Co-Processing Coal and Natural Gas by the Hynol Process for Enhanced Methanol Production and Reduced CO$_2$ Emissions

Prepared by:

Meyer Steinberg

June 19, 1997

Engineering Technology Division
DEPARTMENT OF ADVANCED TECHNOLOGY, BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

19980529 009

Disclaimer

Co-Processing Coal and Natural Gas by the Hynol Process for Enhanced Methanol Production and Reduced CO$_2$ Emissions

Prepared by

Meyer Steinberg
Brookhaven National Laboratory
Engineering Technology Division
Department of Advanced Technology
Upton, New York 11973

June 19, 1997

ABSTRACT

The Hynol Process for conversion of coal and natural gas to methanol as a liquid fuel consists of three consecutive unit operations (1) hydrogasification of coal, (2) steam reforming of the methane formed and added natural gas feedstock, and (3) catalytic methanol synthesis. The Hynol Process is a total recycle process. Using a process simulation computer program, mass and energy balances and yields and efficiency data have been obtained for a range of natural gas to coal feedstock ratios. Although the methanol yield increases with natural gas to coal feed ratio, the cost of feedstock per unit methanol is insensitive over a wide range of feedstock ratios. The Hynol Process produces a 13% increase in methanol yield compared to the equivalent of two separate conventional coal gasification and natural gas reforming plants. The CO_2 emissions are reduced by 22% for the Hynol plant compared to the conventional processes with greater CO_2 reductions at lower gas to coal feedstock ratios. A preliminary cost estimate for a 10,000 Tons/Day Hynol methanol plant indicates a lower production cost than the current cost of methanol by the conventional natural gas reforming plant. The lower unit energy cost for coal is beneficial in reducing the methanol cost in the Hynol Process.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

1   INTRODUCTION

The Hynol Process was originally conceived to process biomass (wood and agricultural products) for the production of methanol with reduced CO_2 emission [1,2]. Effort has also been made to apply the process to municipal solid waste (MSW) feedstock [3]. The Hynol Process in general can be applied to the use of any condensed carbonaceous material as feedstock. A basic feature of the Hynol Process is that natural gas is used as a co-feedstock with the condensed carbonaceous feedstock to produce a higher yield of methanol per unit feedstock than is obtained when using either co-feedstock alone in the conventional process for producing methanol. The reason for the improved yield is that the condensed feedstock has a deficiency of hydrogen compared to carbon, while natural gas has an excess of hydrogen compared to carbon. Thus, the co-feedstock of condensed carbonaceous material with natural gas yields the closest approach to optimizing the hydrogen to carbon content for producing the product methanol. Another feature of the Hynol Process is that it is a complete recycle system maximizing the mass and energy balance. In this paper, we apply the Hynol Process to the co-processing of coal with natural gas.

2   HYNOL PROCESS DESCRIPTION

The Hynol Process consists of three process reaction steps (1) the hydrogasification of the condensed carbonaceous material (wood, coal, etc.) with recycle hydrogen-rich gas to produce a methane-rich gas, (2) the steam reforming of the methane-rich gas together with the addition of the co-feedstock methane to produce carbon monoxide and hydrogen. The excess gas from the methanol synthesis reactor which is rich in hydrogen is recycled to the hydrogasifier at the head end of the process. Figure 1 gives a generalized flow diagram for the Hynol Process. The process chemistry for each unit is given in the following paragraphs.

3   THE HYDROGASIFIER (HGR)

The main reaction taking place in the HGR is between the condensed carbonaceous carbon and the hydrogen in the recycle gas to produce methane:

$$C + 2H_2 = CH_4$$
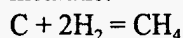
This is an exothermic reaction generating 18 Kcal/mol of CH_4 produced. However, the wood (stoichiometrically $CH_{1.4}O_{0.6}$) or coal ($CH_{0.8}O_{0.1}$) contains oxygen so that two additional reactions must be taken into account:

$$C + H_2O = CO + H_2$$
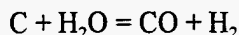
which is endothermic absorbing about 42 Kcal/mol C and

$$CO_2 + H_2 = CO + H_2O$$
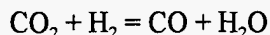
which is energetically about neutral.

