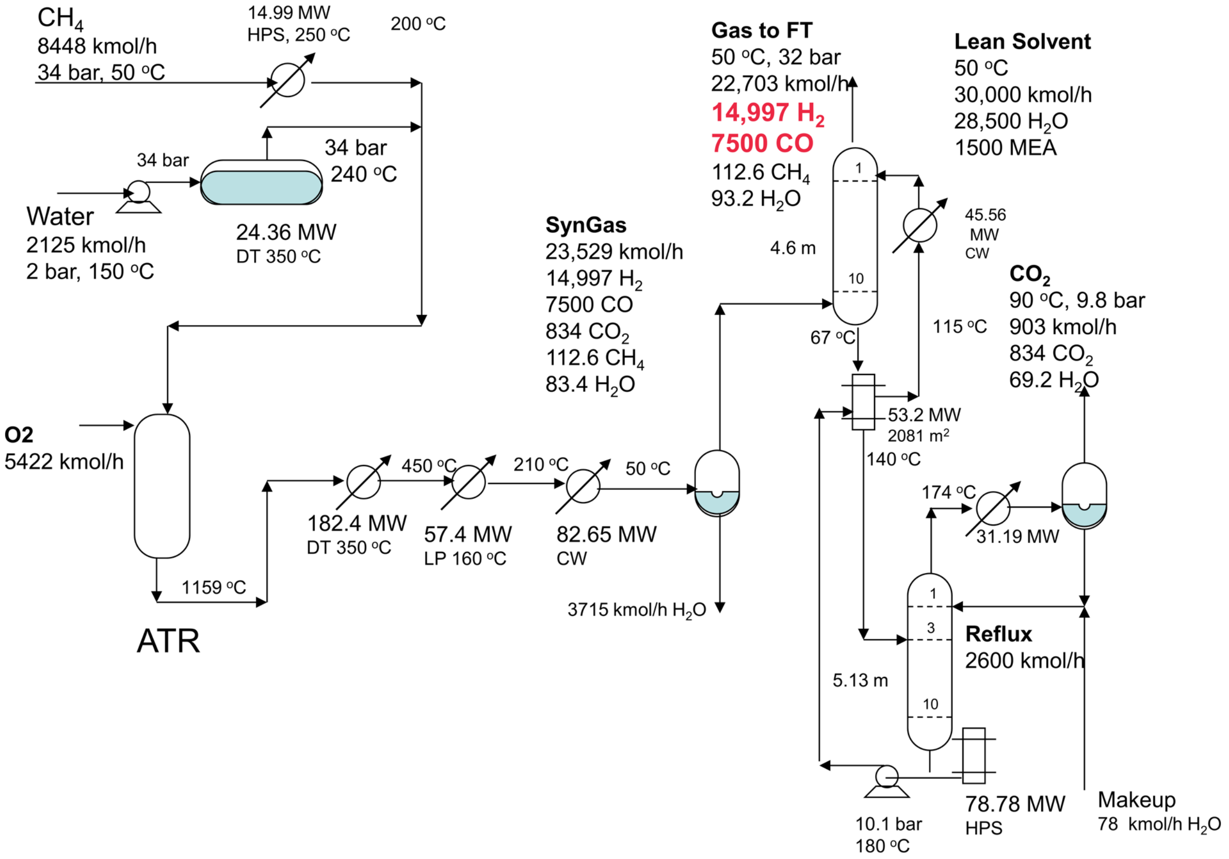

Figure 5. Process flow diagram of modified ATR process to produce 15 000 kmol/h H_2 and 7500 kmol/h CO. Tabulated information on equipment sizing, capital and fuel costs, carbon tax as well as the total annual cost (TAC) is provided in Supporting Information Table S3.

