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KRW OXYGEN-BLOWN GASIFICATION***

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ABSTRACT

An oxygen-blown KRW integrated gasification combined-cycle plant producing hydrogen, electricity, and supercritical- CO_2 , was studied in a full-energy cycle analysis extending from the coal mine to the final destination of the gaseous product streams. A location in the mid-western United States was chosen 160-km from Old Ben #26 mine which ships 3,866 tonnes/day of Illinois #6 coal by diesel locomotive. Three parallel gasifier trains, each capable of providing 42% of the plant's 413.5 MW nominal capacity use a combined total of 3,488 tonnes/day of 1/4" prepared coal. The plant produces a net 52 MW of power and $3.71 \times 10^6 \text{ nm}^3/\text{day}$ of 99.999% purity hydrogen which is sent 100 km by pipeline at 34 bars. The plant also produces $3.18 \times 10^6 \text{ nm}^3/\text{day}$ of supercritical CO_2 at 143 bars, which is sequestered in enhanced oil recovery operations 500 km away. A CO_2 emission rate of 1 kgCO_2/kWh was assumed for power purchases outside the fence of the IGCC plant.

INTRODUCTION

Oxygen-blown gasification is used to convert Illinois #6 coal to synthesis gas [Fig. 1]. After particulate removal, a shift reactor uses steam to convert the CO component of the gas to CO_2 and hydrogen (H_2). Next, H_2S is removed from the stream and processed to produce marketable sulfur. Carbon dioxide is then recovered in a glycol-based process and transported by pipeline for enhanced oil recovery. The gas stream after CO_2 recovery is processed using pressure-swing adsorption (PSA) to recover H_2 at a purity suitable for fuel cells, although there is no restriction on the actual hydrogen end-use. The H_2 stream is transported to end users via pipeline, while the residual gas from PSA—a combination of hydrogen, methane, and light hydrocarbons—is used to generate electricity by combustion turbine combined cycle. Part of the electricity generated supplies the internal needs of the plant, and the excess is sent to the grid.

MINING

The assumed power plant location is 100 mi (160 km) by diesel-rail transport from the Old Ben #26 underground mine in Sesser, Illinois. The plant receives 4,112 tons/day (155.4 metric tonnes/h) of 2 x 4-in. coal, which is prepared to 0 x 1/4-in. with 3.5% weight loss. A summary of this portion of the power cycle appears in Table 1.

INTEGRATED GASIFICATION COMBINED CYCLE CONVERSION

Previous process design studies to characterize integrated gasification combined-cycle (IGCC) power systems with CO_2 -capture technologies were modified using ASPEN[®] modeling to evaluate a configuration producing both merchant hydrogen and electricity [1,2,3,4,5]. The power plant configuration employs three parallel gasifier trains, each capable of providing 42% of the plant's 413.5 MW nominal capacity (for the base case with no CO_2 recovery.) After modification, the plant produces 131 MMscf/day (3.71 million standard cubic m/day) of 99.999% purity hydrogen at 287.7 Btu/scf; 119.9 KJ/g (LHV) which is sent 100 km by pipeline at 34 bars. At 100% efficiency, this could yield 460 MW of power. The plant also produces 112 MMscf/day (3.18 million standard cubic m/day) of supercritical- CO_2 at 143 bars, which is sent 500-km for sequestering in enhanced oil recovery. PSA reject gas goes to a turbine cycle to produce 118 MW. After supplying 66 MW for internal power use this yields 52 MW Net power. The designed plant availability is 95%. This is largely reflected in higher projected maintenance costs.

H_2 PIPELINE

A 100-km pipeline design was prepared and costs were estimated for a high purity hydrogen flow of $3.71 \times 10^6 \text{ nm}^3/\text{day}$ through a 343 mm pipe at 30 bar. There appears to be no economic justification for going to higher pipeline pressures and an internal study of the costs for delivering energy as methane vs. energy as H_2 showed a 13% advantage for methane at 500 psi rising to a 46% advantage at 800 psi. Economic assumptions were for an availability of 95% and capital recovery of 12% to yield transmission costs of 0.171 \$/Mscf; 0.564 \$/GJ. It is very important to observe that the high costs of a dedicated pipeline dictate the high availabilities.

