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ABSTRACT

The U.S. Department of Energy (DOE) is investigating employing CO₂-capture technologies combined with Texaco and Shell integrated gasification combined-cycle (IGCC) power systems that produce both merchant hydrogen and electricity. This represents a high efficiency strategy for using the coal-resource base while being sensitive to the current motivation to reduce greenhouse gas emissions. An oxygen-blown entrained gasifier served as the basis for the study. Comparisons of energy penalties, capital investment, and CO₂ emission reductions were based on the full-energy cycle including mining, coal transportation, coal preparation, gasification, gas treatment, power generation, infrastructure to transfer power or hydrogen to end users, and pipeline transport of CO₂ to sequestration. Technical aspects of H₂ pipelines and supercritical CO₂ pipelines, as well as issues relating to CO₂ sequestering in a variety of host reservoirs were considered. Results from process design and economic simulation of a Benchmark Steam-Methane-Reforming (SMR) system make it possible to test at what price the cost of methane makes coal-base hydrogen economical. An ASPEN model of SMR with heat integration is the basis for a review of performance issues related to natural gas feed composition, desulfurization pretreatment, reforming, gas conversion and purification. Sensitivity studies have been performed to examine the effects of changes in operating pressure, steam-to-carbon ratio, and the use of combustion air preheat. Other parameters that affect hydrogen production and fuel use are reformer reactor inlet and outlet temperatures, shift strategy, reactor temperatures, and PSA design and operation.

Steam-methane reforming model description

Overview

The steam-methane reforming (SMR) process is illustrated in Figure 1. The basic steps leading from the hydrocarbon feed, which we assume to be natural gas, to the high purity hydrogen product are: pretreatment of the raw feed, reforming to synthesis gas, conversion to a hydrogen-rich gas, and purification to hydrogen product specifications. This basic SMR process is supported by a process furnace, which provides heat to raise the gas temperature for the endothermic pretreatment and reforming processes. The furnace also provides heat to raise steam, which is used as a reagent in both reforming and gas conversion. Note that gas conversion, which is exothermic, also provides heat for raising steam. The furnace consumes natural gas as fuel and process gas, which is a residual from the hydrogen purification process.

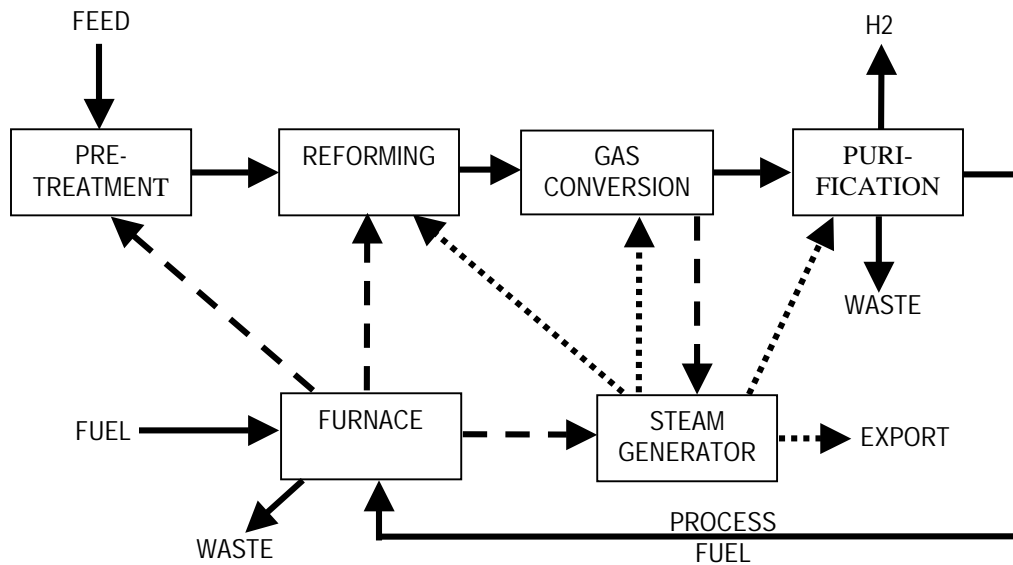


Figure 1, Schematic of SMR Process Showing Heat and Materials Integration

While it provides a highly simplified representation of the process, Figure 1 still illustrates the high level of heat and materials integration used in an SMR plant. Heat exchangers in the furnace flue gas stream heat the feed for pretreatment, pre-reforming, and reforming. The heat recovery steam generator extracts heat for feedwater heating, evaporation, and superheating from the furnace exhaust and from gas conditioning. Steam used as a reagent is partially recovered by condensation from the converted gas stream. A closed water system would clean this water stream and reuse it as boiler feedwater. Steam is also used as a heat source for the MDEA process, which removes CO₂ as a part of the purification process. Purification results in some waste, but also in the recycle process fuel stream. A trade-off in SMR plant design and operation is the distribution of natural gas consumption between feed and fuel. Optimization of plant operating parameters for high hydrogen production results in low process gas production and, consequently, greater fuel use.

Full representation of all these heat and materials interactions results in a model with multiple nested material and energy loops. Such multiple loops can be represented in ASPEN, but result in a model which is difficult to converge as parameters are varied to study the implications of process design choices. To

provide a robust model for sensitivity studies, we have created a simplified model by removing most of the heat exchangers and steam production from the full model. The thermodynamic integrity of the simplified model is assured by setting appropriate reactor temperatures and flow stream temperatures exogenously. Most of the model description below is based on this simplified model, which is represented in Figure 2.

Feed

Steam-methane reforming is commonly used on natural gas or naphtha feedstocks, with the later being an important source of hydrogen in refineries. We have assumed a natural gas feedstock. Natural gas is not a commodity with uniform composition, and the precise composition can have important implications for optimal plant design. Of particular importance is the presence of sulfur compounds, non-methane hydrocarbons, and hydrocarbon liquids. The simple assumption that natural gas is fairly represented as pure methane would not lead to an adequate plant design. We have included equipment to deal with a broad range of natural gas composition. Table 1 provides a representative range of natural gas composition as well as the baseline composition chosen for this analysis and a representative high nitrogen gas composition.

Table 1, Natural Gas Composition, mole %

Component	Normal Range	Baseline	High N ₂ Gas
Methane	87.0 - 96.0	94.9	86.4
Ethane	1.8 - 5.1	2.5	1.2
Propane	0.1 - 1.5	0.2	0.3
iso-Butane	0.01 - 0.3	0.03	0.1
n-Butane	0.01 - 0.3	0.03	0.1
iso-Pentane	trace - 0.14	0.01	
n-Pentane	trace - 0.04	0.01	
Hexanes and higher	trace - 0.06	0.01	0.1
Nitrogen	1.3 - 5.6	1.6	11.8
Carbon Dioxide	0.1 - 1.0	0.7	
Oxygen	0.01 - 0.1	0.02	
Hydrogen	trace - 0.02	0.00	
Mercaptan	4.9 mg/m ³	4.9 mg/m ³	
Water	16 - 32 mg/m ³		
Hydrogen Sulfide	4 ppmv		
HHV, dry, MJ/m ³	36.0 - 40.2		

Sources: Normal Range - Union Gas Limited 2000 - 2002,

<http://www.uniongas.com/NaturalGasInfo/AboutNaturalGas/composition.asp>, accessed 11/5/2002.

