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ALTERNATIVE PROCESS SCHEMES FOR COAL CONVERSION

PROGRESS REPORT NO. 4
SEPTEMBER 1, 1979 - MARCH 30, 1980

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DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

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Abstract

This progress report is divided into two parts. In Part A, the results of the first three progress reports which dealt with the separation of H_2/CH_4 and $H_2/CH_4/CO$ mixtures resulting from coal gasification processes are briefly summarized. The separation calculations were performed for ideal, cryogenic, clathrate (gas-hydrate), and absorption/stripping separation processes. The cryogenic separation indicates the least energy requirement. Work on this phase of the program has been concluded. An experimental coal gasification program is being undertaken.

In Part B, a review summary of existing and developing coal gasification processes is presented. The relative merits of gasifier type, heating method, operating mode, process conditions, and gasifying medium are considered. This is followed by a qualitative appraisal of several selected coal gasification processes based upon the above considerations. It is intended that this report will help focus attention on those areas in which significant process improvements can be realized. The report concludes with a series of recommendations for future work.

TABLE OF CONTENTS

Abstract	iii
Part A. Summary of Gas Separation Work	
I. Conclusions	1
II. Energy Calculations	1
Part B. Summary of Coal Gasification	
I. Introduction	6
II. Reactor Types	12
III. Heating Methods	15
IV. Operating Modes	16
V. Process Variables	17
1. Temperature	17
2. Pressure	18
3. Steam-Oxygen Ratio	20
4. Coal Type	23
VI. Economics of Gasification Processes	25
VII. Advantages and Disadvantages of Various Selected Processes	28
VIII. Conclusions	41
IX. References	44

Part A - Summary of Gas Separation Work

I. Conclusions

In the previous progress reports, the energetics of several gas separation processes were compared. The gas streams arise from such processes as catalytic gasification and hydrogasification. The methods evaluated were ideal separation (Progress Report No. 1), cryogenic and clathrate separation (Progress Report No. 2), and absorption-stripping (Progress Report No. 3). The results of these calculations are summarized as follows: The cryogenic separation of methane and hydrogen required the least energy. Clathrate separations required almost twice as much energy as cryogenic, but the calculation for the cryogenic separation was based on H_2/CH_4 mixtures. The energetics of clathrate separation remain the same for $CO/H_2/CH_4$ systems since only the methane forms a clathrate. The presence of CO in the mixture increases the difficulty of a cryogenic separation. The absorption-stripping separation involves the absorption of methane into cold liquid propane. The energy requirements were roughly two times greater than cryogenic for the H_2/CH_4 separation.

II. Energy Calculations

Ideal separation energies were computed in Progress Report No. 1. The efficiency of a given process will be defined as the ratio of the ideal separation energy to the actual separation energy. For each case, the ideal separation energy has been calculated using the actual separations achieved in the process with which it is to be compared. The initial state will be 100°F and 500 psi and the final state 100°F and 1000 psi (pipeline pressure) in all cases.

An important problem always encountered in determining process efficiencies is the non-equivalence of various forms of energy. The energy computed for an ideal separation is not designated as thermal, electrical or any other form. If such an ideal process required all of the ideal energy as electrical energy generated by a steam power plant, the requisite energy will be approximately tripled due to the Carnot efficiencies.

In order to have a common basis for comparison, all energy requirements will be related back to fuel energy. Electrical requirements will be generated at a Carnot efficiency of 0.35 and thermal requirements at an efficiency of 0.80 is shown in Figure A1.

The energetics of the cryogenic separation of a 60/40 H_2/CH_4 feed stream was calculated in Progress Report No. 2. Separation of a 60/40 $(H_2 + CO)/CH_4$ stream via gas hydrate (clathrate) formation was also calculated in that same report. Finally, calculations for the separation of a 60/40 mixture of H_2/CH_4 by absorption/stripping in cold propane were performed. The results of these calculations are summarized in Tables A1-A3.

Figure A1.