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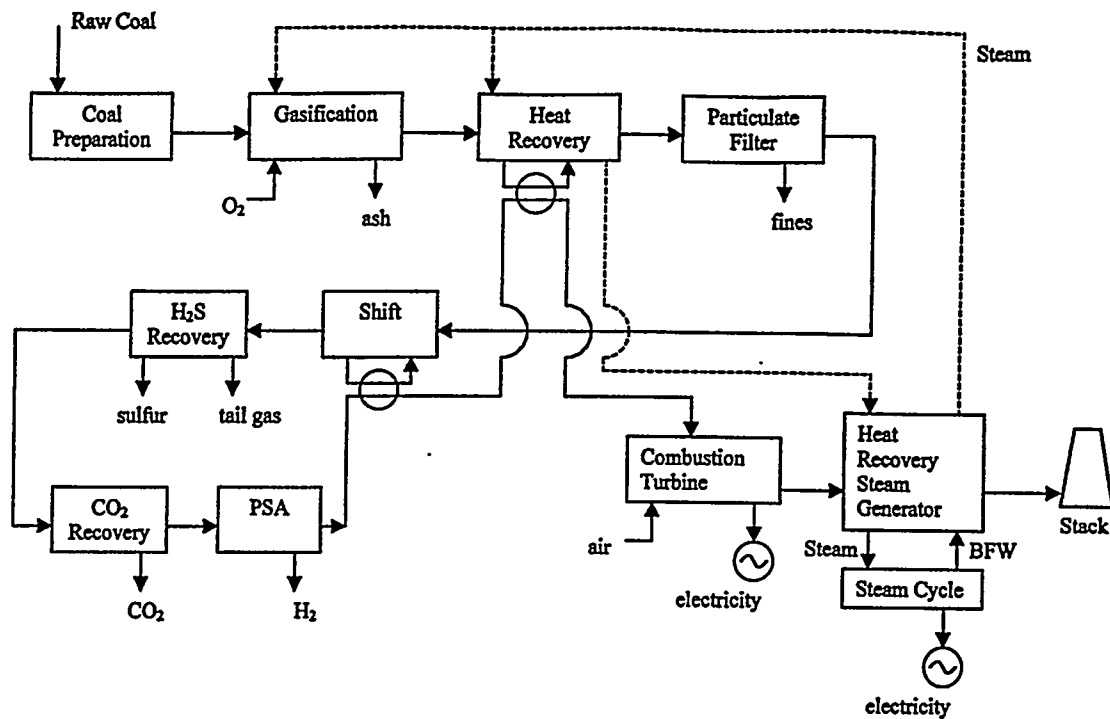


Fig. 1. Integrated Gasification Combined-Cycle Producing Electricity, CO₂ and H₂

Table 1. Energy Use in Coal Mining, Preparation, and Transportation

	Electricity metric units kWh/tonne	Diesel Fuel #2 tonne- km/liter	CO ₂ Emissions kg/tonne coal	Electricity MW	Losses %	Coal kg/h	CO ₂ kg/h
MINING (a)							
Methane emissions (b)			9.63		0.0%	178,981	1,724
Hoisting	6.12		6.12				
Drilling	2.03		2.03				
Ventilation	2.20		2.20				
Dewatering	2.67		2.67				
Break and convey	0.73		0.73				
Ancillary	0.46		0.46				
subtotal	14.21		14.21	2.54	0.0%	178,981	2,543
PREPARATION 2x4-in.	0.44		0.44	0.07	10.0%	161,083	71
TRANSPORT - 161 km							
Mine to IGCC by rail		135	3.27				
General service	0.98		0.98	0.15			
Return to mine		50	1.22				
General service	0.36		0.36	0.06			
subtotal			5.83	0.21	3.5%	155,445	905
PREPARATION 1/4-in. (c)	5.85				6.5%	145,341	

(a) Operations of 250 days/yr at 13 hr/day

(b) Methane emissions of 175 scf/ton counted only as conversion to CO₂ within a 14-yr life

(c) Accounted for in IGCC plant balance

CO₂ PIPELINE

Design and economic assumptions for a supercritical-CO₂ pipeline were compared against current plans for Dakota Gasification Company, Beulah, ND [6] and Shell estimates of CO₂ purchase costs at \$3.25/bbl of oil recovered [7] with a reasonable CO₂ utilization of 5.6 Mscf/bbl oil [8], which would come to a purchase price of about \$0.60/Mscf. Since, the 30-in. Shell Cortez line is unusually large – resulting in economies of scale – previously determined pipeline costs of \$0.77/Mscf CO₂ still appear reasonable.