Baseline - Union Gas Limited

High N₂ Case - Patel, Nitin M., et al, "'Across the Fence' Hydrogen Plant Starts up at California Refinery", Oil and Gas Journal, October 3, 1994, pp. 54 - 61.

ASPEN ISSUES: Components

All expected components in the feed as well as all reaction products must be included in the ASPEN components inventory. Components other than those in the feed as listed above are CO and AR. We have relied on ASPEN built-in physical properties. Since these were not available for iso-propane, we have assumed that all propane will be n-propane.

We have assumed that the feed and the fuel composition are the same, i.e., the fuel is natural gas of the same composition as the feed.

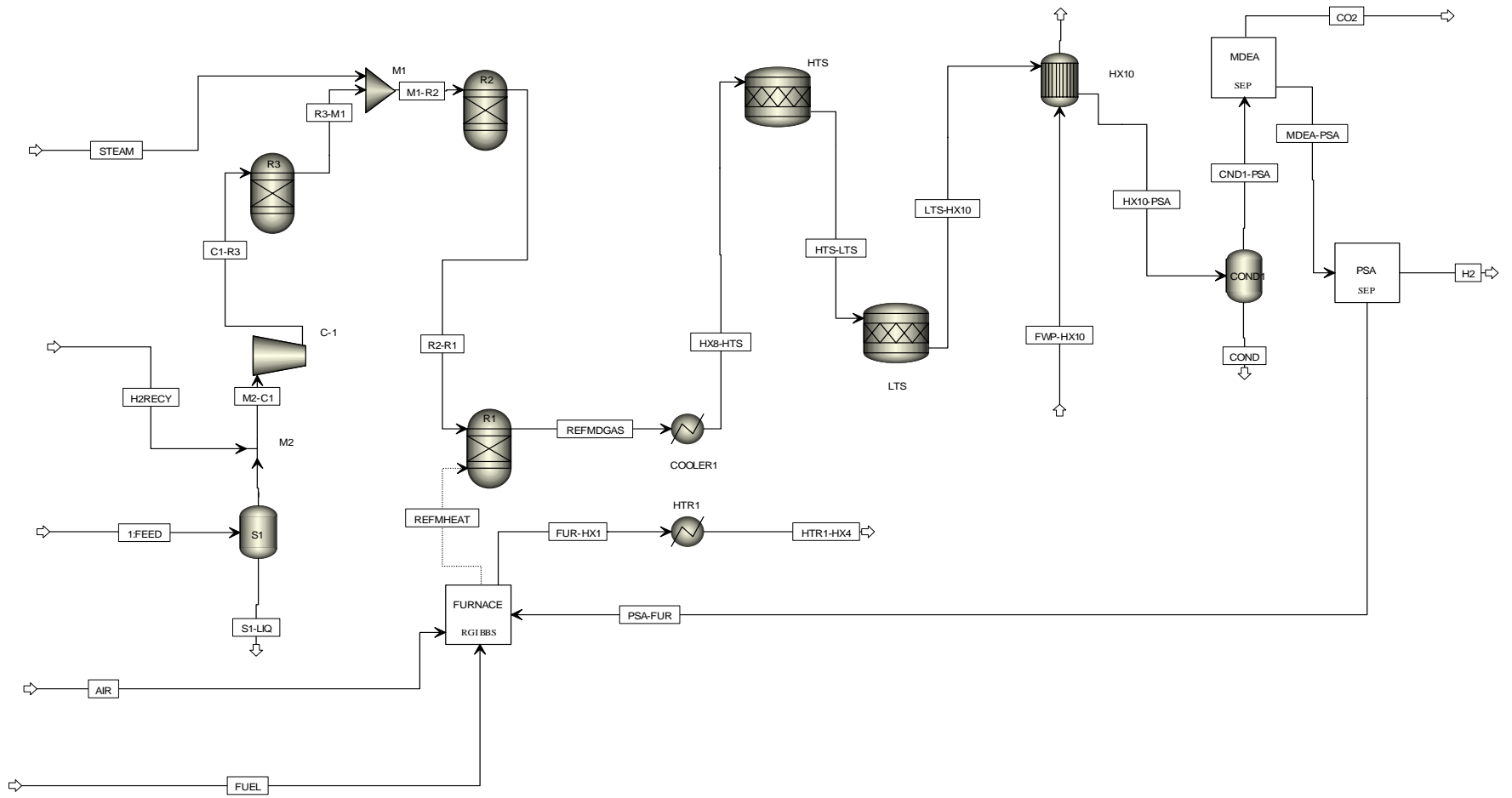


Figure 2, Schematic of ASPEN Model Without Heat Exchange Network

Pretreatment

Reformer limitations dictate minimum quality requirements (composition standards) for the natural gas feed. First, reforming is a catalytic operation, and the catalysts employed are poisoned by even trace amounts of sulfur. Hence, for economical operation, sulfur compounds are removed by pretreatment. Second, reforming is a reaction between methane and steam, so non-methane hydrocarbons must be converted to methane. The elements of the pretreatment system are shown in Figure 3. The feed is first introduced to a flash drum, S1, where liquid phase components are removed. Under the operating conditions expected in our analysis, no liquid phase exists in the feed stream. However, the flash drum is included to allow for other feed specifications. Hydrogen, which is recycled from a hydrogen rich process stream (after CO₂ separation by MDEA but before final purification by PSA) is introduced to the gaseous feed for use in downstream hydrogenation processes. In reactor R3, organic sulfur compounds are hydrogenated, releasing their sulfur as H₂S. While not shown in the figure, H₂S is adsorbed in a zinc oxide bed and reacts to form zinc sulfide, which is removed as a solid waste. In practice, a single reactor vessel can include the catalyst bed for sulfur conversion and the adsorbent ZnO. For high or variable sulfur loadings, more complicated systems using separate reactors for conversion and adsorption are used, or two conversion and adsorption vessels are used in series.

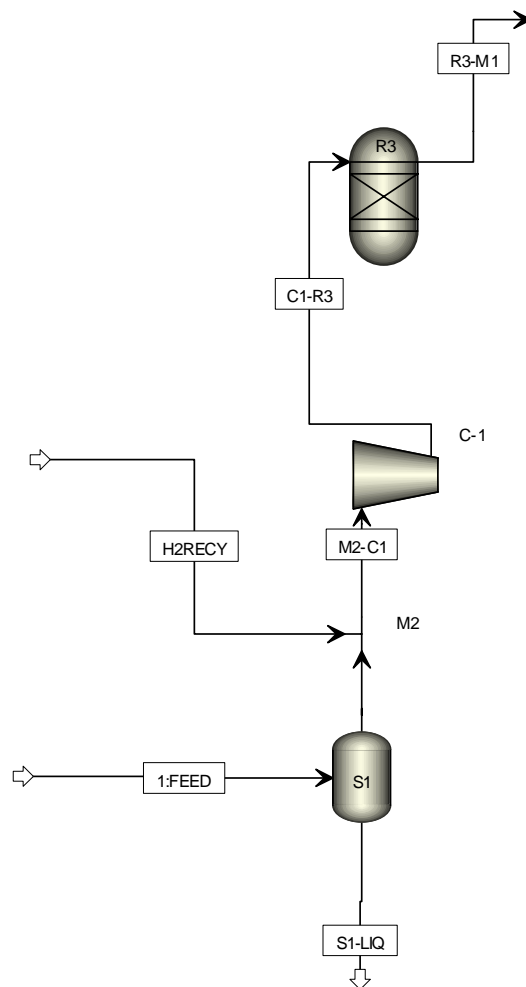


Figure 3, Pretreatment System

A recent Foster Wheeler-designed SMR plant used a desulfurizer temperature of 750F, though they report that a typical temperature for desulfurization is 700F¹. The higher temperature is seen as giving a safety margin to assure complete sulfur removal. Syntex reports that typical operating conditions for feedstock hydrogenation are 500 to 800F (260 to 430C) and up to 50 bar (725 psi)². Baseline operating conditions for this section of the flowsheet are summarized in Table 2.