Table A-1

Ideal vs. Cryogenic Separation

	<u>Feed</u>	<u>Streams</u>	
		<u>Recycle</u>	<u>Product</u>
Amount	1	0.635	0.365
% H ₂	60	92.7	3.0
% CH ₄	40	7.3	97.0

Ideal

Separation 775 calories/g-mole CH₄ separatedCompression 428

Total 1203

1203

Cryogenic

Carnot separation (100% efficient) 1593

" " (40% ") 3982

Compression Costs 444

Total Electrical ; 4426 x 1/0.35 = 12645

$$\eta = \frac{1203}{12645} = 0.0964 = 9.51\%$$

Table A-2

Ideal vs. Clathrate Separation

	Streams		
	<u>Feed</u>	<u>Recycle</u>	<u>Product</u>
Amount	1	0.75	0.25
% (H ₂ + CO)	60	80	0
% CH ₄	40	20	100

Ideal

Separation	735 calories/g-mole CH ₄ separated	
Compression	<u>428</u>	
Total	1163	1163

Clathrate Process

Electric

Feed Gas Compression	5280
Feed Gas Cooling	390
Heat Pump	1829
Water Pumping	<u>429</u>
	7928

Power Recovery (70%)

Product Stream 320x0.7

Recycle Stream 2502x0.7

$$(1975) \quad \frac{(1975)}{5953} \times 1/0.35 = 17008$$

Thermal

Product Stream Heating	603
Recycle " "	<u>4221</u>
	4824 x 1/0.8 = <u>6030</u>
	23038

$$\eta = \frac{1163}{23038} = 0.05 - 5\%$$

Table A-3

Ideal vs Absorption/Stripping

	Streams		
	Feed	Recycle	Product
Amount	1	0.607	0.393
% H ₂	60	96.6	4.4
% CH ₄	40	3.4	95.6
Ideal			
Separation	842		$\frac{\text{calories}}{\text{g/mole CH}_4 \text{ separated}}$
Compression	428		
Total	1270		1270

Absorption/Stripping

Electric

Refrigeration	5862		
Blower	64		
Pumps	333		
Compressors	$\frac{533}{6792} \times 1/0.35$	=	19406

Thermal	$4486 \times 1/0.8$	=	$\frac{5608}{25014}$

$$\eta = \frac{1270}{25014} = 0.0508 = 5.1\%$$

Part B Summary of Coal Gasification

I. Introduction

The reaction of coal with steam, carbon dioxide, oxygen, air, hydrogen, or mixtures of these gases at appropriate temperatures and pressures can result in a substantial conversion of the coal to gaseous products. These gaseous products can be burned directly (fuel gas) or further converted via catalytic processes to other products (synthesis gas).

If hydrogen is used as the gasifying medium, the process is called hydrogasification. Hydrogasification is believed to occur in two stages, rapid devolatilization and hydrogenolysis of the devolatilized matter and a slower hydrogenation of the coal char.¹

The second stage is presumably rate controlling. This reaction is exothermic ($\Delta H = -18$ Kcal/mole) and high pressures (> 1000 psi) are generally employed to obtain high yields. The equilibrium constant is greater than unity at temperatures of about 550°C and lower. Thus, the reaction is favored by high pressure and low temperature. Kinetic considerations require temperatures in the 500° to 1000°C range. The reaction is known to be catalyzed by alkali metal carbonates such as sodium carbonate and potassium carbonate.²

In addition to the relatively severe conditions of temperature and pressure, the cost of hydrogen is also a major consideration, since this must be made via coal gasification, steam reforming of methane (or other feedstocks), electrolysis, or some other process. Current hydrogen production costs are \$6.12/MM Btu for methane reforming and \$9.85/MM Btu for coal gasification.³ Electrolytic hydrogen is about \$22/MM Btu.