RESULTS: FULL-ENERGY CYCLE BALANCES

The energy costs of delivering electricity 100-km from the IGCC plant are presented for three cases; the IGCC base case with no CO₂ recovery (Table 2); the IGCC system with CO₂ recovery (Table 3); the IGCC system developed for this study with H₂ production and CO₂ recovery (Table 4). For the Base-case with no CO₂ recovery; delivered power was 396-MW full-cycle with emissions of 0.83 kgCO₂/kWh. There is a derating with CO₂ recovery. Delivered power becomes 366-MW full-cycle at 0.20 kgCO₂/kWh. An additional derating takes place in the present case with both H₂ production and CO₂ recovery where the hydrogen goes to 3-stage solid-oxide fuel cells. The delivered power now becomes 344-MW full-cycle at 0.22 kgCO₂/kWh. This is the combination of 52-MW busbar at the plant and 298-MW from fuel cells and a steam generator topping cycle.

Table 2. KRW O₂-blown IGCC - Base Case
Basis: Electric power delivery 100 km from station

	nm ³ /d	tons/d	kg/h	Power MW	CO ₂ kg/h	CH ₄ kg/h	N ₂ O kg/h
MINING AND TRANSPORT							
Coal methane emissions						566	
Mining operations & preparation				-2.61	2,614		0.00003
Transport by rail - 161 km				-0.21	905		0.66265
a. Subtotal				-2.82	3,520	566	0.66267
POWER PLANT							
Coal preparation (0-in. x 1/4-in.)		3,845	145,341	-0.85			
O ₂ by cryogenic separation	8,937,000	2,347	88,717	-29.29			
Steam from heat recovery generator			17,254				
Gasifier island				-2.90			
Solid waste		492	18,598				
Sulfur		78	2,948	-4.64			
SO ₂ (gasifier only)		6.92	262		6,157		unknown
Power island				-7.02	320,383		
Miscellaneous (5%)				-2.24			
Subtotal				-44.70	326,540		
Power - gas turbine				627.40			
Power - air compressor and losses				-328.60			
Power - steam turbine				159.40			
GROSS Power Subtotal				458.20			
b. NET Power				413.50			
c. CO₂ PIPELINE AND SEQUESTERING				0.00	0		
d. H₂ PIPELINE				0.00	0		
e. TRANSMISSION LOSS-3.5%				-14.47	0		
f. NET ENERGY CYCLE -Base Case*	0.833		kg CO₂/kWh	396.20	330,060	566	0.66267

*f = a+b+c+d+e.

APPLICATIONS

Carbon dioxide as a supercritical product (143 bar) can be recovered from coal gasification and power production. Where there is an enhanced oil recovery market, this actually is profitable. The need for high-pipeline utilization is critical. Hydrogen can be recovered at high purity (99.999%) for sale from coal gasification, however the need for high pipeline-utilization is critical. Pressures of 35 bar are optimal. Fuel-cell conversion-efficiencies need to approach 77% to match the base-case output. At present, solid-oxide fuel cell efficiencies are 53-58%; while alkaline fuel cell efficiencies are near 70%.

Table 3. O₂-blown IGCC with CO₂

Glycol CO₂ and H₂S recovery; turbine topping
 Basis: Electric power delivery 100 km from station

	nm ³ /d	tons/d	kg/h	Power MW	CO ₂ kg/h	CH ₄ kg/h	N ₂ O kg/h
MINING AND TRANSPORT							
Coal methane emissions						566	
Mining operations & preparation				-2.61	2,614		0.00003
Transport by rail - 161 km				-0.21	905		0.66265
a. Subtotal				-2.82	3,520	566	0.66267
POWER PLANT							
Coal preparation (0-in. x 1/4-in.)		3,845	145,341	-0.85			
O ₂ by cryogenic separation	8,937,000	2,347	88,717	-29.29			
Steam from heat recovery generator			17,254				
Gasifier island				-2.90			
Solid waste		492	18,598				
Sulfur		78	2,948				
SO ₂ (gasifier only)		6.92	262		6,157		unknown
Glycol circulation				-5.80	320,383		
Glycol refrigeration				-4.50			
Power recovery turbines				3.40			
CO ₂ compression to pipeline (143 bar)	3,178,000			-17.30	-260,055		
Power island				-6.90			
Miscellaneous (5%)				-2.86			
Subtotal				-67.01	66,485	0	unknown
Power - gas turbine				580.78			
Power - air compressor and losses				-325.51			
Power - steam turbine				195.30			
GROSS Power Subtotal				450.57			
b. NET Power				383.56			
CO₂ PIPELINE AND SEQUESTERING							
	3,178,000				260,055		
Pipeline booster stations				-1.64	1,637		0.00002
Geological reservoir (1% loss)					-257,454		
c. Subtotal				-1.64	4,238	0	0.00002
d. H₂ PIPELINE				0.00			
e. TRANSMISSION LOSS-3.5%				-13.42			
f. NET ENERGY CYCLE*	0.203	kg CO₂/kWh		365.67	74,242	566	0.66269

*f = a+b+c+d+e.