The conditions favoring high hydrogasification of the carbonaceous material is higher pressure, 30 to 50 atm, and higher temperature, 800 - 900° C. A suitable design for the HGR is a fluidized bed reactor with either sand or the ash from the condensed carbonaceous material to act as a fluidizing medium. The main feature of the HGR is that it is designed so that it is self sufficient in energy not requiring any outside energy to maintain the reaction conditions. The hydrogasification of coal has been studied extensively in the past [4]. Unconverted char from the HGR can be used as a fuel or sequestered. In the case of biomass or coal, impurities such as sulfur may be gasified in the HGR so that a gas cleanup step is required. The sulfur can be removed as calcium sulfide with limestone.

$$CaCO_3 + H_2S = CaS + CO_2 + H_2O$$
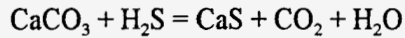
4   STEAM REFORMING (SPR)

The steam reformer, also called the steam pyrolysis reactor (SPR), combines the methane with steam to produce carbon monoxide and hydrogen. Any CO_2 present and hydrogen also produces carbon monoxide.

$$CH_4 + H_2O = CO + 3H_2$$
$$CO_2 + H_2 = CO + H_2O$$
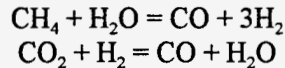
The first reaction is highly endothermic requiring about 60 Kcal/mol of CO produced and the second reaction is about neutral. There is much experience operating steam reformers [5]. The reactor design is usually a nickel catalyst packed tubular reactor which usually operates in the range of 30 to 50 atm and about 1000° C. The co-feedstock methane is added to the HGR gas together with sufficient steam to produce the CO and H_2. The heat required for the endothermic reaction is supplied by combustion of methane with air in a furnace surrounding the catalyst packed tubular reactor. Heat exchangers are used to maintain an energy balance and produce steam for the process.

5   METHANOL SYNTHESIS REACTOR (MSR)

After cooling the gases from the SPR essentially containing H_2 and CO in ratios exceeding 3 is fed to a conventional catalytic methanol synthesis reactor using a copper based low pressure catalyst [6]. The two reactions taking place in the MSR leading to methanol are as follows:

$$CO + 2H_2 = CH_3OH$$
$$CO_2 + 3H_2 = CH_3OH + H_2O$$

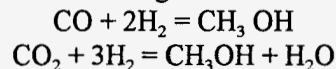Both reactions are exothermic by about 31 Kcal/mol methanol. The reactor must be cooled and the heat recovered as process steam may be used in the process to make up heat balances. A recycle ratio of 5 to 1 is used around the MSR to obtain high methanol conversions. The condensed methanol-water mixture is finally fractionated to produce fuel and chemical grade methanol. None of the gas is wasted. All the hydrogen-rich gas from the MSR is recycled to the HGR.

6   PROCESS SIMULATION

A process simulation computer model was used to obtain mass and energy balances and to perform a parametric analysis. The computer program is based on an equilibrium model. Table 1 gives the elemental analysis of the bituminous coal used and the typical composition and flow rate of the gas feed to each of the major reactors as shown in Figure 1. Table 2 gives the results of the yields, efficiency and CO_2 emissions as a function of natural gas to coal feed ratio.

The conclusions drawn from the process simulations are as follows:

1.   As the total natural gas to co-feedstock ratio increases, the methanol yield per unit coal increases significantly, while the methanol to total natural gas feedstock decreases only slightly.

2.   The temperature of the gas to the HGR necessary to make the HGR energy self-sufficient decreases with increasing natural gas to coal feed ratio.