The reaction of coal with CO₂ results in the production of CO via the Boudouard reaction

The equilibrium constant is greater than one at temperatures of 700°C and higher. Conversion of CO₂ is favored by low pressure. The kinetics of the graphite reaction with CO₂ have been shown to be 200 times faster than that of direct hydrogenation at 1000°C. Producer gas (essentially CO) can be generated by reacting coal with oxygen (or air) to supply the CO₂. If an external source of CO₂ is available from a CO₂ recovery process, then a thermally balanced process would result from the combustion of 0.426 moles of carbon per mole of carbon gasified.

If Klbel- Englehard chemistry were suitably developed so that the reaction of CO with water

were competitive with Fisher-Tropsch, producer gas technology might become competitive with conventional steam gasification.

The gasification of coal with steam is the most common method for conversion of coal to gaseous products. The reaction is highly endothermic and actually takes place in two stages. The first stage is devolatilization to produce char plus volatiles (methane, phenols, tars, oils, naphtha, H_2S , NH_3 , some CO and H_2). The second stage is the reaction of steam with char.

Little energy is required for the devolatilization step. On the other hand, the second stage is energy intensive. This reaction is conducted at elevated temperatures (650° to 1800°C) and usually at elevated pressures (1 atm to 100 atm).

The CO produced by the water gas reaction can react with water via the CO shift reaction to produce more hydrogen and CO_2 .

It can be shown that three independent chemical equations are sufficient to characterize the six component (C , CO , CO_2 , H_2 , H_2O , CH_4) carbon-hydrogen-oxygen system.

		$\Delta\text{H} \text{ (Kcal/mole)}$
Water Gas	$\text{C} + \text{H}_2\text{O} = \text{CO} + \text{H}_2$	+ 32
Boudouard	$\text{C} + \text{CO}_2 = 2\text{CO}$	+ 42
Hydrogenation	$\text{C} + 2\text{H}_2 = \text{CH}_4$	- 18

From these equations, one can derive a number of other dependent equations.

Since these reactions are occurring simultaneously, the composition of the raw gas depends on conditions of temperature, pressure, H/O ratio, and approach to equilibrium. In addition, depending on the type of gasifier, the devolatilization products alter the raw gas composition. In some systems they are rapidly removed and in others they are reformed in the gasifier to CO and H₂ via reactions such as

or oxidized in the combustion zone (for air or O₂ blown gasifier) via

The rate of steam gasification at 1000°C with graphite is about 5 times greater than CO₂ gasification and 1000 times that of direct hydrogenation.⁴ The reaction is known to be catalyzed by alkali metal compounds⁵ such as Na₂CO₃, K₂CO₃, KOH, etc., substances which also catalyze the C-CO₂ reaction and the C-H₂ reaction.

Steam gasification is used for the generation of fuel gas or synthesis gas. Since the water gas reaction is highly endothermic, the heat of reaction is frequently supplied by combusting part of the coal in the gasifier itself using air or oxygen. If air is used, the resulting low Btu gas (100 to 250 Btu/SCF) contains 45 to 55% N₂. The use of oxygen raises the Btu content to 300 to 450 Btu/SCF due to the elimination of N₂ in the product gas. If a high Btu gas is desired, it is generally necessary to shift the product gas to a 3/1 H₂/CO ratio followed by catalytic methanation. Since methane has 1000 Btu/SCF, any gasification process which

generates large quantities of methane in the raw gas has a thermal efficiency advantage if the resulting product is to be used as a fuel gas.

The thrust of much of the so-called second generation gasification programs in the United States has been aimed at the generation of significant quantities of methane in the gasifier itself. Hygas, Bi-gas, and Synthane generate 16 to 18% methane, while hydrane produces a raw gas with about 68% methane.⁶ The Exxon catalytic gasification employs coal impregnated with 10 to 20% K_2CO_3 , temperatures of 650° to 750°C, and 50 atm pressure. The gasifier effluent, after scrubbing and acid gas removal, is cryogenically separated into pure methane product and a CO, H_2 , CH_4 recycle stream.⁷

If the desired product is synthesis gas, the presence of methane in the product gas is no longer as desirable and indeed may interfere with subsequent processing necessitating its removal. Consequently, gasification schemes which produce no methane become more attractive for synthesis gas production.