Table 2, Operating Parameters for Pretreatment Equipment

Flowsheet Element	Parameter	Baseline
Feed stream	Temperature	70 F
	Pressure	20 bar
Flash tank	Temperature	70 F
	Pressure drop	-0.5 PSI
H2 recycle stream	Temperature	100 F
	Pressure	20 bar
	Flow rate	Set by design specification to assure 2% H2 in the reagent stream ³
Compressor	Outlet Pressure	30 bar
	Isentropic efficiency	0.72
Desulfurizer	Temperature	650 F
	Pressure drop	-25 psi
	Effectiveness	The reactor is assumed to achieve equilibrium concentrations. ⁴

The heat exchange network is not included in Figures 1 and 2. Natural gas feed is heated by compression and then by heat exchange with flue gas from the reformer furnace. In the full model with the heat transfer network, the temperature of the inlet stream is fixed at the desired reactor inlet temperature. Sufficient energy is drawn from the flue gas stream to achieve this temperature. The endothermic reactions then result in a slightly lower reactor exit temperature. In the simplified model discussed here, the reactor temperature is fixed and the equilibrium gas mixture is calculated based on that temperature. The heat duty for the reactor is calculated based on the heats of reaction and the sensible heat difference between the inputs and the products. This heat duty is the energy to be supplied by heat exchange with the flue gas.

¹ (Fleshman, James, et al, "New Hydrogen Plant Design Achieves Low Cost and High Efficiency", [wysiwyg://115/http://www.fwc.com/publications/tech_papers/oil_gas/am99_07.cfm](http://www.fwc.com/publications/tech_papers/oil_gas/am99_07.cfm), accessed 3/08/02.)

² "Syntex Purification Catalysts", ICI Group 518W/029/1/PUR, report accessed through the Syntex web site.

³ The Foster Wheeler plant referred to in footnote 1 does not use a hydrogen recycle stream or a hydrogenation reactor because the gas only contains light sulfur compounds. We assume that this is an unusual circumstance and that our feed requires hydrogenation for removal of mercaptans.

⁴ In an actual plant design, reactor parameters would be given a safety factor to assure a close approach to equilibrium. This can be achieved with excess catalyst and temperature adjustment.

Reforming

The steam-methane reforming reaction is: $\text{H}_2\text{O} + \text{CH}_4 \rightarrow \text{CO} + 3\text{H}_2$. This is a highly endothermic reaction which is supported by heat from the reformer furnace. This support is direct, through the heating of the catalyst-filled tubes that form the reactor, and indirect, through raising steam with a heat recovery steam generator. The reforming process is represented in the flow diagram section of Figure 4.

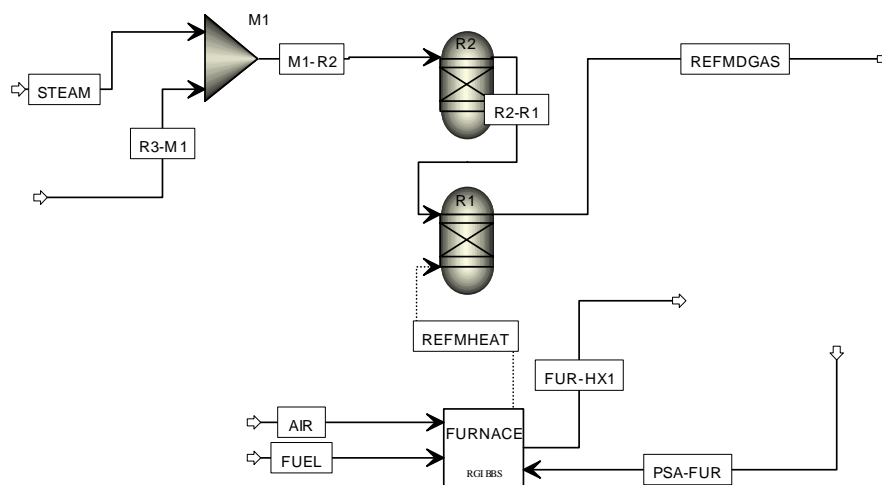


Figure 4, Pre-Reforming and Reforming with the Reforming Furnace

Gas from the desulfurizing reactor and ZnO beds, R3 in Figure 3, is mixed with steam at an appropriate temperature and pressure in mixer M1, which may be incorporated in the pre-reforming reactor, R2. A separate mixer is used for the ASPEN model to facilitate comparison of the reactor feed and product stream compositions. The reformer model incorporates three separate equilibrium reactors. The first is the pre-reformer, R2, which is used to break down higher hydrocarbons to methane. The second is the primary reformer, R1, which accomplishes most of the methane reforming, though some methane reforming will occur in the pre-reformer. The third equilibrium model represents the reformer furnace, which combines air, natural gas fuel, and process fuel (rejected at the PSA). Heat from the furnace is transferred to the primary reformer and, through cooling of the flue gas, to the pre-reformer, desulfurizer, and steam generator. The reforming reaction takes place at high temperature, so the flue gas leaving the primary reformer is still at a very high temperature and contains sufficient sensible heat to accomplish these duties as well as to provide some steam for export.

Before entering the pre-reformer the feed stream, M1-R2, is heated by heat exchange with the furnace flue gas. We assume a reactor temperature of 950F for the pre-reformer. This is consistent with a minimum temperature of 500C suggested by IEA⁵ and with an application example for Synertix pre-reforming catalyst⁶. The stream will experience some temperature drop in passing through the pre-reformer, consistent with the endothermic reactions taking place. A drop of about 125F has been reported on natural gas feedstock (Patel, 1994). Synertix provides an example with a temperature drop of 175F. ASPEN results are consistent with this range of values. The pre-reformed gas stream is then reheated to about 1200F by heat exchange with the reformer furnace flue gas. It is then introduced to the primary reformer, R1, which operates above 1500F by direct heat exchange with the integral furnace that surrounds the reactor tubes. Methane conversion is favored by higher temperature, but metallurgy limits the practical operating temperature. Baseline operating conditions for equipment in the reforming section are summarized in Table 3.

⁵ Precombustion Decarburization, IEA Greenhouse Gas Program, Report # PH2/19, p. 22.

⁶ "Pre and Post Reforming", <http://www.synertix.com/refineries/hydrogen-reforming.htm>, accessed 3/15/02.