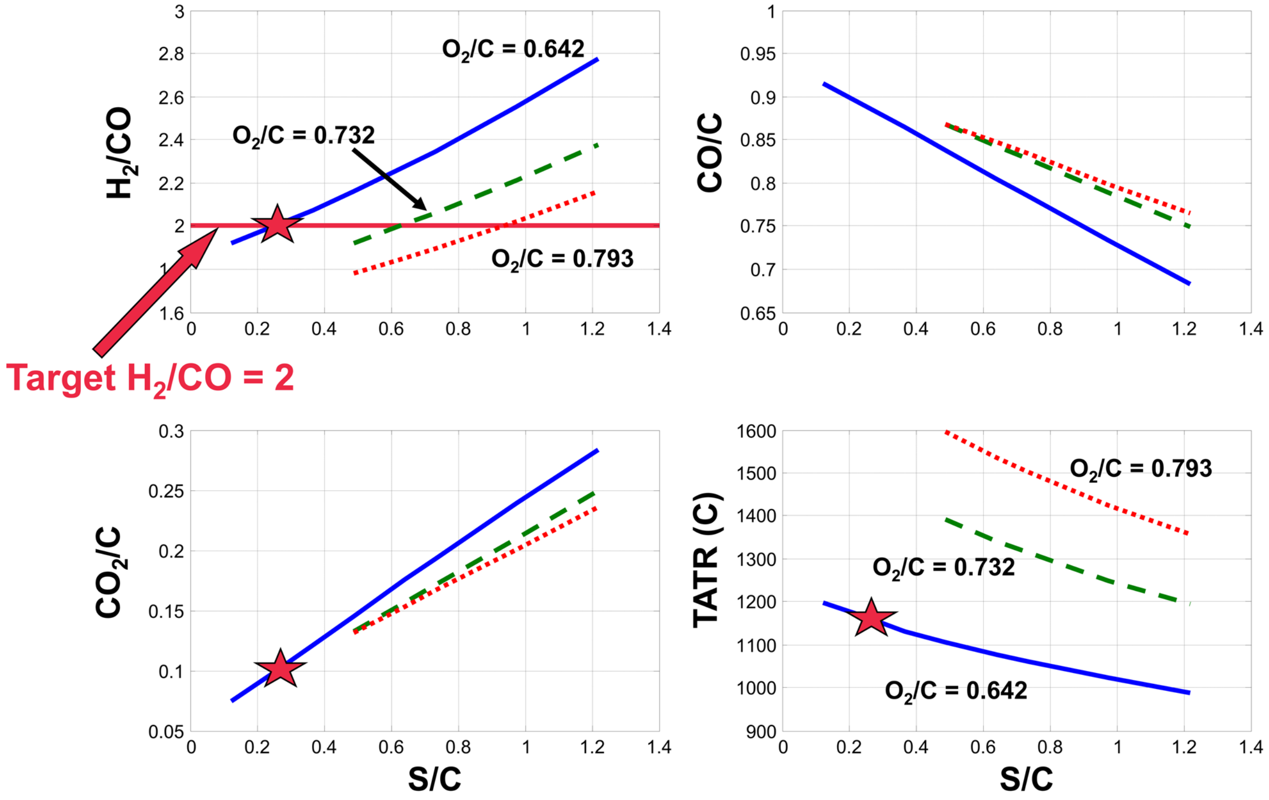

Figure 6. Effect of O_2/C and S/C ratios on ATR process.

reaction and to heat the process stream to high temperature. This type of unit is called an autothermal reactor (ATR) that combines a partial oxidation reaction in the top portion followed by a SMR reaction at the bottom. Note that the amount of water fed is much smaller than in the SMR units because high methane conversion can be attained by using high temperatures. There is less need to have excess water to drive up the methane conversion.

The reactor is a single adiabatic vessel that is much less complex than a fired furnace. However, the vessel must be refractory lined to withstand very high temperatures and must be design for high pressure (35 bar). There are many combinations of steam-to-methane ratios (S/C) and oxygen-to-methane ratios (O_2/C) that yield the desired hydrogen-to-carbon monoxide (H_2/CO = 2) in the syngas leaving the ATR. Figure 6 shows the effects of changing the S/C and O_2/C ratios. As the oxygen is reduced, the steam must be reduced to achieve the desired H_2/CO = 2. Lower oxygen also reduces the temperature in the ATR reactor. The amount of CO_2 produced increases as the S/C ratio increases.

The point marked with a star is selected as the design point. It uses less of the expensive oxygen fresh feed and gives reasonable ATR temperature, in addition to minimizing CO_2 emissions. The flowsheet shown in Figure 5 is based on this design.

It is instructive to compare this ATR process (Figure 5) with the SMR/ATR process (Figure 1). There are many significant differences.