2

3. The carbon conversion (coal carbon to gasified carbon) in the HGR increases with natural gas to coal feed ratio.

4. Interestingly enough, the CO_2 emissions per unit energy remains about the same over the range of feedstock ratios. The CO_2 emission includes the CO_2 emitted in the process and the CO_2 from the combustion of the methanol product.

The natural gas to coal feed ratio choice depends on the economics of the process. A first order estimate mode in Table 3 assuming plant capital cost for a fixed methanol production rate is approximately the same for the range of feedstock ratios shown in Table 2, indicates a rather constant raw material cost per unit methanol based on current U.S. coal costs in the range of $20 to $30/ton and current U.S. natural gas costs in the range of $2.00 to $2.50/MM BTU. The reason for this is that the feedstock cost, under these conditions, is mainly dominated by the natural gas cost. Because of this cost insensitivity, the choice of feedstock ratio then becomes dependent on the availability of the feedstock materials. A feedstock ratio choice can also be based on a reasonably achievable carbon-conversion in the HGR. From experience, we assume the HGR carbon conversion efficiency can be obtained up to about 81.5% resulting from a feedstock ratio of 1.59.

7   COMPARISON OF HYNOL WITH CONVENTIONAL PROCESSES

The conventional process for methanol production is based on the steam reforming of natural gas. The process consists of a steam reformer, shift reactor and methanol synthesis reactor [7]. When coal is used as a feedstock, the coal is gasified with steam and oxygen in a gasifier. The resulting gas is shifted with steam to adjust the CO/H_2 ratio and is then fed to a methanol synthesis reactor [7]. Table 4 compares the Hynol Process using co-feedstocks of coal and natural gas with the conventional coal gasification and natural gas reforming plant each operating separately with the same quantities of feedstock as in the Hynol plant when the feedstock ratio is 1.59. It can be seen that the Hynol plant products 6 times more methanol per unit of coal than the conventional coal gasification plant and 1.4 times more than the natural gas reforming plant. Thus, the Hynol plant products 13% more methanol than the sum of the two conventional coal gasification and methanol reforming plants. The CO_2 emission is even more significant in that the Hynol plant products 22% less CO_2 emissions than the two conventional plants. The CO_2 emissions become less by 35% when the NG/coal decreases to 0.84. The CO_2 emission takes into account the CO_2 emitted by the methanol production plants and that generated by the combustion of methanol. It should be noted that methanol used as fuel in internal combustion automotive engines can be 30% more efficient than gasoline driven engines thus further reducing CO_2 emissions [9]. An even greater reduction in CO_2 emission by a factor of at least 2.5 can be achieved when using methanol in a direct fuel cell for automotive power [10].

8   PRELIMINARY COST ESTIMATE FOR THE HYNOL PROCESS

A preliminary cost estimate is made for the production of methanol from a coal/natural gas Hynol plant with the following economic assumptions.

1. Assume a world size plant producing 10,000 T/D methanol.
2. Capital cost estimated at $800 million based on estimates of a similar Hynol plant with wood as feedstock [2].

3. Plant factor of 90%, operating 328.5 days/yr.
4. Cost of coal = $25/ton = $27.75/ton MF coal.
5. Cost of NG = $2.50/MSCF = $118.80/ton methane.
   These feedstock costs reflect current U.S. conditions.
6. O and M cost based on percentage of capital investment; 1% for labor, 2% for maintenance, 1% for power and 2% for catalysts and miscellaneous for a total O and M charge of 6% on capital investment.
7. Capital charges based on a 80/20 debt/equity ratio and includes depreciation, return on investment (ROI), interest charges of debt and taxes; this amounts to a total of 19% on capital investment.