Table 3, Operating Conditions for Reforming Section Equipment

Flowsheet Element	Parameter	Baseline
Steam feed	Temperature	950 F
	Pressure	30 bar
Desulfurized feed to pre-reformer	Temperature	950 F
	Pressure	28.5 bar
Pre-reformer	Temperature	950 F
	Pressure drop	25 psi
	Effectiveness	The reactor is assumed to achieve equilibrium concentrations.
Pre-reformed feed to primary reformer	Temperature	1200 F
	Pressure	27 bar
Reformer	Temperature	1500 F
	Pressure drop	25 psi
	Effectiveness	The reactor is assumed to achieve equilibrium concentrations.

Gas Conversion

The synthesis gas from the reformer is rich in H₂ and in CO. The shift reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$, can be used to increase the H₂ content. Equilibrium for this reaction favors the products at low reaction temperatures, but high temperature is required to achieve a practical reaction rate. This dilemma is normally addressed through the use of a two stage shift system. In the first stage, a high temperature is required, typically 350C (662F)⁷ reactor inlet temperature. The temperature will increase in the reactor due to the exothermic nature of the shift reaction. At this temperature, the reaction is promoted by a low cost iron-based catalyst and reduces the CO concentration to a few percent. In the second stage of shift, a lower temperature is used (190 - 210C or 374 - 410F)⁸ to increase the equilibrium concentration of H₂. A more expensive, copper-based catalyst is required to achieve equilibrium at a reasonable rate. These catalysts are sulfur intolerant and require operation above the gas dew point. Alternatives to the two stage shift might be preferred for some installations. These include a single-stage high temperature shift or a single-stage medium temperature shift. These options result in higher CO concentrations in the product gas. Figure 5 is a schematic of the shift conversion system from our simplified model.

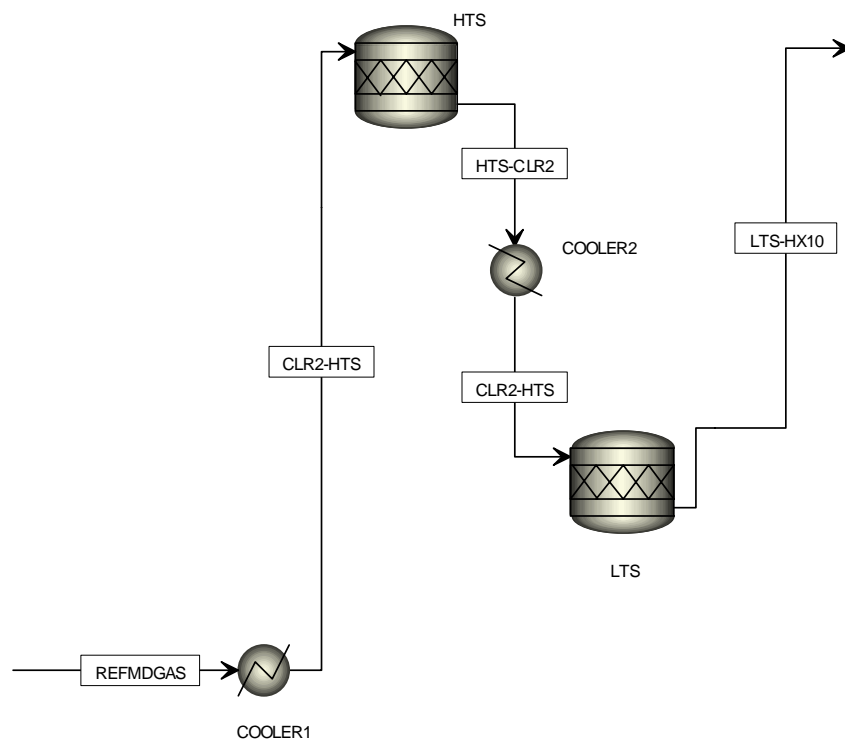


Figure 5, Two-Stage Shift Conversion System

Our ASPEN models use fixed conversion efficiencies to represent the shift reactors. Conservative vessel sizing and catalyst loading assure a close approach to equilibrium at the design operating temperatures. In an actual plant and in the full model with heat exchange, the two coolers exchange heat between the hot gases and the steam and feedwater heating systems. The reformed gas at the entrance to cooler1 is available at a very high temperature. In coal gasification power plants using a shift to produce hydrogen for use in a combustion turbine, the best application of this thermal energy would include fuel gas preheating. In subsequent studies, we will use these models to investigate alternative heat exchange networks to find the optimal use for available process heat. Table 4 is a summary of operating conditions.

⁷ "Steam Reforming", <http://www.synetix.com/refineries/hydrogen-steamreforming.htm>, accessed 3/15/02.

⁸ *ibid*

Table 4, Operating Conditions for Conversion Section Equipment

Flowsheet Element	Parameter	Baseline
Reformed gas	Temperature	1500 F
	Pressure	19.5 bar
Cooled gas feed to high temperature shift	Temperature	662 F
	Pressure	19 bar
High temperature shift	Outlet Temperature	802 F
	Pressure drop	15 psi
	Effectiveness	The reactor is assumed to achieve 90% CO conversion.
Cooled feed to low temperature shift	Temperature	400 F
	Pressure	18 bar
Low temperature shift	Outlet Temperature	415 F
	Pressure drop	15 psi
	Effectiveness	The reactor is assumed to achieve 90% CO conversion.
Shifted gas to purification	Temperature	415
	Pressure	17

Purification

The shifted synthesis gas has a high concentration of H_2 , but it also includes a high concentration of CO_2 and H_2O , as well as residual methane and small amounts of carbon monoxide and nitrogen. To produce a high quality hydrogen product as required for fuel cell applications, the gas is purified by removal of CO_2 in an MDEA process, removal of moisture by condensation and drying, and removal of other contaminants in a PSA (pressure swing adsorption) unit. These processes are complicated, requiring a complex model of their own for complete representation. Because our focus is the gas composition and the internal workings of the SMR process steps, we have represented these purification steps as simple separation processes, set to achieve design performance goals. The simplified model is represented in Figure 6. Operating parameters are listed in Table 5.

