

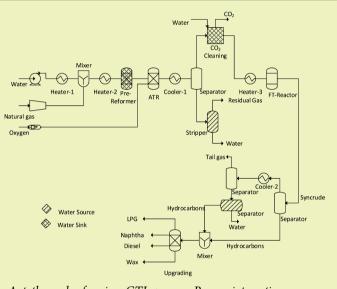
Water and Energy Issues in Gas-to-Liquid Processes: Assessment and Integration of Different Gas-Reforming Alternatives

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Supporting Information

ABSTRACT: The substantial discoveries of shale gas are leading to increasing attention of gas-to-liquid processes using Fischer-Tropsch chemistry. Traditionally, focus has been given to the reaction schemes, while major issues such as energy and water matters have been handled subsequently. There is a need to examine the impact of selecting the reforming technology on issues pertaining to sustainability such as energy and water usage. This paper analyzes energy and water generation and management options for three primary alternatives for the production of syngas: steam reforming, partial oxidation, and autothermal reforming. A combination of thermodynamic models and computer-aided simulation is used to quantify those aspects. Trade-offs are established for the use of a desired H2:CO ratio on water and energy usage. Also, systematic process integration techniques are used to identify the impact of energy and mass integration on the usage of energy and water in the process and to benchmark the process performance.



KEYWORDS: Gas reforming, Partial oxidation, Steam reforming, Autothermal reforming, GTL process, Process integration

INTRODUCTION

The search for opportunities to reduce dependence on petroleum and find an economic way to ship fuels has sparked a special interest in natural gas (NG). According to the International Energy Outlook 2013,¹ natural gas consumption is projected to increase during the next few years in the industrial and electric power sectors due to its relatively low price promoted by the recent shale gas discoveries. Also, the efficient use of natural resources is a key piece for a gas-to-liquid (GTL) process, either as a feedstock or as part of a utility system. Fuels produced through GTL processes have become a good alternative to transportation fuels because they contain a high cetane number with excellent combustion properties, low sulfur, and are easy to transport.² A GTL-derived fuel can be used in engines as blended or net diesel.^{3–5} FT products are sulfur-free and eco-friendly compounds.⁵

Fischer–Tropsch (FT) chemistry is an effective approach to convert natural gas to long-chain hydrocarbons. An FT-based GTL process typically involves three primary stages: syngas synthesis, FT synthesis, and upgrading. There are different alternatives to syngas generation, which could amount up to 40% of the total investment, thus driving a particular interest to optimize the syngas production stage. Available technologies are partial oxidation (POX), steam-methane reforming (SMR), and autothermal reforming (ATR). These options have been addressed by researches and are employed by several industries such as Shell,³ which uses POX; Rentech,⁶ which uses SMR; and Sasol,⁷ Exxon Mobile,⁴ and Syntroleum,⁸ which use ATR.

Some works have been developed aiming to improve the GTL process economics or the environmental or operational aspects. Gandrick et al.⁹ considered the recycling of the light gas from FT synthesis and refining areas to fire gas turbines to produce electricity and the reuse of the gas turbines to produce superheated steam. Martin and Grossmann¹⁰ proposed a superstructure for the optimization of FT-diesel production through biomass gasification, with the objective of minimizing energy consumption. Rafiee and Hillestad¹¹ searched for CO₂

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        Received:
        July 30, 2013

        Revised:
        October 14, 2013

        Published:
        October 24, 2013
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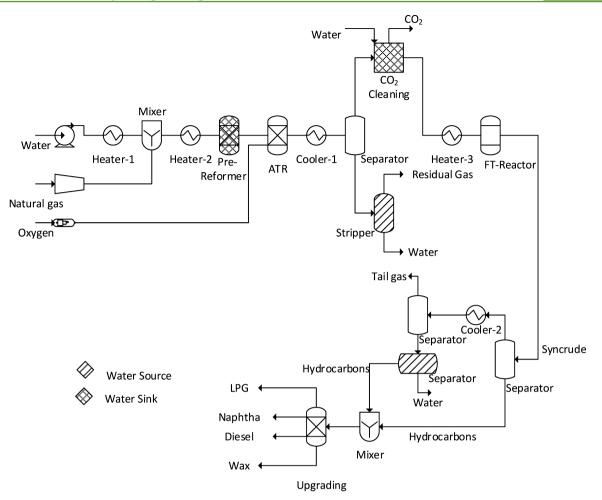


Figure 1. GTL process based on ATR.

removal allocation based on economic objectives. Swanson et al.¹² considered the recycle of the syngas coming from the FT to increase the CO conversion, while the unconverted syngas along with the fuel gas from hydro-processing is flared in a gas turbine to produce power, and the heat is recovered in a steam generator for a biomass-to-liquid process. The potential for process integration has been recently explored. Bao et al.¹³ reported that GTL processes show high potential for energy integration. In terms of water management, Gandrick et al.⁹ proposed the reuse of the wastewater recovered from FT-synthesis as makeup in the cooling tower and steam for the process.