The results of the preliminary cost estimate is shown in Table 5. The unit production cost which includes ROI, turns out to be $124/ton or $0.41/gal of methanol. The traditional selling price and production cost of methanol for a conventional natural gas reforming plant has been $0.45/gallon. Because of the mandatory requirement for the addition of MTBE to gasoline which is produced from methanol, the demand has increased the selling price last year to almost $2/gallon. It has since dropped to the present level of about $0.57/gallon [8]. Thus, the estimated cost of methanol for the coal/natural gas co-feedstock Hynol plant at $0.41/gas is highly competitive. It should be noted that even if the capital investment has been under-estimated by 20%, the cost of methanol would only increase by 10% to $0.45/gas which is still competitive with the conventional process. Besides the improved yield of methanol compared to the conventional processes mentioned earlier, the cost of coal which makes up about 25% of the feedstock energy cost of the plant is less than half the cost of natural gas on a unit energy basis. The result is a lower overall unit feedstock cost and, as shown earlier, this factor appears to be insensitive to the natural gas/coal feedstock ratio.

9   CONCLUSIONS

The Hynol Process operating with coal and natural gas as feedstocks yields at least 13% more methanol than the equivalent of two separate conventional steam-oxygen coal gasification and natural gas-steam reforming plants. The CO_2 emissions become even less with lower gas to coal feedstock ratios. Use of methanol fuel cells for automotive power could significantly decrease CO_2 emission compared to convention IC engines. A preliminary cost estimate for a 10,000 T/D Hynol methanol plant indicates a production and selling price cost lower than that for current conventional natural gas steam reforming plant. The Hynol cost for methanol appears to be insensitive to the natural gas to coal feedstock ratio over a wide range.

10   REFERENCES

1.   M. Steinberg and Y. Dong, "Process and Gyroratios for the Production of Methanol from Condensed Carbonaceous Material," U.S. Pat. RE 35,377 (November 12, 1996).

2.   M. Steinberg and Y. Dong, "Hynol—An Economic Process for Methanol Production from Biomass and Natural Gas with Reduced CO_2 Emission," BNL-49733, Brookhaven National Laboratory, Upton, New York (October 1993).

3.   REM Capital Corp., "Waste to Methanol Project Summary," Internal Report (September 3, 1994).

4.   M. Steinberg, "The Flash Hydropyrolysis and Methanolysis of Coal with Hydrogen and Methane," Int. J. Hydrogen Energy 12, No. 4, pp. 251-66 (1987).

5.   D.E. Redler and M.V. Twigg, "Steam Reforming" in Catalyst Handbook, 2nd Ed., M.V. Twigg ed., Wolfe Publishing Co., London (1989).

6.   S. Lee, Methanol Synthesis Technology, CRC Press, Inc., Boca Raton, Florida (1990).

7.   C.E. Wyman, R.L. Bain, N.D. Hinman and D.J. Stevens, "Ethanol and Methanol from Celluosic Biomass," in Renewable Energy Sources for Fuels and Electricity, Ed. T.B. Johanssen et al., p. 914, Island Press, Washington, D.D. (1992).

8.   Hart's Oxy-Fuel News, Vol. VIII, No. 47 (December 2, 1996).

9.   Motor Vehicle Emission Laboratory (MVEL), "An Analysis of the Economic and Environmental Effects of Methanol as an Automotive Fuel," EPA Report No. 0730, Ann Arbor, Michigan (September 1989).

10. World Car Conference '96, Bourns College Engineering Center for Environmental Research and Technology, University of California, Riverside, California (January 21-February 4, 1996).

APPENDIX A

Table 1
Feedstock and Gas Feed Conditions to Each Reactor

Bituminous coal feed to HGR - elemental analysis, wt% moisture free MF
(coal feed contains 10% moisture)

C	-	73.33
H	-	4.97
O	-	7.90
Ash	-	9.13
S	-	3.12
N	-	1.55

Gas flow rate (Kmol/h) and composition (Vol. %) based on 100 Kg/hr coal for 100 Kg/hr NG addition to SPR and 39.3 NG to Reformer Furnace. Methanol Production = 345 Kg/100 Kg MF Coal.