Table 4. KRW O₂-blown IGCCGlycol CO₂ and H₂S recovery; PSA H₂ recovery; turbine topping; 3-stage solid oxide fuel cell

	nm ³ /d	tons/d	kg/h	Power MW	CO ₂ kg/h	CH ₄ kg/h	N ₂ O kg/h
MINING AND TRANSPORT							
Coal methane emissions						566	
Mining operations & preparation				-2.61	2,614		0.00003
Transport by rail - 161 km				-0.21	905		0.66265
a. Subtotal				-2.82	3,520	566	0.66267
POWER PLANT							
Coal preparation (0-in. x 1/4-in.)		3,845	145,341	-0.85			
O ₂ by cryogenic separation	8,937,000	2,347	88,717	-29.29			
Steam from heat recovery generator			17,254				
Gasifier island				-2.90			
Solid waste		492	18,598				
Sulfur		78	2,948				
SO ₂ (gasifier only)		6.92	262		6,157		unknown
Glycol circulation				-5.80	320,383		
Glycol refrigeration				-4.50			
Power recovery turbines				3.40			
CO ₂ compression to 143 bar	3,178,000			-17.30	-260,055		
H ₂ PSA purification to 31 bar	3,710,000			-3.18			
H ₂ cryo-storage for pipeline				-0.92			
Power island				-1.81			
Miscellaneous (5%)				-3.07			
Subtotal				-66.22	66,485	0	unknown
Power - gas turbine				244.53			
Power - air compressor and losses				-169.48			
Power - steam turbine				42.93			
GROSS Power Subtotal				117.98			
b. NET Power				51.76			
CO₂ PIPELINE & SEQUESTERING	3,178,000				260,055		
Pipeline booster stations				-1.64	1,637		0.00002
Geological reservoir (1% loss)					-257,454		
c. Subtotal				-1.64	4,238	0	0.00002
H₂ PIPELINE OUTLET (21 bar)	3,710,000						
H ₂ 3-stage SOFC (58% of 460.0 MW)				266.80			
Steam Generator (85% of 36.8 MW)				31.28			
d. Subtotal				298.08	0	0	0.00000
e. TRANSMISSION LOSS-3.5%				-1.81			
f. NET ENERGY CYCLE*	0.216	kg CO₂/kWh		343.56	74,242	566	0.66269

*f = a+b+c+d+e

FULL ENERGY CYCLE ANALYSIS OF GREENHOUSE GAS FORCING

Recent consideration of full-energy cycle analysis for power production (9) have emphasized the importance of greenhouse gases such as methane and N₂O in addition to other than carbon dioxide. Modeling results suggest that a molecule of methane is equivalent to 56 molecules of CO₂ in its climate-forcing impact, while each N₂O molecule is equivalent to 280 molecules of carbon dioxide (10). These "equivalent CO₂ impacts" were used as the basis for Fig. 2 which shows the equivalent CO₂ emissions to provide 396-MW of electricity 100-km from the IGCC system.