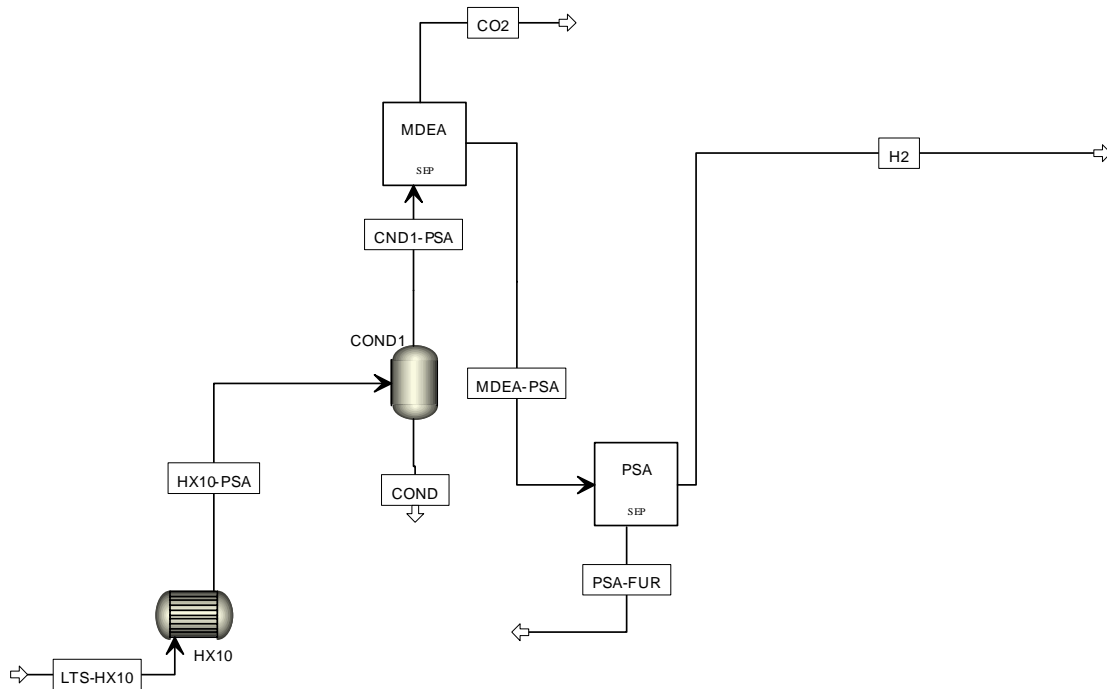


Figure 6, Purification System

The hot, hydrogen rich stream from the low temperature shift is cooled against a feedwater stream in HX10, resulting in a stream temperature as low as practical given the feedwater flow rate. Our full model with heat exchange suggests that a temperature of about 200F may be achieved. Further cooling to 100F may be accomplished with quenching in the condenser. Condensate is sent to water treatment. The cooled gas is treated in an MDEA chemical absorption system for removal of CO_2 . A removal efficiency of 95% is practical. Glycol drying of the CO_2 is necessary if the CO_2 byproduct is to be condensed, compressed, and transported to a sequestration site. The highly concentrated hydrogen stream from the MDEA is treated in the PSA unit to achieve hydrogen purity of up to 99.999%. The PSA waste gas stream includes unrecovered hydrogen, CH_4 , CO , and other contaminants. This stream is valuable as a process fuel and is used in the reformer furnace to reduce the overall system fuel requirement.

Table 5, Purification Section Operating Parameters

Flowsheet Element	Parameter	Baseline
H2-rich gas from low temperature shift	Temperature	415 F
	Pressure	17 bar
Cooled gas from feedwater heater	Outlet temperature	200 F
	Pressure	16.5 bar
Condenser, quench	Temperature	100 F
	Pressure drop	5 psi
MDEA	Temperature	100
	Pressure	16 bar
	CO ₂ recovery	95%
PSA	H2 Recovery	90%
	Contaminants in H2 product stream	Assumed to be 0.001% of product stream
	Fuel gas composition	calculated

Model Results

Selected stream compositions for the baseline case are presented in Table 6. Descriptive titles have been chosen for the streams rather than names from the model nomenclature. The following observations relate to this data:

1. The NG feed is virtually hydrogen-free. The hydrogen content increases following the desulfurizer, reflecting the addition of recycle H_2 according to the design specification that it should be 2% of the feed stream to the desulfurization reactor to assure complete hydrogenation of sulfur compounds. H_2S is formed in the desulfurizer as expected, but it is not shown in the desulfurized stream because it has been removed in ZnO beds.
2. The desulfurizer also reduces hydrocarbons to methane, consuming H_2 in the process. This is expected in the prereformer, but occurs here because the desulfurizer is represented as an equilibrium reactor. The use of catalysts that favor the conversion of sulfur compounds, but are less effective in promoting the conversion of other organic compounds is not recognized by an equilibrium reactor. In the next update of the model, we will change the reactor specification to REQUIL, which allows the specification of selected reactions that are expected to achieve equilibrium.
3. Further reduction of non-methane hydrocarbons occurs in the pre-reformer along with some methane reforming. The presence of the steam, which is introduced prior to this stage, is evident in the high H_2O flow in the pre-reformed gas.
4. The reformed gas composition shows that substantial reforming has been accomplished at the higher temperature extant in the primary reformer. Under baseline conditions, nearly 75% of the methane in the desulfurized stream has been converted. Correspondingly, a significant concentration of CO is now evident.
5. The reduction of CO in the high temperature shift is 90%, consistent with the specification in the RSTOIC reactor used to represent the shift. For both the high and low temperature shifts the reactor will be changed to REQUIL in the next update. The increase in hydrogen corresponds to the reduction in CO.
6. A further 90% reduction in CO is accomplished in the low temperature shift. A corresponding increase in H_2 is accomplished.
7. Ninety percent of the hydrogen in the PSA input is recovered as product. We do not have precise correlations, but the recovery percentage is reduced as higher purity hydrogen is recovered. The high pressure of the product stream and the low pressure of the waste fuel stream reflects the nature of PSA operations.
8. The process fuel stream from the PSA includes substantial methane and hydrogen. The assumed separation efficiency for hydrogen will have little effect on the mass flow rate or caloric value of this stream. This is mainly a function of other process variables as discussed below.

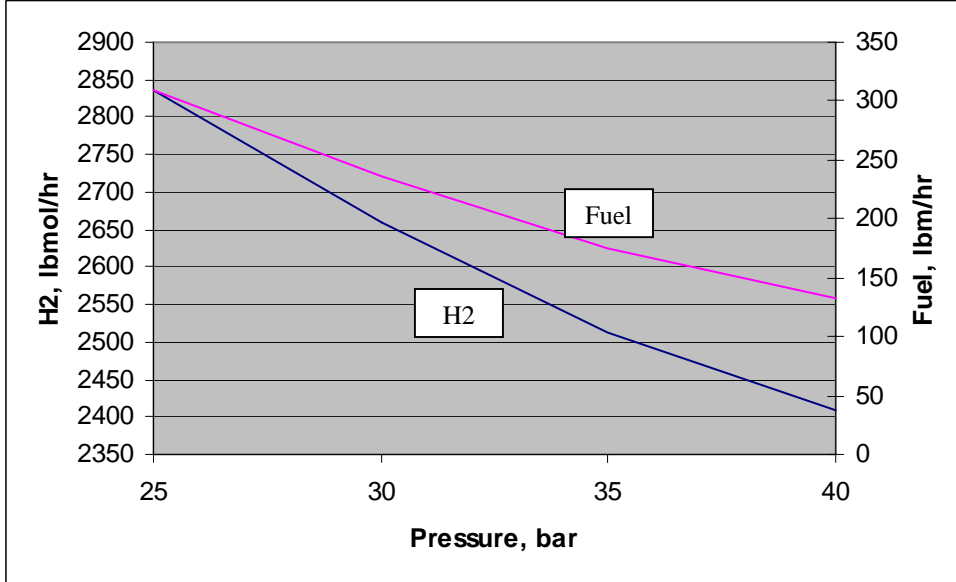
Sensitivity studies have been performed to examine the effects of changes in operating pressure, steam-to-carbon ratio, and the use of combustion air preheat. Other parameters that affect hydrogen production and fuel use are reformer reactor inlet and outlet temperatures, shift strategy and temperatures, and PSA design and operation.

Higher pressure operation is favored because of reduced equipment size. However, higher pressure favors the reactants in the reforming reaction, because four moles of product are formed for each two moles of reactant. This means that less hydrogen is formed at higher pressures. Offsetting this is availability of more methane in the PSA waste fuel gas. This reduces the demand for fuel as an input. The reduced fuel demand and reduced hydrogen production are illustrated by model predictions shown in Figure 7. The pressure is that immediately following the feed compression.