Feed to	1-HGR	2-SPR	3-MSR
Press, atm	30.00	25.00	40.00
Temp. °C	552.00	400.00	100.00
Rate Kmol/hr	16.93	48.16	53.70
Gas Comp. Vol. %			
CO	3.53	2.80	18.19
CO_2	1.61	0.95	4.31
CH_4	3.39	22.86	1.36
H_2O	13.18	57.01	0.55
H_2	76.15	15.84	75.10
N_2	1.19	0.54	0.48
MeOH	0.94	0.00	0.00

Table 2
Methanol Yields, Efficiency and CO_2 Emissions

Bituminous Coal Feedstock 100 Kg/hr MF
NG = natural gas

NG Feedstock, Kg	50	75	100	125
NG Fuel for Reforming, KG	33.5	46.5	59.3	72.2
Total NG/MF Coal Ratio	0.84	1.22	1.59	1.97
C Conversion in HGR, %	57.3	69.7	81.5	93.4
Thermal Efficiency, %	59	63	65	67
Temp. of Gas to HGR, °C	899	693	552	458
Methanol Product, Kg	204	275	345	415
MeOH/MF Coal Kg/Kg	2.04	2.75	3.45	4.15
MeOH/Total NG Kg/Kg	2.44	2.26	2.17	2.10
CO_2 Emissions Lbs/MMBTU	191	193	194	194

Table 3
Feedstock Cost as a Function of Natural Gas to Coal Ratio

Natural Gas Cost - $2.50/MMBTU = $118.80/ton Methane
Coal Cost = $25/ton ($27.75/ton MF)

|				
Feedstock NG/MF Coal Ratio, Tons/Ton	0.84	1.22	1.59	1.97
Methanol Produced				
MeOH/MF Coal Ratio, Tons/ton	2.04	2.75	3.45	4.15
MeOH/NG Ratio, Tons/ton	2.44	2.26	2.17	2.10
Feedstock Cost				
MF Coal - $/ton MeOH	13.60	10.10	8.05	6.69
NG - $/ton MeOH	48.67	52.54	54.72	56.55
Sum Feedstock, $/ton MeOH	62.27	62.64	62.77	63.24

Table 4
Comparing Coal/Natural Gas (NG) Hynol Process with Conventional Coal Gasification and Natural Gas Reforming Processes for Methanol Production

Factor	Hynol Process	Conventional Coal Gasification	Processes NG Reforming
Feedstock			
MF Coal, Kg	100.00	100.00	---
Total NG, Kg	159.3	---	159.3
Oxygen, Kg	---	80.0	---
Thermal Eff., %	65.1	50.8	64.0
Carbon Conversion, %	67.1	25.1	78.0
Methanol Yield			
MeOH/Coal	3.45	0.57	---
MeOH/NG	2.17	---	1.56
MeOH Product, Kg			
		$\underline{57}$	$\underline{249}$
Total MeOH, Kg	345	306	
% MeOH Hynol Increase Over. Conv. Process	13%		
CO_2 Emission			
		$\underline{550}$	$\underline{180}$
Lbs CO_2/MMBTU	194	249	
% CO_2 Reduction by Hynol Compared to Conv. Processes	22%		

Table 5
Preliminary Cost Estimate for Methanol Production by Hynol Process

Natural Gas/MF Coal Feedstock Ratio = 1.59
MeOH Plant Capacity = 10,000 T/D
Capital Investment = $800 x 10^6
Plant Factor = 90% (328.5 p, Days/yr)