1. More methane and more oxygen must be fed in the ATR process because all the endothermic heat of the SMR reaction must come from burning some of the methane. In the SMR/ATR process, some of the heat is provided in the furnace/reactor (67.4 MW).
2. More water is also fed, which makes the vaporizer duty larger.
3. More high-temperature energy is recovered in Dowtherm and LP steam production because the flow rate of gas leaving the ATR is larger (more methane, oxygen and water fed).
4. More CO_2 is produced (834 vs 282 kmol/h), so the absorber/stripper unit has a larger load. Column diameters are larger and stripper reboiler duty is larger.

In the following sections, detailed economic comparisons of the five alternative flowsheets are presented.

■ ECONOMIC BASIS AND PROCESS DESIGN ASSUMPTIONS

The capital investment, the energy requirements, the carbon dioxide generation and the consumption of raw materials for the five alternative processes are all different and are itemized in the corresponding tables. But each of the processes produces the same amount of syngas for feeding to the FT process with the same desired H_2/CO ratio of 2.

Methane and Oxygen Costs. A number of assumptions were made in the development of the flowsheets shown in Figures 1–5. The most important economic assumption involves the method of accounting for the energy requirements and carbon dioxide production. Energy is consumed and produced at different levels (electricity, Dowtherm at 350 °C, high-pressure steam at 254 °C, low-pressure steam at 160 °C and furnace duties in the fired reactors and furnaces). Energy is also required to generate electricity to drive compressors. With an overall thermal efficiency of 33% and assuming a natural gas lower heating value of 50 MJ/kg, one MW of electricity requires the combustion of 0.003 79 kmol/s of CH_4. For all of the other energies, a thermal efficiency of 75% is assumed, so one MW of furnace duty, steam or Dowtherm requires the combustion of 0.001 667 kmol/s of CH_4.

Carbon dioxide is produced in each of the processes and some is consumed in the DMR reactor. It is also produced in the combustion of methane to generate the required energy at various levels. Because each mole of CH_4 generates a mole of CO_2 in the combustion process, the overall carbon dioxide that is produced and carries a carbon tax debit includes that coming from both the process and fuel combustion. A carbon tax of \$21 per 1000 kg is assumed and included in the economics.

Reaction equilibrium is assumed in the heated SMR and DMR reactors (Aspen *RGibbs* reactor model) to predict reactor performance. This assumption should be valid because of the high temperatures involved and the resulting fast kinetic reaction rates. A power-law kinetic *RPlug* model is used for the RWGS reactor because temperature decreases along the length of the reactor due to the endothermic reaction and the exit composition depends on the temperature profile. The Aspen Peng–Robinson physical property package is used in all units except in the CO_2 removal unit (absorber, stripper and heat exchangers) in which the Amines package is used.

The economic objective function used in this paper is total annual cost (TAC), which includes the cost the methane consumed in both the process and in the generation of energy, the cost of oxygen, the carbon tax and an annual capital cost (capital investment divided by a 3 year payback period). A detailed discussion of these items is given below, which are based on information derived from Turton et al.[34] and Luyben.[35] The cost of cooling with cooling water is assumed to be negligible, so all water-cooled heat exchangers have only capital costs.

Oxygen is consumed in the ATR processes, and it is provided as a liquid (LOX) so that it can be pumped to the high pressures required. A base-case price of \$80 per 1000 kg is assumed, but the effects of variations in price are considered later. A base-case price of methane of \$5 per 1000 SCF is assumed, but the effects of variations in price are considered later. Carbon dioxide is consumed in the DMR and RWGS processes. It assumed to be free, but available at low pressure from whatever source is used. Possible sources include H_2 production separation units or oxy-fired gas turbine systems. The alternative for these processes for the disposal of their CO_2 is to compress the gas to high pressure for sequestration. Thus, it may be more economical for them to give it to the syngas plant for little or no charge.

Capital Investment and Equipment Sizing. Each of the units in a given flowsheet has a capital cost for purchase and installation. The big ticket items are the SMR and DMR reactor/furnaces, the compressors and the large heat exchangers.