Table 6, Composition of Principal Streams for the Baseline Case

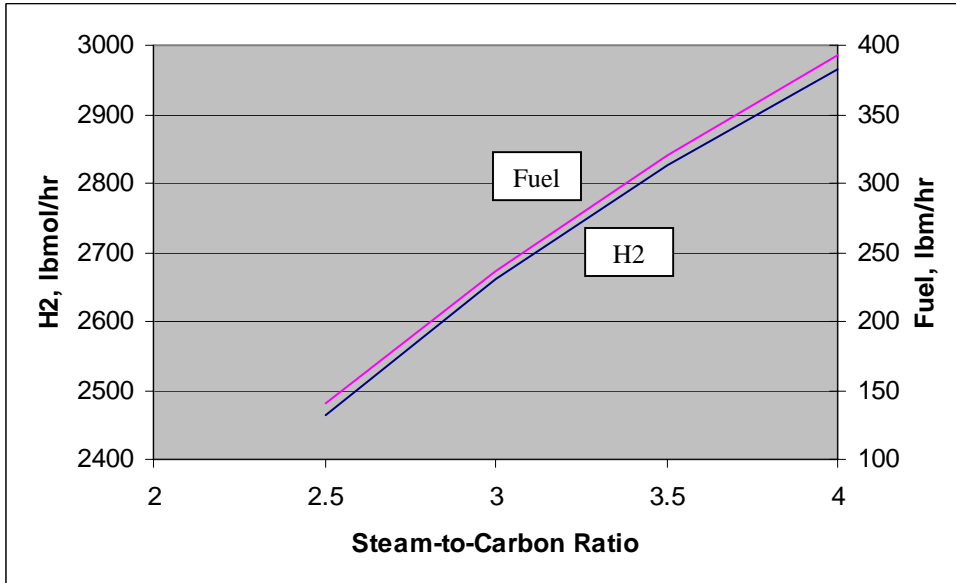
	NG Feed	Desulfurized	Prereformed	Reformed	HT Shift	LT Shift	PSA IN	PSA Fuel	PSA H2
Mole Flow lbmol/hr									
CO	0.000	0.457	0.952	413.301	41.330	4.133	4.133	4.135	0.000
CO2	7.000	4.047	76.955	329.034	701.005	738.202	36.907	36.917	0.000
H2	0.050	8.567	301.418	2546.779	2918.750	2955.947	2955.943	295.677	2660.349
H2O	0.000	5.850	2895.047	1978.539	1606.568	1569.371	16.895	16.899	0.000
CH4	948.500	1011.836	938.964	274.543	274.543	274.543	274.541	274.334	0.000
O2	0.200	0.00E+00	2.24E-27	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
N2	16.000	16.000	16.000	16.000	16.000	16.000	16.000	16.000	0.000
AR	0.000	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
CH4O	0.000	4.00E-07	1.89E-05	5.46E-04	5.46E-04	5.46E-04	1.04E-04	1.04E-04	0.00E+00
C2H6	25.000	2.79E-01	1.47E-02	1.10E-02	1.10E-02	1.10E-02	1.10E-02	1.10E-02	0.00E+00
C3H8	2.000	5.66E-04	1.51E-06	1.62E-06	1.62E-06	1.62E-06	1.62E-06	1.62E-06	0.00E+00
ISOBUTE	0.300	9.38E-07	1.15E-10	1.08E-10	1.08E-10	1.08E-10	1.08E-10	1.08E-10	0.00E+00
N-BUT-01	0.300	1.09E-06	1.47E-10	2.34E-10	2.34E-10	2.34E-10	2.34E-10	2.34E-10	0.00E+00
N-PEN-01	0.200	1.83E-09	1.26E-14	2.86E-14	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
N-HEX-01	0.100	0.00E+00	9.36E-19	3.15E-18	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
TERT--01	0.350	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
H2S	0.000	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Total Flow lbmol/hr	1000	1047	4229	5558	5558	5558	3304	644	2660
Total Flow lb/hr	16909	17003	71688	71688	71688	71688	12856	7491	5363
Total Flow cuft/hr	18668	33333	151623	335067	229907	172638	98213	18557	79211
Temperature F	70	737	814	1500	791	413	100	100	100
Pressure psi	290	405	375	350	325	300	203	15	200

Figure 7, Sensitivity of Fuel Use and H₂ Production to Pressure



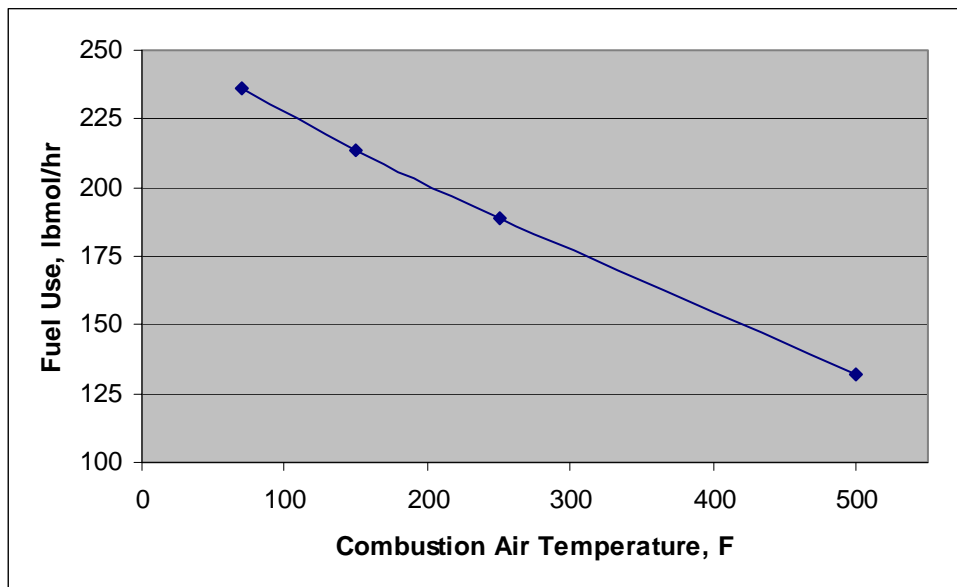
The steam-to-carbon ratio is the mole ratio of steam to carbon in the feed to the reformer. This ratio will also affect both hydrogen production and fuel consumption. Hydrogen production is increased because the higher steam concentration will favor the product hydrogen in both the reforming and shift reactions. However, this benefit is achieved at the cost of higher fuel consumption both to make the steam and to replace the waste fuel, which is less available as more hydrogen is produced. These effects are shown in the model results summarized in Figure 8.

Figure 8, Sensitivity of Fuel Use and H₂ Production to Steam-to-Carbon Ratio



An important strategy for reducing fuel consumption is to preheat the combustion air against the exiting furnace flue gas. Figure 9 shows the predicted fuel consumption as a function of combustion air temperature. This benefit must be traded against the necessary capital investment and other possible applications for the sensible heat in the flue gas.