Traditionally, publications in the area of GTL have selected a specific reforming technique and tracked the yield and product distribution. While this is a worth objective, there is a need to examine the impact of selecting the reforming technology on issues pertaining to sustainability such as energy and water usage. We address in this paper several aspects related to such issues: (a) A comparative analysis is developed for assessing the impact of the use of different reforming technologies on energy and water usage. A process flowsheet based on each reforming alternative is developed, and a combination of thermodynamic models and computer-aided simulation is used to rigorously quantify the impact on energy and water usage. (b) Trade-offs are established for a desired syngas ratio of 2.0 on water and energy usage. (c) Systematic process integration techniques are used to establish performance targets for energy and water usage and to benchmark the performance of the process.

Process Description. The FT-based GTL process consists of the following main systems: gas reforming for syngas production, syngas synthesis using FT reaction, and separation and upgrading.

The integration of these components to generate the GTL process technologies considered here are shown in Figures 1 -3. The major points of each individual system are briefly described below.

Gas Reforming for Syngas Production. This section summarizes the basic chemistry involved in the three primary gas-reforming technologies. For more information on reforming of natural and shale gas, the reader is referred to literature on the subject (e.g., Noureldin et al.¹⁴).

Partial Oxidation (POX). The chemical reaction carried out in this option is below.¹⁴

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$$
 $H_{298K}^0 = -36 \text{ kJ/mol}$

This method employs an air separation unit because nitrogen-free oxygen is required in the feed. The partial combustion can be catalytic or noncatalytic.^{15,16} Efforts have been made to achieve the partial oxidation at low temperatures (for instance, between 300 and 1000 °C with a rhodium catalyst¹⁶ or using platinum as catalyst with a temperature lower than 1200 °C¹⁷) because at the high reaction temperatures currently used (between 1200 and 1500 °C) the operating cost is high and soot formation is observed.¹⁸

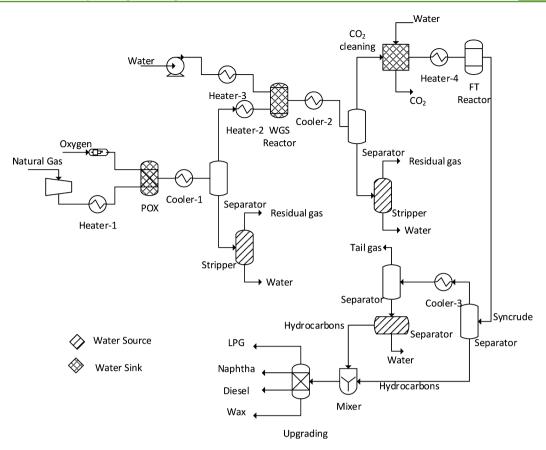


Figure 2. GTL process based on POX.

Steam–Methane Reforming (SMR). SMR is a catalytic process carried out in a mult-itubular reactor commonly packed with nickel as a catalyst.¹⁸ It has a high H_2 generation and requires heat because the reaction is endothermic. Typical designs provide a system to recover the heat from flue gases to preheat the inlet stream.¹⁹

CH₄ + H₂O → CO + 3H₂
$$H_{298K}^0 = 206 \text{ kJ/mol}$$

CO + H₂O ↔ CO₂ + H₂ $\Delta H_{298K}^0 = -41 \text{ kJ/mol}$

A water-gas shift reaction is part of this process.