1. DMR and SMR furnace/reactor capital cost: based on heat duty using the correlation in Turton et al.[34]
2. DMR and SMR furnace/reactor size to find amount of catalyst: based on a maximum heat flux of 9000 Btu/h-ft^2.[30]
3. DMR and SMR catalyst cost: \$18,000/m^3.
4. ATR vessel size: based on a 5 s residence time.
5. ATR vessel capital cost: 10 times normal vessel cost with aspect ratio $L/D = 10$; $10 \times 17\,640 \times (D^{1.066}) \times (L^{0.802})$ with diameter and length in meters.
6. ATR exit temperature = 1159 °C; oxygen feed varied to give this temperature.
7. SMR exit temperature = 1000 °C; reactor/furnace duty varied to give this temperature.
8. DMR exit temperature = 1000 °C; reactor/furnace duty varied to give this temperature.
9. RWGS reactor operated adiabatically with inlet temperature 1151 °C to produce the required CO.
10. DMR uses a FEHE designed for a 20 °C hot-end approach temperature differential with an overall heat-transfer coefficient $U = 0.17$ kW K^{-1} m^{-2}.
11. Overall heat-transfer coefficient $U = 0.28$ kW K^{-1} m^{-2} in gas/steam and gas/Dowtherm heat exchangers, and $U = 0.20$ kW K^{-1} m^{-2} in gas/water cooled heat exchangers.
12. Heat-exchanger capital cost = $7296 \times (\text{area}^{0.65})$ with area in m^2.

Table 3. Economics Summary

	TAC (10^6 \$/y)	capital (10^6 \$/y)	carbon tax (10^6 \$/y)	feed and fuel methane (10^6 \$/y)	oxygen (10^6 \$/y)	fuel/CO_2 (kmol/h)
SMR/DMR	359.2	49.69	13.09	329.5	0	3297
SMR/RWGS	373.0	57.17	15.63	338.7	0	3765
SMR/ATR	382.2	21.78	0.802	277.7	96.60	(276)
SMR/RWGSMOD	386.5	56.48	17.89	349.8	0	4023
ATR	399.9	18.23	1.788	270.4	121.6	(730)

13. Compressor and drive capital cost: 3 times the correlation given in Turton et al.[34] (based on Aspen Economic Analysis results).
14. Fat solvent inlet temperature to stripper: 140 °C.
15. Absorber and stripper vessels: $17\,640 \times (D^{1.066}) \times (L^{0.802})$.
16. Separator drums: design for a maximum vapor velocity or for a 5 min liquid holdup, whichever gives the larger diameter (aspect ratio $L/D = 2$).

■ ECONOMIC COMPARISON

Table 3 presents an overall comparison of the five alternative processes while other corresponding tables give details of equipment sizes, capital investment, carbon tax, energy requirements and methane consumption (fresh process feed plus fuel burned). It is clear from the Table 3 that energy costs for all processes considered are higher by an order of magnitude than the corresponding capital costs, in agreement with the assumptions made in this paper. Thus, most of the processes effectiveness, as well as their relative competitiveness will depend of the ability to minimize CH_4 and/or LOX input, as well as their costs. With base-case costs assumed, the process with the lowest TAC is the dual-reactor SMR/DMR plant at 359.2 M \$/y showing its potential in cost-effective and sustainable CO_2 utilization. Its capital costs are slightly lower than SMR/RWGS and SMR/RWGSmod with the major capital costs coming from SMR reactor and compression train. The DMR reactor and its catalyst costs comprise 2/3 of the SMR costs as calculated from their corresponding heat duty, MW. The total amount of CH_4 for both feed and fuel is also lower than in both SMR/RWGS and SMR/RWGSmod due to the consumption of CO_2 as a raw material. Notably, net CO_2 consumption in SMR/DMR process is only little higher or almost equal to that in both SMR/RWGS and SMR/RWGSmod (1875 vs 1835 vs 1675 kmol/h, respectively) but the amount of fuel gas to the SMR furnace of SMR/DMR is almost half of that in SMR/RWGS and SMR/RWGSmod (287.9 vs 536.3 MW, respectively).

Table 3, however, clearly shows limitations of using SMR for syngas production with high capital costs as compared to the competing ATR processes. Overall, the process with the smallest capital investment is the simple single vessel ATR with the capital costs being halved when compared to the SMR processes. Capital cost is not a determining factor overall as it comprises only a fraction of the TAC. More importantly, ATR based processes also have the smallest methane cost because it does not use methane as furnace fuel. Finally, because of the high temperature, process heat can be efficiently recovered downstream effectively yielding an energy producing process. Dowtherm and high pressure steam generate 730 kmol/h CH_4 equivalent, when compared to the need 3297 to 4023 kmol/h of CH_4 equivalent in SMR based processes. This is concomitant with a very low estimated carbon tax for both ATR based processes, 1 order of magnitude smaller than in the SMR based processes. However, both of the ATR processes consume expensive oxygen. In fact, LOX composes ~30% of the total feedstock cost in ATR and ~36% in SMR/ATR. Interestingly, decreasing input of LOX from ATR to SMR/ATR is counterbalanced by the increase in CH_4 as feed and fuel that seems to provide a less expensive alternative at the case base assumptions. Finally, substituting fraction of the CH_4 with readily available no cost waste CO_2 provides an edge to the SMR/DMR process due to the 10 M \$/y savings in natural gas. The dynamic interplay among the costs of raw materials (natural gas and LOX), carbon tax applied and the TAC of the process considered will be further investigated in the following sensitivity analysis.