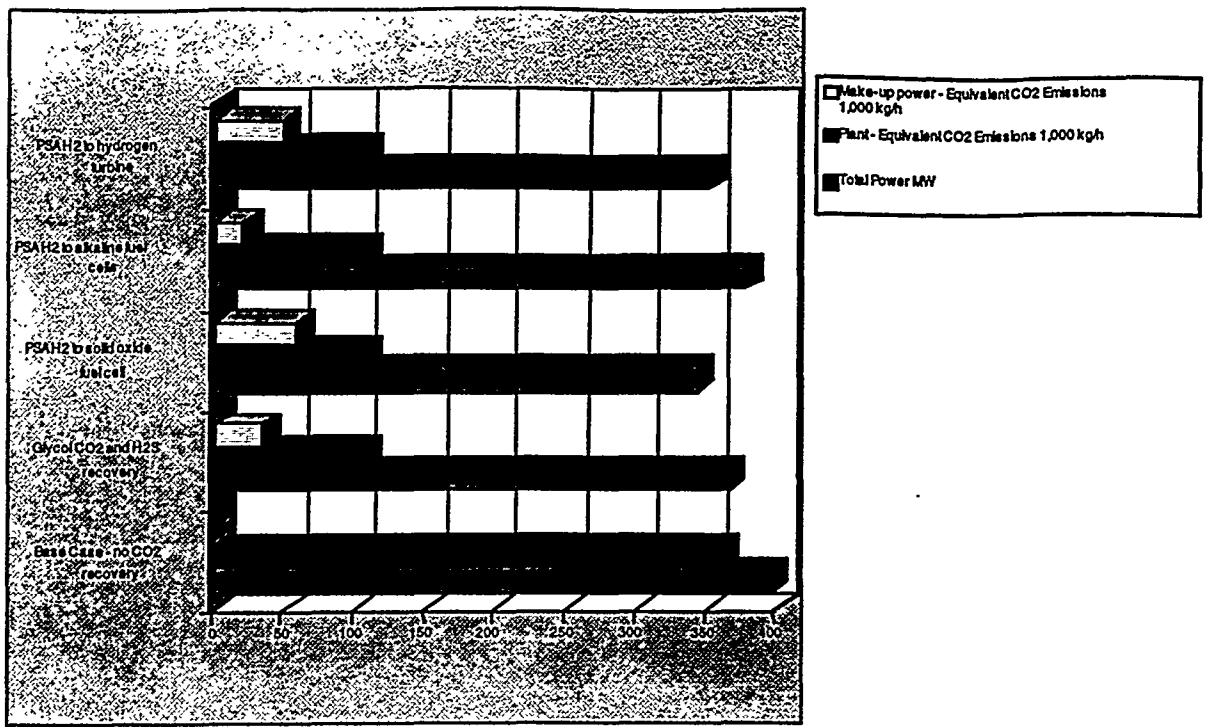


Fig. 2. Equivalent CO₂ Greenhouse Emissions 396 MW Net-Cycle.

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REFERENCES

1. Gallaspy, D.T., et al., 1990. "Southern Company Service's Study of a KRW-based GCC Power Plant," EPRI GS-6876, Electric Power Research Institute, Palo Alto, CA.
2. Doctor, R.D., Molburg, J.C., Thimmapuram, P.R., Berry, G.F., and Livengood, C.D., 1994. "Gasification Combined Cycle: Carbon Dioxide Recovery, Transport, and Disposal," ANL/ESD-24, Argonne National Laboratory, Argonne, IL.
3. Doctor, R.D., Molburg, J.C., and Thimmapuram, P.R., 1996. "KRW Oxygen-Blown Gasification Combined Cycle: Carbon Dioxide Recovery, Transport, and Disposal," ANL/ESD-34, Argonne National Laboratory, Argonne, IL.
4. Doctor, R.D., J.C. Molburg, P.R. Thimmapuram, "Oxygen-Blown Gasification Combined Cycle, Carbon Dioxide Recovery, Transport, and Disposal," Proceedings of the 3rd Intl. Energy Agency Carbon Dioxide Disposal Symposium, Cambridge, MA, USA, 9-11 Sept. 1996, H.J. Herzog, Ed., Pergamon Press, Oxford; simultaneous publication in Energy Conservation and Management, 28 (Suppl.):575-580 (1997).
5. Doctor, R.D., Molburg, J.C., Thimmapuram, P.R., Berry, G.F., and Livengood, C.D., and Richard A. Johnson, "Gasification Combined Cycle: Carbon Dioxide Recovery, Transport, and Disposal," Proceedings of the 2nd Intl. Energy Agency Carbon Dioxide Disposal Symposium, Oxford, UK, 29-31 March, 1993, P.W. F. Reimer, ed., IEA Greenhouse Gas R&D Programme, Pergamon Press, Oxford (1993); simultaneous Publication in Energy Conservation and Management, 34(9-11):1113-20 (1993).
6. "Big Canadian Miscible CO₂ EOR Project," Oil & Gas J. (July 7, 1997).
7. Moritis, C., "EOR Survey and Analysis," Oil & Gas J. (Apr. 15, 1996).
8. Hsu, C. et al., "Production Report," Oil and Gas J. (Oct. 23, 1995).
9. Smith, I.M., Greenhouse Gas Emission Factors for Coal-The Complete Fuel Cycle, International Energy Agency, London, UK, Nov. 1997.
10. Bryant, E., Climate Process and Change, Cambridge, 1997, p. 119.