Autothermal Reforming (ATR). Combustion and steam reforming are combined in the same reactor to obtain a proper syngas ratio for the FT reactor.⁵ The heat from the oxidation reaction provides the heat required by steam reforming, leading the process to be autothermal.^{18,19}

$$CH_4 + 1.5O_2 \rightarrow CO + 2H_2O \quad \Delta H_{298K}^0 = -519 \text{ kJ/mol}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H_{298K}^0 = 206 \text{ kJ/mol}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad H_{298K}^0 = -41 \text{ kJ/mol}$$

FT Synthesis. The syngas goes to the FT synthesis stage, where the CO and H_2 are converted into paraffins, olefins, oxygenates, and acids. The components found in the products depend on the catalyst employed. The products follow the Anderson–Schulz–Flory (ASF) distribution, modeled by

$$\frac{W_n}{n} = (1 - \alpha)^2 \alpha^{n-1}$$

where W_n corresponds to the mass fraction of hydrocarbons with *n* carbons, and α is the chain growth probability of the molecules to form longer chains.^{20,21}

Different types of reactors are commercially used, such as fluid bed, circulating-catalyst, tubular fixed bed, and fixed slurry bed. A fluid bed reactor is used at high temperatures to produce olefins with low molecular weight. Circulating-catalyst reactors provide the cooling required through the product recycle.²² The fixed bed reactor is filled with catalyst inside of the tubes, and a cooling fluid circulates on the outside of the tubes. A slurry bed reactor operating at low temperatures is regarded as the most efficient process for FT clean diesel. The difference among these reactors consists basically on the phases involved in the reaction and the catalyst distribution.^{23–25}

Depending on the temperature level, the FT process technology is divided into high (HTFT) and low (LTFT) temperature Fischer–Tropsch. HTFT temperatures range between 300 and 350 °C at 2.5 MPa, and the conversion can reach up to 85%.¹⁸ LTFT ranges between 220 and 240 °C at 2–2.5 MPa. Choosing the catalyst is an important factor, as discussed in the literature.^{18,22,26,27} Cobalt-based catalysts achieve a high conversion, can be used at low temperatures, favor paraffin production, and decrease undesired product generation. Iron catalysts work at high temperatures, and a water–gas shift reaction leads to undesired products.^{26,27} The desired syngas ratio in FT reactor inlet is typically 2 to 2.1, according to the reaction,²⁷

$$nCO + 2nH_2 \rightarrow (-CH_2 -)_n + nH_2O$$

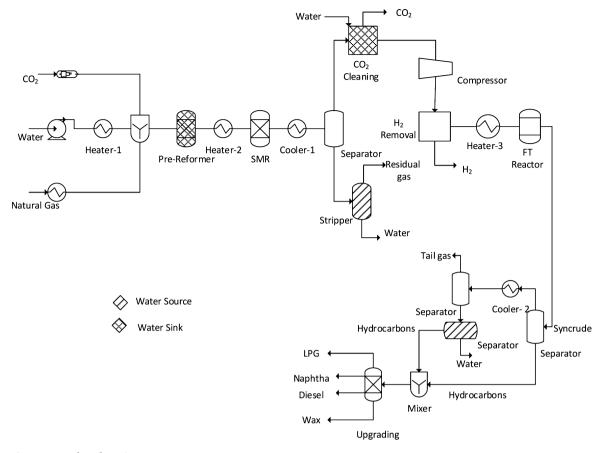


Figure 3. GTL process based on SMR.

Some syngas production process is needed to adjust the syngas ratio (the ratio of hydrogen to CO) before it is fed into the heavy paraffin synthesis reactor.³

The synthesis gas conversion is carried out on a cobalt-based catalyst at low temperatures. The products are mostly paraffins, which become longer at high chain growth probability values. Having paraffins in the upgrading section improves the yield as well as the product properties.²⁸

Use of Separation Processes. Once the reaction stages have been implemented, the FT outlet is separated into high quality fraction products. The different boiling points of the components allow the use of distillation columns. The lighter components are separated first, while oxygenates are extracted in the liquid phase. Extractive distillation and fractionation can be used to separate olefins or to convert them into naphtha and diesel. In some cases, for instance when a cobalt-based catalyst is used, paraffin products are upgraded using a hydrogenation unit and then fractionated. Although several technologies can be used to obtain different product fractions, in this work the upgrading step was simulated as a simple separation process, which was suitable for the objective of carrying out an overall water and energy analysis.

Development of GTL Process Flowsheets. We now consider the process flowsheets that arise from the implementation of the three reformers to convert natural gas into liquid fuels, namely, ATR, POX, and SMR. The approach includes the assessment of key aspects for each flowsheet, such as feedstock usage, power consumption, heat requirements and the effects of potential water and energy integration.

Data were collected for the design the GTL flowsheets, and ASPEN Plus simulations were carried out for each case,

complemented with an overall analysis for heat recovery and water use management. A base capacity of 50,600 bbl of liquid product/day was assumed. This is essentially the process capacity for which a break-even point was reported by Bao et al.,¹³ where natural gas prices of \$8.00/MMBTU were assumed. Such process capacity would yield suitable profitability for recent declining prices for natural gas reaching \$3.50/MMBTU.