Synthesis gas is subsequently converted to desired products by various syntheses. These syntheses are all catalytic, activation of carbon monoxide and hydrogen being necessary to lower the activation energy and to provide suitable chemical reaction pathways. Table 1 outlines some of the processes together with catalysts and operating conditions.^{8,9} Catalytic methanation has been previously mentioned in connection with high Btu fuel gas production. Methanol synthesis is established technology, 6.36×10^9 lbs having been produced in 1978 (number 22 in order of production). It also provides a direct route to

Table 1

Summary of Synthesis Gas Conversion Processes

Process	Main Reaction (s)	ΔH kcal/mole	Temp. where $K_p \neq 1$	Process Temp.	Pressure (psia)	Typical Catalysts	Comments
Water Gas Shift	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	-7.8 (927°C)	<827°C	315-485°C 250°C	rxn. independent of pressure	chromia promoted iron oxide copper oxide zinc oxide alumina	Generally run with 2 to 4 times stoichiometric steam. Conversions as high as 99% based on CO. High temperature catalyst used in first reactor for higher rates, low temperature in 2nd reactor for equilibrium
Methanation	$\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$	-49.3 (25°C)	<627°C	Inlet 300°C Outlet 500°C	300-1000	nickel ruthenium	Heat removal is major engineering problem. Carbon deposition can be a problem at H_2/CO ratios less than 3.
Methanol Synthesis	$\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$	-25 (350°C)	<405°C	375°C 270°C	3000 750	zinc oxide=chromia copper, zinc, and chromium oxides	Characterized by low equilibrium conversions at temperatures of industrial interest. Heat removal is also a problem. Methanol can be converted over certain zeolite catalysts to high octane gasoline in high yield.
Higher Alcohol Synthesis	$2n\text{H}_2 + n\text{CO} \rightleftharpoons \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1)\text{H}_2\text{O}$ $(n+1)\text{H}_2 + (2n-1)\text{CO} \rightleftharpoons \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1)\text{CO}_2$	-30Kcal -CH ₂ -	280-350°C 320-430°C	400°C	1500-2500	modified methanol catalysts (alkali promoted)	Not practical on commercial scale. Isobutanol is a major product. More selective syntheses are needed.
Isosynthesis	$\text{CO} + \text{H}_2 \rightarrow \begin{cases} \text{isobutane} \\ \text{isobutene} \\ \text{other branched} \\ \text{+ linear aliphatics} \end{cases}$			400 -450°C	4500-9000	thoria, thoria-alumina thoria-2rO	Developed in Germany for producing branched aliphatics for high octane gasoline. Pressure requirements are extreme. Alcohol formation below 375°C, CH ₄ , C ₂ H ₆ , C ₃ H ₈ above 475°C.
Fischer Tropsch	$n\text{CO} + 2n\text{H}_2 \rightleftharpoons n\text{CH}_2$ $2n\text{CO} + n\text{H}_2 \rightleftharpoons n\text{CH}_2 + n\text{CO}_2$ $n\text{CO} + 2n\text{H}_2 \rightleftharpoons n(\text{CH}_2)_n\text{OH}$ $+ (n-1)\text{H}_2\text{O}$	-39.4 -48.9 -30		180°-200°C	atmospheric	Cobalt-thoria on kieselguhn	Straight chain hydrocarbons mostly saturated. Appreciable monoolefins (peak at C ₃ -C ₄). Branch chain hydrocarbons mostly monomethyl. < 1% oxygenates.
				220-350°C	300-430	cobalt-thoria- magnesia promoted iron	Catalyst life increases. Hydrocarbon yield 10-15% higher. Alcohols are about 5%. Product distribution depends on reactor type and operating conditions. Mainly hydrocarbons products.
				100-150°C	725-14000	ruthenium	High molecular weight straight chain paraffins.
				400-150°C	2000	alkalized iron turnings	} 30-50% oxygenates, mostly straight chain alcohols.
				180-200°C	70-700	reduced ammonia catalysts	
				180-200°C	300-750	precipitated iron oxyl	
Kolbel-Englehardt	$3n\text{CO} + n\text{H}_2\text{O} \rightleftharpoons n(\text{CH}_2)_3 + 2n\text{CO}_2$	-59.8	<500°C	200-260°C	15-	Fischer-Tropsch catalysts	Work in this area begun in 1949 and discontinued in early 1950's due to petroleum availability. Up to 75% of product mix is olefinic. 45-60% is C ₈ -C ₁₀ hydrocarbons.