Figure 9, Sensitivity of Fuel Use to Combustion Air Temperature



Since this model of SMR was developed as a baseline for comparison against the performance of coal-based H₂ production with CO₂ sequestration, the rate of production and fate of CO₂ from the SMR process is of particular interest. In the coal case, virtually all of the carbon in the feed coal is present in the synthesis gas and is available for capture by the CO₂ recovery systems. In the SMR case, a furnace produces CO₂ separate from the process gas stream. This CO₂ is diluted by nitrogen from the combustion air and is, therefore, not readily captured. The balance of the CO₂ is captured from the process gas stream during the H₂ purification process. We have applied our SMR model to clarify how operating parameters affect the total CO₂, captured CO₂, and exhausted CO₂. The results are summarized in Figures 10, 11, and 12. As shown in these figures, only about one half of the CO₂ produced is available for capture and sequestration. Use of O₂ firing of the furnace would improve the situation, and might be a useful retrofit strategy. However, new plants using oxygen would probably employ partial oxidation not SMR.

Figure 10, Sensitivity of CO₂ Production to Operating Pressure

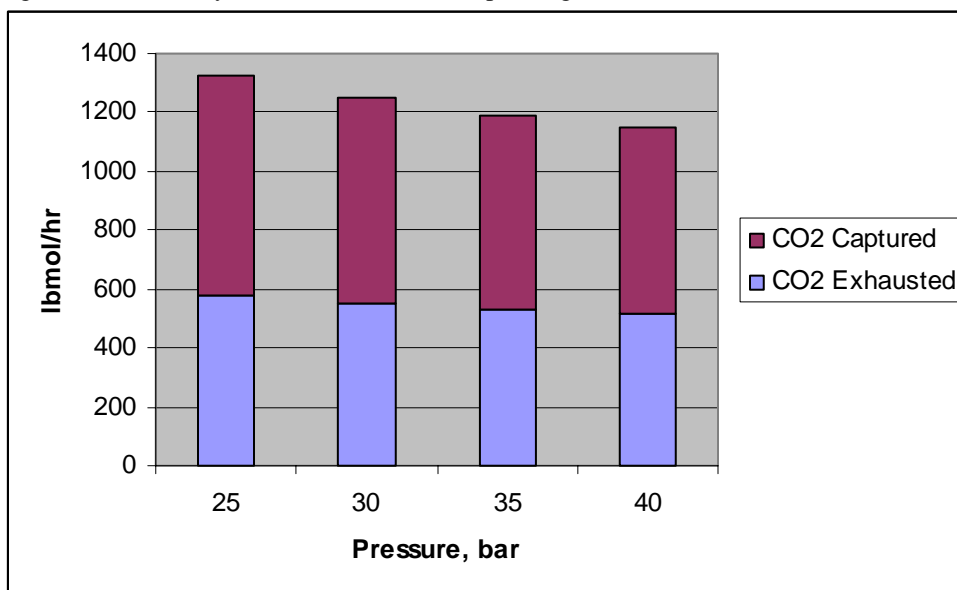


Figure 10 shows a decline in total CO₂ produced. This is consistent with the fact that the higher pressure reduces the concentration of products from the reforming reaction. Hence, less CO₂ is produced, as-well-as less H₂. The methane that is not reformed is available for use in the furnace, thus reducing the fuel demand. However, this does not reduce net CO₂ emissions from the furnace, shown here as CO₂ Exhausted. That reduction is achieved because the reforming reactor heat demand is reduced as less reforming is accomplished.

Figure 11 shows the sensitivity of CO₂ production to changes in the steam-to-carbon ratio. In this case, both the captured and exhausted CO₂ increase substantially as the ratio is increased. This is consistent with the increase in fuel use and in hydrogen production shown in Figure 8. Any increase in H₂ production is accompanied by an increase in CO₂, which is formed in the shift reactor from CO produced in the reformer. This increase in CO₂ emissions combined with the increase in fuel use might discourage operation at high steam-to-carbon ratios. On the other hand, high H₂ output may be justified to maximize the use of capital. A model such as this would have critical input to an economic analysis of policies such as carbon emission taxes.

Figure 11, Sensitivity of CO₂ Production to Steam-to-Carbon Ratio

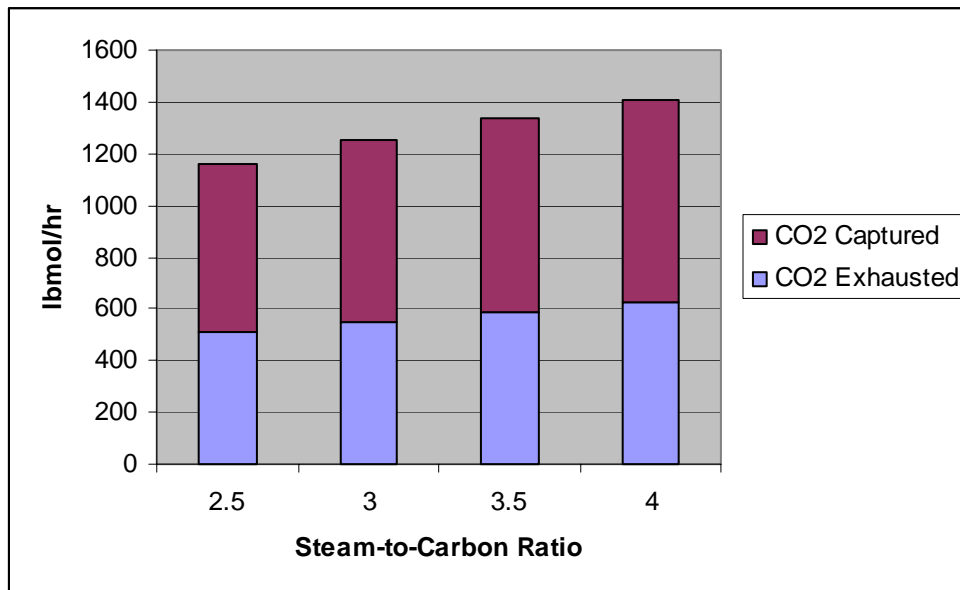
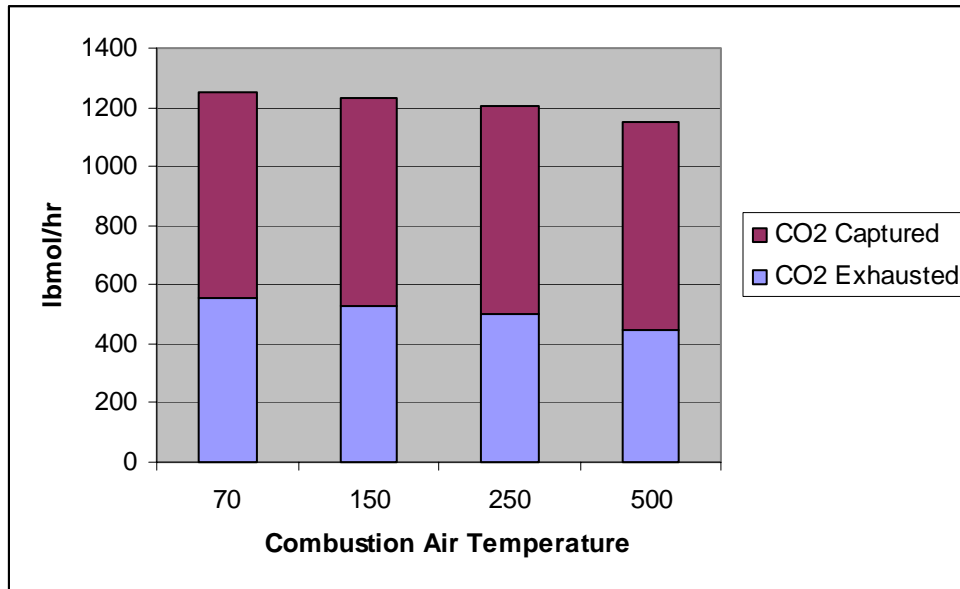


Figure 12 shows a substantial decline in CO₂ exhausted as the combustion air temperature is increased. This is expected as combustion air preheat naturally reduces the fuel demand of the reforming furnace. The affect on captured CO₂ is insignificant. The more likely trade-off would be between air preheat and the production of steam for export. Our full, integrated model will be applied to this analysis when it is completed.