Each of the syngas technologies requires different equipment and conditions to produce a H_2 :CO ratio equal to 2. The FT and upgrading sections were considered to be the same. The synthesis gas conversion is assumed to occur on a cobalt-based catalyst at low temperatures. The flowsheet description for each case is given below. Water sources and sinks are identified for each flowsheet. Water sources refer to those parts of the process where water is produced, while water sinks refer to pieces of equipment where water is consumed. The natural gas composition that was assumed in this work for each of the three technologies is given in Table 1.

Table	1.	Composition	of	Natural	Gas

component	composition (% mol)
CH_4	95.39
C_2H_6	3.91
C ₃ H ₈	0.03
CO ₂	0.59
N_2	0.08
temperature (°F)	100
pressure (psia)	310

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Syngas Process Using ATR. Figure 1 shows the GTL flowsheet when ATR is used in the syngas synthesis section. Natural gas is first compressed from 310 to 435 psia, mixed with saturated steam, preheated to 700 °F and sent to a prereformer to convert higher hydrocarbons into syngas to decrease the coking formation at high temperatures.^{19,29} The outlet stream and oxygen from the air separation unit are sent to the autothermal reformer; the syngas produced at 435 psia is cooled and water is separated, while the gas stream goes to a separator where 99.96% of CO₂ is removed by using water at 295 psia. The syngas is heated to 428 °F and fed to the FT reactor, for which the product distribution has been modeled as an ASF distribution, with a chain growth probability of 0.9.9,30 The syncrude at 362 psia is separated into vapor and liquid phases. The liquid phase is sent to a mixer, while the vapor stream is cooled and a tail gas is extracted. The tail gas contains a mixture of short-chain hydrocarbons, CO, CO₂, and hydrogen. The residual gas exiting the stripper contains traces of CO, CO₂, and hydrogen. Water is separated, and the remaining stream is sent to the mixer and then to a distillation column to obtain different hydrocarbon fractions, such as LPG, naphtha, diesel, and waxes.

Table 2 reports the reformer feedstock requirements for each GTL technology. For the case of the process based on ATR,

Table 2. Feed Consumption for the Syngas Production Stage (lbmol/h)

	ATR	POX	SMR
NG	59,084	57,761	55,116
O ₂	40,708	38,088	_
H ₂ O	35,352	_	236,374
CO ₂	-	_	47,445

the molar ratio of oxygen to natural gas at the inlet is 0.69, while that of water to natural gas is 0.6. The amount of O_2 was increased to reach the H₂:CO ratio to 2 to keep consistency with the other two processes. It is important to mention that the temperature increases as O_2 increases.

The pre-reformer and the autothermal reformer are modeled as adiabatic reactors using the ASPEN Plus RGibbs model, which is based on a Gibbs minimization reactor. The thermodynamic property method used was Peng–Robinson. The FT product was approximated as paraffins, with $\alpha = 9$ (using cobalt as catalyst the product distribution is mainly paraffin), from which a global reaction was estimated with the stoichiometric coefficients for each component. The attempt to model products from C1 to C100 caused convergence difficulties in ASPEN PLUS; therefore, we grouped hydrocarbons from C30 to C100 within the carbon C30 cluster.⁵

Syngas Process Using POX. For the process based on POX, natural gas is compressed from 310 to 435 psia and preheated to 700 °F, while oxygen from the air separation unit (ASU) is compressed to the same pressure. Both components are sent to the partial oxidation reformer where an exothermic reaction takes place. The syngas stream is cooled to 120 °F, and water is separated. The gas stream is heated to 572 °F and sent to a water–gas shift (WGS) reactor using saturated steam at 435 psia, where the H₂:CO ratio is adjusted to 2. The product is cooled to separate the water and is sent to a separation unit where 99.85% of CO₂ is removed. The stream enriched with CO₂ contains small amounts of water. The syngas stream is heated to 428 °F and is fed to the FT reactor. The syncrude

product exits at 362 psia and is separated into vapor and liquid phases. The liquid is sent to the mixer, while the vapor is cooled to 104 $^{\circ}$ F. Tail gas is extracted, and water is separated. The remaining stream goes to a mixer, and the mixture is sent to a distillation column to obtain different hydrocarbon fractions.

The molar ratio of oxygen to natural gas is 0.66 (Table 2). The amount of water is calculated from the stoichiometric ratio in the water gas shift reaction. Figure 2 shows the base diagram for the GTL flowsheet using POX.