high octane gasoline through the Mobil M process.

There is currently also a resurgence of interest both in higher alcohol synthesis and in Kölbel-Englehardt chemistry.

II. Reactor Types

There are three major types of reactors used in coal gasification systems: fixed bed, fluidized bed, and entrained flow. In the fixed bed systems, the reactive gases are passed through the bed in either co-current or countercurrent flow, the latter being the predominant contacting scheme. Coal is introduced at the top of the gasifier with steam (and air, O_2 , or heat exchange media) being injected at the bottom. Ash is removed at the bottom either dry or as a molten slag. The gasifier can be conveniently divided into four zones from bottom to top: (1) ash zone; (2) heated zone (frequently an oxidation zone where coal is combusted with air or O_2); (3) reduction (gasification) zone where CO and H_2 are produced; and (4) devolatilization zone where feed coal is devolatilized with hot product gas.

The advantages of fixed bed gasification are as follows:

- (1) high carbon conversion due to high residence time of coal
(~ 1 hour)
- (2) product gas contains no solids
- (3) lower operating temperatures than entrained or fluidized gasifiers
- (4) devolatilization leads to increased methane which is useful for fuel gas production

The disadvantages of fixed bed gasification are:

- (1) caking coals generally require expensive pretreatment
- (2) gasifier requires sized coal (1/2 in. to 2 in.)(15 to 40% of mined coal may be too small for fixed bed gasifiers.)
- (3) devolatilization leads to increased methane which is a disadvantage for synthesis gas production
- (4) tars generated by devolatilization must be removed from product gas.

Entrained flow gasifiers react pulverized coal with a cocurrently fed gasifying medium at high temperatures and short residence times. The ash is removed either dry or as a molten slag depending upon operating temperatures.

Entrained flow gasifiers have the following advantages:

- (1) all coals can be gasified without any pretreatment. The coal particles are separated from each other by the flowing gas streams and are gasified so rapidly that there is no time for agglomeration.
- (2) no by-product formation. The cocurrent flow leads to devolatilization followed by oxidation and/or reforming so that hydrocarbons, tars, phenolics, etc. are not present in the raw gas. This is useful for synthesis gas production.
- (3) highest overall energy production per unit reactor volume.

The disadvantages are:

- (1) CO/H_2 ratios tend to be high ($\sim 2/1$) so that shifting the product gas is required.
- (2) low methane content reduces fuel gas heating values.

- (3) exit gases have a high loading of ash
- (4) entrained flow gasifiers require the highest temperatures due to short residence times. This leads to thermal efficiency losses.

Fluidized bed gasifiers operate with crushed or fine coal. They generally operate at temperatures between fixed bed and entrained flow gasifiers. The residence times are also intermediate. The state of development of these gasifiers leaves much room for potential improvement.¹⁰

The advantages of fluidized bed gasification are:

- (1) excellent gas-solid contacting
- (2) ability to handle small particles and fines
- (3) intermediate characteristics between those of fixed bed and entrained flow lead to smaller advantages and smaller disadvantages in general.