■ RAW MATERIAL COSTS SENSITIVITY ANALYSIS

All economic comparisons depend on the assumptions made. This is particularly true for the prices of raw materials because they are typically 1 order of magnitude larger in most chemical processes than energy or capital costs. How are the economic comparison affected by the assumed prices of oxygen and natural gas and how would their fluctuations affect the overall economics? We explore this question in this section. The two processes compared are the SMR/DMR process and the SMR/ATR processes.

Oxygen Price. Because the SMR/DMR process does not consume oxygen, its TAC remains constant at \$359,200,000 per year. At the current \$80 per 1000 kg of oxygen, the TAC of the SMR/ATR process is \$382,200,000 per year. However, as shown in Figure 7, if the price of liquid oxygen drops to \$62 per 1000 kg, the two processes have about the same TAC. It becomes apparent that availability of inexpensive electrical power necessary to obtain LOX facilitates SMR/ATR use making it more cost efficient than SMR/DMR.

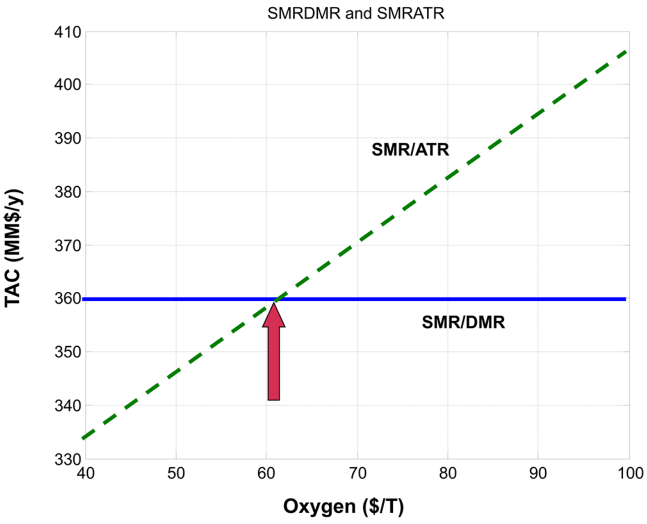

Figure 7. Effect of LOX price on the TAC of SMR/ATR and SMR/DMR processes.

Methane Price. Both processes consume methane fresh feed, but the SMR/ATR uses less methane as fuel because it provides the heat for the endothermic SMR reaction (8195 kmol/h for SMR/ATR vs 5885 kmol/h for SMR/DMR). Therefore, the price of natural gas has more of an effect on the TAC of the SMR/DMR process in terms of feed and fuel costs. Figure 8 compares how natural gas price affects the two processes under two different conditions. The first case assumes that the oxygen price remains constant at \$80 per 1000 kg. In this case, higher natural gas prices make the SMR/ATR process more economical. However, it is more reasonable to assume that there is a significant dependence of the oxygen price on the price of natural gas because it is a major expense in the production of liquid oxygen in compression work. We approximate this dependence by scaling the oxygen price with the methane price, as shown in the following relationship:

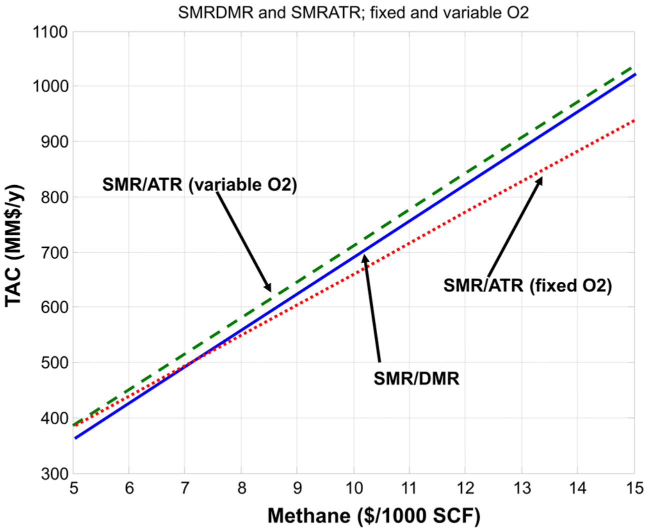

Figure 8. Effect of natural gas price on the TAC of SMR/ATR and SMR/DMR processes.