Production Cost						$ MM/Day
Coal = 2900 x $27.75/ton				=		0.08
Natural Gas = 4608 x $118.75				=		0.55
O and M =	0.06 x	$\dfrac{\$800\ MM}{328.5}$		=		0.15
Total Capital Charge =	0.19 x	$\dfrac{\$800\ MM}{328.5}$		=		0.46
Total Production Cost				=		1.24
Unit Production Cost				=		$124/ton
Selling Price				=	$\dfrac{124}{303}$ =	$0.41/gal
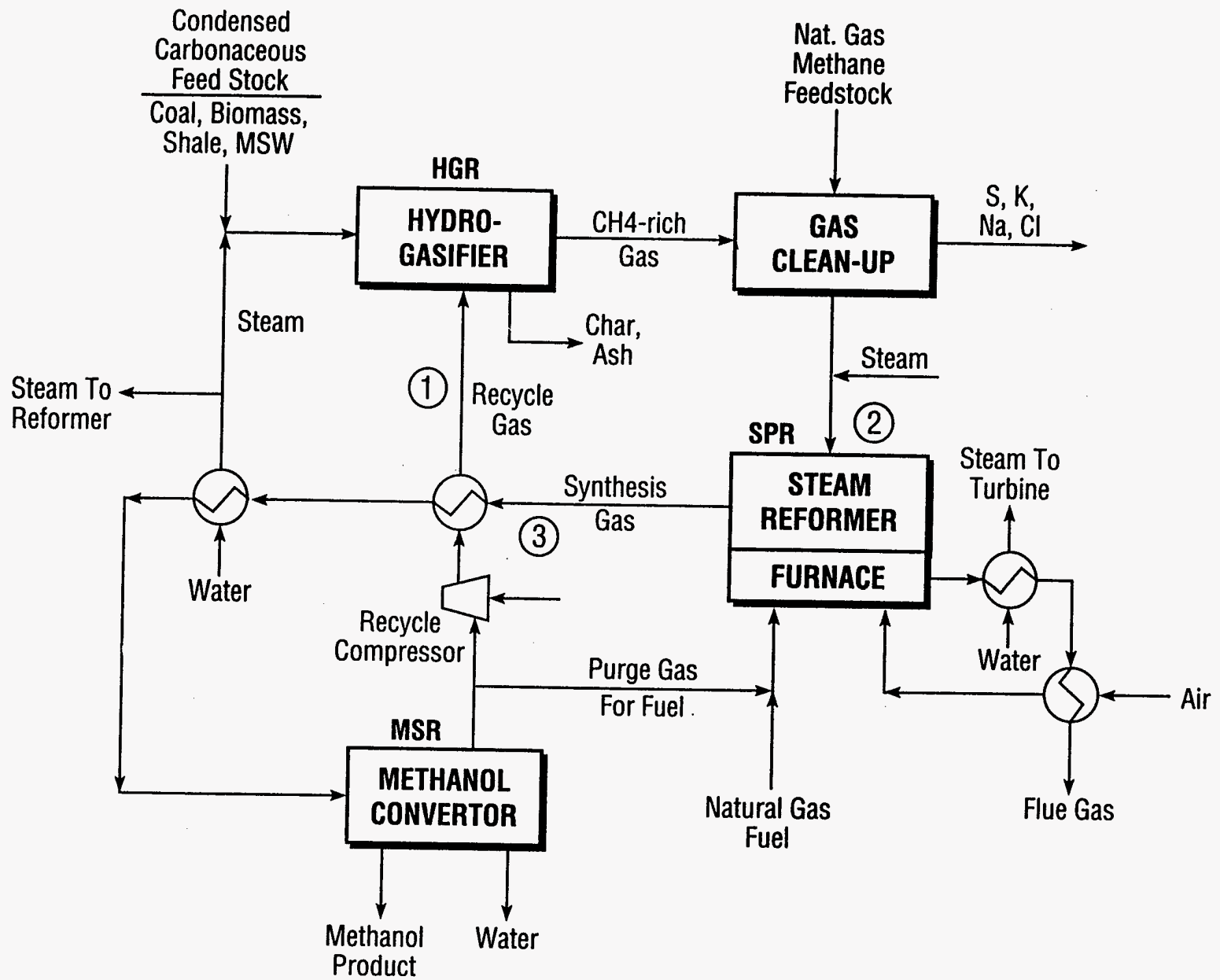
THE HYNOL PROCESS
Figure 1

Report Number (14) BNL—65453

_____

_____

_____

Publ. Date (11) 19970619

Sponsor Code (18) DOE/FE, XF

UC Category (19) UC-125, DOE/ER

DOE