The partial oxidation reformer is modeled using the ASPEN Plus RGibbs model, while the water-gas shift reactor is modeled with the REquil model, which is driven by an equilibrium-based calculation. The FT reactor is modeled similarly as in the ATR case.

Syngas Process Using SMR. In this case, natural gas is heated to 471 °F and mixed with saturated steam at 310 psia and CO2 at the same pressure. The stream is fed to a prereformer, which operates adiabatically at 310 psia, to convert higher hydrocarbons into syngas. The product stream is preheated to 1000 °F and sent to the steam-methane reformer (the reformer operates at 295 psia, a lower pressure with respect to the other two cases). Syngas at 1625 °F is cooled to 120 °F, and water is separated, while the gas stream goes to a separator where 99.95% of CO_2 is removed using water as a separating agent. The treated gas is compressed to 377 psia and taken for H₂ removal to adjust the H₂:CO ratio to 2; 34% of the H₂ contained in the syngas is removed, along with traces of water, CO₂, and CH₄. The adjusted syngas is heated to 428 °F and fed to the FT reactor, which operates at 362 psia. The remaining part is the same as in the other two cases.⁹ Figure 3 shows the basic flowsheet for this process.

The molar ratio of water to methane in the feed stream is 4.5, while that of water to CO_2 is 5. The pre-reformer and steam reformer are modeled using an ASPEN Plus RGibbs model. The FT reactor is modeled similarly as in the two previous cases. A summary on base data and operating conditions for each GTL process is available in the Supporting Information.

RESULTS AND DISCUSSION

The first point to analyze is related to the consumption of raw materials for each option. The implications for power

Table 3. Resources Consumption for Each Technology

	ATR	POX	SMR
overall water consumption (lbmol/h)	36,200	4720	239,705
power demand (MW)	287	269	183

Table 4. Water Uses for Each Flowsheet with Each Reformer

	input	generation/depletion
ATR	pre-reformer, CO_2 removal	reformer, pre-reformer, FT reactor
РОХ	reformer, WGS reactor, CO ₂ removal	reformer, WGS reactor, FT reactor
SMR	pre-reformer, CO_2 removal	reformer, pre-reformer, FT reactor

requirements are briefly discussed. Water use and integration is then considered, followed by an energy analysis and the potential implications of energy integration.

Implications of the Reaction Paths. The conversion of natural gas into liquid fuels using the ATR technology requires more water than the POX process. In ATR, water is used to

Table 5. Water Balance for Each Process Flowsheet with Each Reformer (lbmol/h)

	input	generation/depletion	discharge
ATR	36,300	49,681	84,940
POX	4725	46,865	50,660
SMR	239,919	-18,537	217,152

Table 6. Overall Water Analysis for Each Technology

	ATR	POX	SMR
(water produced, bbl)/(liquid product, bbl)	2.07	1.24	5.29
(water feed, bbl)/(liquid product, bbl)	0.95	0.12	6.33

 Table 7. Minimum Water Requirements after Direct Recycle

 (lbmol/h)

	fresh water	discharge
ATR	0	48,640
POX	0	45,935
SMR	22,767	0

Table 8. Water Balance for Each Technology (lbmol/h)

	ATR	POX	SMR
water in	36,300	4725	239,919
generation	49,681	46,865	-18,537
water out	84,940	50,660	217,152
losses	1041	930	4230
water production ^a	48,640	45,935	0
^a Target values assuming	direct recycle.		

Table 9. Water Composition from FT Synthesis

component	% wt
water	98.88
nonacid oxygenated hydrocarbons	1.00
acidic oxygenated hydrocarbons	0.09
other hydrocarbons	0.02
inorganic components	0.01

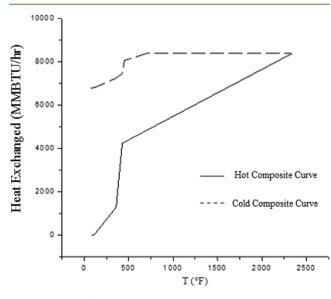


Figure 4. Pinch diagram for GTL process with ATR technology.

obtain CO with a steam reaction, while in POX water is only used to adjust the H₂:CO ratio through the water–gas shift

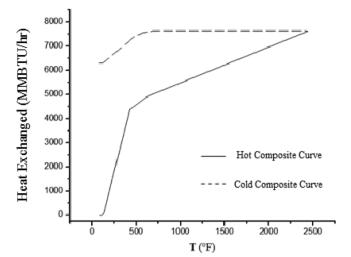


Figure 5. Pinch diagram for GTL process with POX technology.

reaction. The POX outlet syngas ratio is 1.8; the amount of water needed is small and corresponds to the CO conversion

$$f_{\rm CO} = \frac{SR_{\rm out} - SR_{\rm in}}{SR_{\rm out} + 1}$$

where SR_{out} is the syngas ratio in the water—gas syngas reactor outlet, and SR_{in} is the syngas ratio in the inlet.