The disadvantages are:

- (1) narrow range of operating conditions due to fluidization requirements
- (2) caking coals require pretreatment
- (3) carbon conversions (85 to 90%) are lower than fixed bed
- (4) high ash loading in exit gas

III. Heating Methods

The reactions of coal with steam and with carbon dioxide are highly endothermic so that the heat of reaction must be supplied by any of several methods. The method most commonly employed is the injection of air, oxygen, or enriched air into the coal bed directly so that the highly exothermic combustion reactions supply the requisite heat.

Since roughly 42 Kcal/mole must be supplied (including the heat necessary to vaporize the water), roughly 30% of the coal must be burned in the gasifier to achieve thermoneutrality. If oxygen is used, additional coal will be required for its generation. If air is used, a low Btu gas of about 100 to 250 Btu/SCF results. This gas has limited uses except for on-site fuel gas since its energy content is too low for economical pipeline transport and the nitrogen content makes this gas unsuitable for synthesis gas processes. If processes which operate efficiently with a dilute synthesis gas stream were developed, a considerable savings in coal gasification might be realized through the elimination of the expensive oxygen plant (see remarks below).

Several process schemes for supplying the reaction heat have been proposed and piloted. Heat exchange media have included hot ash (Agglomerating Ash Process, Battelle/Union Carbide), hot char (Cogas), and hot gas (Pintsch-Hildebrand), to mention just a few. Electrical heating has also been proposed along with process heat from HTGR (high temperature gas reactors). The CO_2 acceptor process couples the exothermic reaction

of dolomite with CO_2 to the carbon-steam reaction

The removal of CO_2 also enhances the water gas shift reaction.

At the present time, the cost of electricity precludes its use for supplying the process heat. Nuclear process heat still remains a possibility, but the future status of nuclear power is unclear. A differential economic analysis by Shinnar¹¹ comparing direct oxygen-blown gasification with processes using separate air-blown combustors (from which process heat is derived by transfer of char, ash, inerts, etc.) shows that for syngas production the advantage of direct is +\$30 to +\$265/mscf and for fuel gas -\$20 to +\$195/mscf. The gain through elimination of the oxygen plant is offset by air compression, turbine power recovery, SO_2 scrubber, incremental gasifier cost, and incremental CO_2 removal. The CO_2 acceptor process which also has no O_2 plant requires a separate regenerator and it is difficult to thermally balance the reactions among the three fluidized beds.

IV. Operating Mode

The temperature of operation determines the condition of the ash in the gasifier. The two most common modes are dry ash and slagging. At high temperatures below the ash fusion temperature,* the ash tends to agglomerate and such operation is usually undesirable. In general, slagging operations take place at 1200°C ($\sim 2200^\circ\text{F}$) and higher while dry ash gasifiers operate at 1000°C (1800°F) or lower.

There are several advantages to operating a gasifier as a slagger:

---

* The ash fusion temperature depends on the ash composition and so there is some variability from coal to coal.

- (1) the design of the gasifier itself is simplified since there is no need for grates and mechanical devices for ash removal.
- (2) for oxygen blown gasifiers, the steam/oxygen ratio can be optimized so that high thermal efficiencies result. (Not all slagging gasifiers, however, run at this optimum.)
- (3) the higher operating temperatures with attendant higher rates increase the volumetric throughput of the reactor.

The principle disadvantage of the slagger is that it produces a low H_2/CO ratio, usually in the vicinity of 1/2. Most synthesis gas processes require at least 1/1 H_2/CO (e.g. Fischer-Tropsch) to prevent coking of the catalyst while methanol synthesis requires 2/1 H_2/CO and a catalytic methanation most often employs a ratio of 3/1. The development of synthesis gas catalysts that operate with 1/2 H_2/CO ratios or provide internal water gas shift would be worthwhile avenues of investigation. In most cases, it is more economical to separately shift to higher H_2/CO ratios than to try to generate the required ratio in the gasifier itself by increasing the H_2O/O_2 ratio.¹² For other cases, it remains a break-even proposition.