Steam-methane-reforming with heat integration

We have developed an ASPEN model of SMR with many of the heat integration opportunities represented. The ASPEN process diagram for this model is appended. The observations made here regarding updating reactor representations apply to this full model. In addition, at this time, the full model does not reliably converge to a solution although a converged case is represented. The case shown in the process diagram is a converged case, but some of the operating parameters are not consistent with known operating practice. The model fails to converge when these values are adjusted. We feel that this model is close to working, but have set it aside in favor of the simpler model discussed above. We will resume development of this model as future project resources permit. Until then, the model without heat integration will be used to study SMR as the baseline for commercial hydrogen production. Most of the issues of heat integration can be addressed by the use of heaters and coolers, as the simpler model demonstrates. Further, when the "equation-oriented" strategy now being introduced into ASPEN is extended to complex heat exchanger networks, the convergence problems should be eliminated. The diagram of the ASPEN system with the full heat exchanger network and the full heat and material balance are presented.

Further Model Development

The observations made here regarding updating reactor representations applies to this full model. In addition, at this time, the full model does not reliably converge to a solution. The case shown in the process diagram is a converged case, but some of the operating parameters are not consistent with known operating practice. The model fails to converge when these values are adjusted. We feel that this model is close to working, but have set it aside in favor of the simpler model discussed above. We will resume development of this model as future project resources permit. Until then, the model without heat integration will be used to study SMR as the baseline for commercial hydrogen production. Most of the issues of heat integration can be addressed by the use of heaters and coolers, as the simpler model demonstrates. Further, when the "equation-oriented" strategy now being introduced into ASPEN is extended to complex heat exchanger networks, the convergence problems should be eliminated.

This model better represents the complexity of heat transfer in the SMR plant, and would be useful for the analysis of tradeoffs such as export steam vs. air preheating, optimum steam-to-carbon ratio and other issues related to the optimal application of process heat. In addition, the full model is essential as the basis of a cost analysis for economic optimization of the plant. This is important for policy studies involving CO₂ taxes, variations in costs with fuel quality, and other analysis affected by the tradeoff of capital and operating costs.

The simple model should be an excellent basis for further development and optimization of the heat transfer network. Since the simple model provides a complete set of heat duties and temperatures for heat sources and heat consumers, it provides the basic information needed for pinch analysis. These are a few of the ways in which the SMR modeling activity started here can be extended to:

- quantify the carbon emission implications of H₂ production from SMR and alternative technologies.
- evaluate the technical and environmental implications of alternatives in process design and operations.
- assess the potential effectiveness of CO₂ control policies and strategies as compared against a Steam-methane-reforming technology
- clarify the potential emission benefits of operational changes or retrofits to existing SMR plants.

The development of the model for this purpose would permit us to improve the assessment of when coal gasification for hydrogen production will become economical.

Economic Assessment of Steam-Methane Reforming

At present, steam-methane reforming dominates the market for hydrogen production and to assess the economics of hydrogen production as currently practiced, a top-down analysis was employed. Hence, even though the ASPEN modeling could be used for steam-methane reforming equipment sizing and determination of capital and operating costs, published data about contracted costs for “turn-key” systems was employed. The ASPEN simulation was then used to fill in the details about issues of unit operations which were not disclosed in the reports.

For a typical facility providing 50-million scf/d (120,500 kg/d) of hydrogen, the Direct Capital Cost comes to \$30 million.⁹ When installation is complete and inventories of catalysts and solvents are purchased, this maps into a Total Plant Investment of \$82 million. An availability of 95% may be anticipated from this facility, which will operate with an efficiency of 78% LHV, or 84% HHV.¹⁰ Operating costs, utilities and catalyst replacement costs are available in the literature and have been adopted here.^{11,12,13} The SMR facility will export steam at a modest price to offset operating costs.

Using a current natural gas price of \$2.85/MM Btu, cost for the production of H₂ comes to \$0.83/kg [the basis for these figures is shown on the following page.] Purchase of natural gas account for 55% of this price, capital equipment charges are 28%, and operating and maintenance accounts for 17% of costs. At the current facilities 1366 tons CO₂/d is emitted to the atmosphere.

⁹ Meyers, Robert, Handbook of Petroleum Refining Processes, (2nd Ed.), McGraw-Hill, 1997, p. 6.50

¹⁰ Patel, Nitan (Air-Products), et al., “Across the Fence Hydrogen Plant Starts up at California Refinery,” Oil & Gas J., Oct. 3, 1994, p.54

¹¹ Bassett, L.C., “Hydrogen - Buy it or Make it?,” Chemical Engineering Progress, March 1980, p. 93

¹² Probst, Ronald and Harris Gold, “Water in Synthetic Fuel Production,” MIT Press, 1978, p. 224

¹³ AlKabbani, A.S., “Reforming Catalyst Optimization,” Hydrocarbon Processing, July 1999, p.61

Steam-Methane Reforming with CO₂ Capture Costs

While the natural gas gets split between reagent feed and fuel use for the furnace, because of the PSA blow-down serving as a feed to the furnace, there actually is a significant emission of CO₂ at low pressure (44%) as well as at high pressure. The capture costs of this low pressure CO₂ will exceed those of a typical stack emission because the feed to the furnace is high in H₂ fuel resulting in an 8% concentration of CO₂ in the stack gas at atmospheric pressure as compared to the typical 15% CO₂ in a furnace.

Earlier reported efforts on surveying cost-effective CO₂ recovery systems with the TransAlta Corporation and Initially, Fluor-Daniel (Greenville, SC) performed a design study for an monoethanolamine (MEA) scrubber to remove CO₂ from flue gas for a PC-fired boiler using low sulfur sub-bituminous coal. For these atmospheric systems, the capture and compression of CO₂ for delivery at the fence came to \$49.62/ton.¹⁴ In marked contrast, the capture and compression of the CO₂ from the MEA system in the SMR at high pressure should come to \$7/ton CO₂. Using a current natural gas price of \$2.85/MM Btu, costs for the production of H₂ with CO₂ capture comes to \$1.12/kg. This is an increase of 35%.

¹⁴ Doctor, Richard D., John C. Molburg, Norman F. Brockmeier, and Marshall Mendelsohn, "CO₂ Capture for PC-Boilers using Flue-Gas Recirculation: EVALUATION OF CO₂ RECOVERY, TRANSPORT, AND UTILIZATION," Carbon Sequestration Program Review Meeting, Pittsburgh, PA, Feb. 11-14, 2002.