Both ATR and POX require oxygen and water. However, the ATR option consumes oxygen and water in the reformer for the syngas synthesis, and POX uses water in order to fix the syngas ratio in the water–gas shift (WGS) reactor. Because controlling the syngas ratio with the water inlet to the WGS reactor seems easier than controlling the oxygen inlet and temperature in the autothermal reformer, POX probably offers better potential for operability.

The reactions need to provide a desired syngas ratio of 2.0 are given below.

For the ATR case:

 $CH_4 + H_2O \rightarrow CO + 3H_2$ steam reforming

 $CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$ oxidation reforming

 $CO + H_2O \leftrightarrow CO_2 + H_2$ water-gas shift

It should be noted that the three reactions take place in the reformer.

For the POX case:

 $CH_4 + 0.5O_2 \rightarrow CO + 2H_2$ partial oxidation reforming

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
 water-gas shift

In this case, the first reaction takes place in the reformer, and the second one is needed for the adjustment of the H_2 :CO ratio and takes place in a different unit.

Both cases look fairly similar, but the decision on where to feed the water to reach a syngas ratio of 2.0 changes the global view. Water requirements change depending whether the objective is to favor or to avoid the steam reforming reaction. The steam reformer requires a high amount of water to carry out the steam reaction, even if not all of the water reacts. The reformer outlet syngas ratio is 3, a lower value because when CO_2 is fed, the amount of H_2 produced per mole of CO decreases because of the dry reforming reaction (CO_2 produced

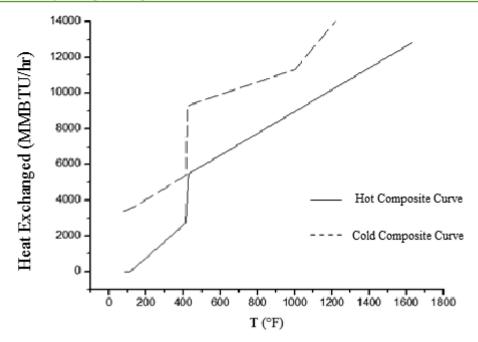


Figure 6. Pinch diagram for GTL process with SMR technology.

Table 10. Energy Requirements (MMBTU/h)

	ATR	POX	SMR
ł	efore energy integr	ration	
heating	1589	1340	15,673
cooling	8373	7629	12785
	after energy integra	ition	
minimum heating	0	0	6,239
minimum cooling	6784	6289	3351

Table 11. Summary of Water/Energy Nexus for Each GTL Process

	ATR	POX	SMR
water consumption (lbmol/h)	36,300	4725	239,919
power requirements (MW)	287	269	183
heating (MMBTU/h)	1589	1340	15,673
cooling (MMBTU/h)	8373	7629	12,785

is recycled to meet the feed requirements). The following reactions explain this point

 $CH_4 + H_2O \rightarrow CO + 3H_2$ steam reforming

 $CH_4 + CO_2 \rightarrow 2CO + 2H_2$ dry reforming

 $CO + H_2O \rightarrow CO_2 + H_2$ water-gas shift

 $CH_4 + H_2O \rightarrow CO + 3H_2$ global reaction

The global reaction in the steam–methane reformer is similar to the first reaction (steam reforming). This is translated into a bigger reformer size and higher heating requirements, but with no CO_2 emissions and a better feed ratio for the FT reactor.

The SMR case uses H_2 removal to adjust the H_2 :CO ratio to 2, but another alternative could be the use of a reverse water—gas shift reaction, which requires CO_2 to be fed to the reactor. Therefore, an extra unit is needed, along with a heating operation to reach the high temperature required in the reactor.

From the analysis of the three cases, one can see that steam reforming does not lose oxygen (it comes out with carbon monoxide, which is a product of interest), while oxygen is lost as water in POX due to the full combustion process. On the other hand, ATR has a double loss of oxygen as water and carbon dioxide because of the full combustion and the water gas shift reaction. The yield of methane to carbon monoxide is unaffected in POX reforming. Because the oxygen conversion to CO is limited by the number of available carbons in the feed, the additional oxygen comes out as water. From here and supported by the global reaction for the steam reforming case, the POX and SMR options offer better yields of methane to CO than the ATR process, where the yield is lower due to the amount of carbon lost as carbon dioxide.