V. Process Variables

Temperature

The rates of the various coal gasification reactions increase with increasing temperature. At the same time, the composition of the raw product gas is also heavily dependent on the temperature. Although the situation is complicated by the fact that there are several simultaneous reactions and that equilibrium is generally only approached, a few

generalizations concerning the effect of temperature can be made.

High temperatures (1800°F) favor high hydrogen and carbon monoxide production with the H_2/CO ratio approaching 1 at a H/O ratio of 2. Lower temperatures favor the formation of methane and carbon dioxide. As mentioned previously, temperatures above 2200°F generally lead to ash fusion and slagging operation. If the temperatures are too low (< 1600°F) carbon conversions are generally poor and the resulting char is difficult to sell. For hydrogasification processes, the char is generally used to make the hydrogen.

Pressure

Higher pressures in the gasifier favor the formation of methane and carbon dioxide relative to carbon monoxide and hydrogen. This is especially advantageous for the production of fuel gas. Table 2 contains equilibrium data for the C, H, O system at various temperatures, pressures, and H/O ratios.¹³ It should be remembered that equilibrium with respect to all the simultaneous reactions occurring in a gasifier is rarely achieved. Increasing the H/O ratio increases the concentration of H_2 and CH_4 relative to CO and CO_2 while decreasing this ratio has the converse effect.

In addition to affecting the raw gas composition, operation at elevated pressures presents some operating advantages:

- (1) higher gasification rates per unit reactor volume.
- (2) lower compression costs since it is cheaper to compress the reactant gases than the product gases (reactant gas volume/product gas volume = 0.20-0.25).

Table 2

Equilibrium Compositions in the C, H, O System

P atm	T °F	H/O	1			10			20			50			100		
			1500	2000	2500	1500	2000	2500	1500	2000	2500	1500	2000	2500	1500	2000	2500
		1	32.6	33.2	33.3	26.9	32.1	33.0	23.2	31.0	32.7	17.9	28.5	31.9	14.1	25.6	30.7
		2	48.6	49.8	49.9	43.7	47.9	49.5	34.0	46.2	48.9	26.1	42.1	47.5	20.4	37.5	45.5
		3	58.1	59.7	59.9	46.9	57.4	59.3	40.3	55.2	58.7	30.8	50.1	56.8	24.1	44.5	54.2
CO		1	60.9	66.5	66.7	40.7	65.3	66.6	32.9	64.0	66.5	23.5	60.5	66.2	17.7	56.1	65.8
		2	45.9	49.9	50.0	36.7	49.1	50.0	25.1	48.2	50.0	18.0	45.9	49.9	13.6	42.8	49.8
		3	36.8	39.9	40.0	25.1	39.4	40.0	20.4	38.8	40.1	14.7	37.1	40.1	11.1	34.7	40.1
CH ₄		1	0.4	0.1	0.0	2.3	0.5	0.1	4.3	1.0	0.3	6.4	2.1	0.7	7.9	3.4	1.2
		2	0.9	0.1	0.0	3.8	1.2	0.3	9.2	2.2	0.6	13.6	4.5	1.5	16.7	7.2	2.7
		3	1.3	0.2	0.0	8.8	1.7	0.5	13.0	3.1	0.9	19.0	6.4	2.1	23.3	10.1	3.9
CO ₂		1	4.0	0.1	0.0	18.0	1.1	0.1	23.5	2.0	0.2	30.0	4.6	0.5	34.1	7.8	0.9
		2	2.3	0.0	0.0	7.3	0.6	0.0	13.7	1.2	0.1	17.6	2.6	0.3	20.1	4.5	0.5
		3	1.5	0.0	0.0	6.8	0.4	0.0	9.0	0.7	0.1	11.7	1.7	0.2	13.3	3.0	0.3
H ₂ O		1	2.1	0.1	0.0	11.5	1.0	0.1	16.1	2.0	0.3	22.1	4.3	0.7	26.2	7.2	1.4
		2	2.3	0.1	0.0	8.4	1.2	0.2	18.0	2.2	0.3	24.7	4.8	0.8	29.2	8.0	1.5
		3	2.3	0.1	0.0	12.4	1.1	0.2	17.3	2.1	0.3	23.8	4.7	0.8	28.1	7.7	1.5

(3) gas purification and synthesis are more economical because of smaller vessels.