$$\text{oxygen price} = 40\left(1 + \frac{\text{methane price}}{\$5 \text{ per } 1000 \text{ SCF}}\right)$$

Half of the price of oxygen is associated with capital investment and other fixed and variable costs that do not change with natural gas price. The other half of the price varies directly with the cost of energy.

As shown in Figure 8, in this more reasonable case, the TAC of the SMR/DMR remains lower than that of the SMR/ATR process.

Carbon Tax. The SMR/ATR process produces carbon dioxide (282 kmol/h). The SMR/DMR process is a net consumer of CO_2 (1875 kmol/h). However, the SMR/ATR process uses less methane as fuel in other parts of the process (carbon tax is \$801,400 per year) than does the SMR/DMR process (carbon tax is \$13,090,000 per year).

The somewhat unexpected result is that higher carbon tax makes very little change in the TAC of the SMR/ATR process, but it does affect the TAC of the SMR/DMR process. Figure 9 shows these effects.

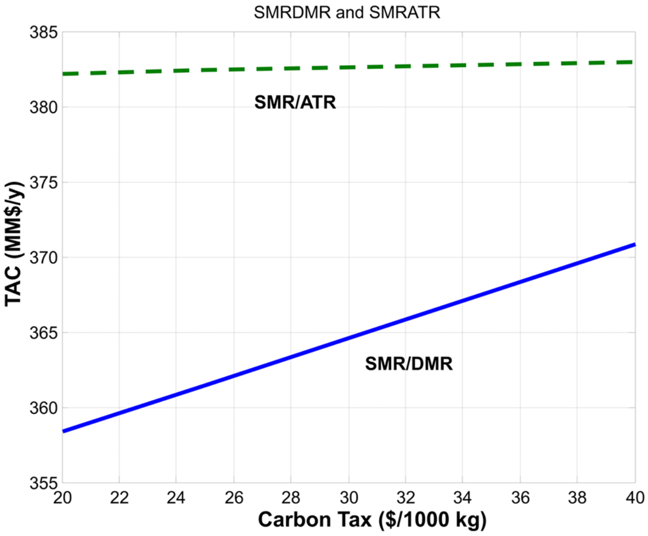

Figure 9. Effect of carbon tax on the TAC of SMR/ATR and SMR/DMR processes.

CONCLUSION

Several alternative configurations of the syngas production with H_2:CO ratio of 2 at 32 bar were evaluated to be supplied to FT synthesis units. A total annual cost economic objective function was used that considered the cost of raw material feeds, the capital costs of the process equipment, the cost of the methane fuel required to meet the energy requirements and the carbon tax resulting from the CO_2 generated in the process and generated in the methane fuel combustion. At base case assumptions, the combination of SMR/DMR process has the smallest total annual cost (TAC) of all the configurations considered. The economic comparisons were fairly insensitive to the prices of the raw materials (oxygen and natural gas). Importantly, even though SMR/DMR is a net CO_2 consumer, it also consumes more methane than its nearest competitors, SMR/RWGS and SMR/ATR, thus reacting negatively to the carbon tax increase. Although ATR based processes had lowest capital investment costs due to the rather simple reactors, the need to consume LOX rendered these processes more expensive at the base-case assumed prices.

Future work will study the dynamic control of the SMR/DMR process. Plantwide control of this process is expected to be nontrivial because there are two independently operating units. The individual control structures must be coordinated to produce the desired H_2/CO ratio to feed to Fischer−Tropsch.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00368.

Detailed equipment and economics information for SMR/ATR, modified SMR/RWGS and ATR processes (PDF).

AUTHOR INFORMATION

Corresponding Author

*J. Baltrusaitis. E-mail: job314@Lehigh.edu. Phone: +1-610-758-6836.

Notes

The authors declare no competing financial interest.

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