Power Requirements. Table 3 gives a comparison of the water and power requirements for each technology. The cases based on POX and ATR require power to operate the NG and O₂ compressors, but the major requirements are related to the need for compressing oxygen as part of the air separation unit. Our calculations on the power requirements were developed from the information given in the Idaho report⁹ to separate a given amount of O₂. In the POX process, 76% of the amount of oxygen coming from the ASU unit is converted into CO, while in the ATR case 45% of the total amount of oxygen is converted into CO. Also, 40% is lost as water, and the rest in the production of CO_2 . This is due to the total oxidation and WGS reactions that take place in the ATR reactor. The result is that the POX and ATR processes show similar oxygen requirements, and therefore, the power requirements for both cases are also similar.

For the case based on SMR, power is needed to compress the CO_2 stream, as well as to raise the water pressure and the syngas pressure. Also considered was the power needed for the SMR reactor heating system for the air blower and for the flue gas extractor. Overall, the SMR option shows lower power requirements despite the need for an additional compressor to reach the FT conditions. The highest power requirement for this case is due to the CO_2 compressor.

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Water Usage. The GTL processes are now analyzed in terms of water consumption and their potential for water integration as a basis for a proper management of basic resources. The analysis was based on a direct recycle of water sources to water sinks to establish targets for minimum water consumption and minimum discharge.

Table 4 shows the points in the flowsheet where water is fed and produced or depleted before it is discharged after the separation units for each option, while Table 5 gives the water balance for each case. Some differences in the water balances reported in Table 5 are observed, and they are due to losses in items such as tail gas, stipper, and CO₂ recovery streams. It can be noted how SMR is the most intensive process in terms of water consumption and water discharge. The amount of output water is lower than the amount fed because water reacts in the reformer in higher amount than its production in the FT reactor. At the same time, ATR has the highest water output because the water fed is added to the amount produced by reaction. The net generation of water is about the same for the ATR and POX cases, but the latter shows lower potential for water recovery. The net water consumption of the autothermal reformer is lower than the water requirements for the watergas shift reactor of the POX alternative. The FT reactor generates the same amount of water for the three cases. SMR requires more water for CO₂ cleaning, which contributes to make the most intensive option in terms of water requirements.

GTL flowsheets could be viewed as water-producing processes because the production of water is higher than that of the main product. Table 6 shows a comparison of the amount of water produced in relation to the liquid product, as well as the consumption of water for each barrel of liquid product. It can be observed that even when the SMR process produces more than five times water with respect to the liquid product, it consumes more water than the amount it produces. As for the other two options, the POX process produces 10 times more water than the amount it consumes, while the ATR process produces twice the amount of water it requires for its operation.

If a direct recycle is considered (assuming that all water fed can be recovered from the output water), the results given in Table 7 for minimum fresh water consumption and amount of water disposal are obtained. The options based on ATR and POX would show no need for fresh water consumption, while the SMR-based process would have no water discharge. Also, a global process balance shows that both ATR- and POX-based technologies produce water. Table 8 shows an overall water balance and the result of implementing a direct recycle scheme for water integration for the three technologies. The GTL process using ATR as syngas synthesis technology has the highest potential (in terms of flow rates) to provide a water surplus that could be supplied to other processes, while the steam reformer option is an overall water-consuming process. If water recycling is implemented, ATR and POX present similar potentials for net water generation for the overall process.

The simple direct recycle analysis developed here does not consider the issues of pollutants that would need special treatment and that would affect the synthesis of a complete mass integration network. The issue of water recycling needs to be complemented by taking into account the water impurities of the potential sources and required purities or allowed impurities, so that graphical³¹ or mathematical programming approaches³² can be used to design more formal water integration networks. Water composition of FT synthesis on

cobalt catalyst at low temperatures consists of water-soluble oxygenated compounds. Table 9 shows a typical composition.¹⁹ The oxygenated compounds are mostly C5–C10, main alcohols are C1–C5, and carboxylic acid corresponds to C1–C5 carbons.²⁹ The amount of undesired compounds is low because the cobalt catalyst favors the paraffin generation, and the high chain growth probability promotes longer paraffin and minimizes the undesired light products.³ Simple treatment can be carried out to clean the water streams using distillation and anaerobic biological treatment; the effluent would be suitable for discharge into the environment or for reuse within the process.

Thermal Energy Requirements. Heating and cooling requirements were evaluated for each alternate process, and pinch technology was then used to establish targets for energy integration. A minimum approach temperature difference of 10 °F was assumed. The analysis is limited to the prediction of minimum utility requirements; therefore, no integration networks were designed at this stage of develpment. The targeting procedure can then be complemented with the synthesis of heat integration networks using the principles of pinch methodology³³ or the application of mathematical programming techniques.^{34,35}

If we take as a basis the GTL process using SMR, the reforming technology shows higher heating and cooling requirements than the alternate reforming schemes. A significant amount of heat is needed to keep the temperature in the reformer, produce steam from water, and preheat the inlet stream to the reformer. The high temperature (as well as high flow rate) from the reformer product stream could be used to produce high-pressure steam. The FT reactor also needs a high amount of cooling, which means that it could be used to produce steam, in this case medium-pressure steam.

The heating requirements by the ATR process are higher than those of the POX option. Even though heating the WGS reaction and preheating the inlet stream are needed in the POX alternative, the amount of steam required in the autothermal reformer of the ATR case is more significant. Also, ATR requires more cooling, even though the reformer outlet temperatures are very similar because the product flow rate coming from ATR is higher than the POX product stream. In both cases high-pressure steam can be generated using the reformer product stream, and middle-pressure steam can be obtained from the heat duty of the FT reactor. For the three cases, the heat duty required by the FT reaction is the same.

When energy integration was considered, it was found that for the ATR and POX cases the reformer product stream and the FT reactor are sufficient to satisfy the heating requirements. The reformer product stream still shows some heat excess; such an amount could be shared with other processes or used to generate steam.

Figures 4–6 show the results from the pinch analysis that provided the minimum heating and cooling requirements for each case. In the ATR and POX cases, the pinch point is located at the highest temperature, so that only cooling is required. This is a consequence of the high heat load and high temperature of the reformer product stream. Some detail on the process conditions that led to the pinch analysis for energy targeting of the three process flowheets is availabe in the Supporting Information.

The SMR case requires more heating than cooling. Even when all the heat from the hot stream is higher than that required from the cold streams, the amount that could be integrated is limited by thermodynamic feasibility. Heat is provided only from the reformer products and the FT reactor output.

Table 10 summarizes the original energy requirements for each case and the potential effect of energy integration. The utility consumption for the three cases can be significantly reduced through the implementation of energy integration techniques. The SMR process shows the lowest cooling requirements, but it is the only option with heating requirements; the amount of 6239 MMBTU/h needed for heating after integration reflects the endothermic operation of the reformer.

Some Points on Energy/Water Nexus. It can be observed that the alternative with the lowest energy consumption shows the highest water consumption. This is the consequence of the high power in a GTL process associated with the production of pure oxygen needed for the syngas synthesis. When syngas is produced by partial oxidation or in combination with steam reforming, the water consumption lowers but the power requirements for the production of pure O₂ increase. At the same time, the case with the highest water consumption presents the highest heating and cooling requirements. Heating is mostly due to the significant amount of water that needs to be processed in the vapor phase for syngas generation, as well as to the energy required for the endothermic reaction of methane and water. Cooling utilities are needed to cool the product stream from the reformer, which has a high flow rate because it contains a significant amount of excess water. Table 11 gives a summary of the major energy/water implications for each of the three GTL alternatives here considered.

CONCLUSIONS

An analysis of three gas-to-liquid technologies, partial oxidation (POX), steam-methane reforming (SMR) and autothermal reforming (AR) has been presented. On the basis of their reaction paths, feedstock requirements and some of their implications have been assessed. Targets for water and energy requirements for each technology have been calculated, and the potential effect of the implementation of process integration strategies on the usage of water and energy on the process has been assessed. An overall water analysis for the GTL technologies shows that the highest water consumption is due to its direct use as a reactant in the syngas production step. Also, this factor is translated into lower power requirements and higher need for energy from process utilities for the overall process. If process integration techniques are implemented, technologies based on ATR and POX show the best potential because they can become self-sufficient in both water and heat requirements.

ASSOCIATED CONTENT

S Supporting Information

Supporting Information regarding operating conditions for each GTL process and thermal data for the energy integration analysis has been prepared. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Funding from Mexico's Consejo Nacional de Ciencia y Tecnología (CONACyT) and Qatar National Research Fund (QNRF NPRP 4-1191-2-468) is gratefully acknowledged.

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