(4) waste heat recovery is facilitated at higher pressures.

(5) increased methane (for fuel gas production).

It can be shown that a gasifier should not be operated at a pressure much lower than the pressure required for downstream processing of the gas. In fact, there is a significant penalty associated with atmospheric pressure gasifiers. This results from the requirement of product gas compression and the requirement that all high temperature equipment be rated at 200 psi. Not until pressures of 500 psi and higher are specified do the increasing steel and fabrication costs offset these gains. Thus the optimal pressure range for coal gasifiers is 200 to 500 psi.¹⁵

Steam-Oxygen Ratio

For the oxygen blown gasifier, the steam-oxygen ratio is a major variable affecting gasifier performance. By examination of the stoichiometric constraints imposed by the reactions

(assuming no methane formation) and by imposing thermoneutrality, Shinnar has shown that, for the case of no excess carbon, oxygen or steam, the reaction can be written as

The two limiting cases are:

All intermediate cases $0 < x < 1$ are of course accessible. Case A has a $\text{H}_2\text{O}/\text{O}_2$ ratio of 1.6 and H_2/CO ratio of 0.45 but consumes more O_2 than B. Case B has a $\text{H}_2\text{O}/\text{O}_2$ ratio of 8.2 and a H_2/CO ratio of ∞ , i.e. no CO. When O_2 and steam preparation are included, the thermal efficiencies become 81% for A and 72% for B. The low CO_2 content of A is also an additional advantage.

If methane formation is accounted for, a similar analysis combining the equations

leads to

The two limiting cases are

$$x = 1$$

The thermal efficiencies are 86% and 87% for C and D, respectively.

However, while reactions A and B are realizable in standard gasifiers,

C and D are subject to severe thermodynamic and kinetic constraints.

In order to achieve the requisite rates at the low temperatures required for high CH_4 formation, the gasification must be catalyzed. If the

desired end product is SNG, then this may indeed be a desirable process.

But if either fuel gas or synthesis gas is desired, there is no strong incentive to go the high pressure, catalyzed gasification processes for fuel gas and a strong disincentive for synthesis gas.

The conclusion drawn from considerations of stoichiometrics, kinetic, and equilibrium constraints is that gasifiers operating near reaction A

($H_2O/O_2 = 1.6$) have several advantages:

- (1) Gasifier temperatures are in the slugging range.
- (2) Cold gas efficiency⁺ is higher.
- (3) Net thermal efficiency⁺⁺ is higher.
- (4) Low CO_2 production.

The low H_2/CO ratio is a disadvantage for synthesis gas production since for synthesis gas production since most processes require $H_2/CO \geq 1$.

There is an incentive here for the development of synthesis gas processes capable of operating at low H_2/CO ratios so that the high thermal

$$^+ \text{Cold gas efficiency} = \frac{\text{LHV clean gas}}{\text{net LHV coal}}$$

$$^{++} \text{Net thermal efficiency} = \frac{\text{energy out} - \text{energy in impurity (H)}}{\text{net LHV coal}}$$

efficiencies of these gasifiers can be maintained.

Coal Type

As is well known, the term coal is applied to a wide spectrum of carbonaceous materials of varying chemical compositions and physical and chemical properties. The ASTM system (Table 3) classifies coals by fixed carbon content and volatile matter for higher rank coals (high volatile A through unthracite) and by calorific content for lower rank coals (high volatile A through lignite). The primary factors for coal gasification are coal reactivity and coal caking.

In general, United States coals can be divided into eastern and western coals. The western coals are mostly lignites and sub-bituminous coals with high volatiles and low calorific content. They tend to be more reactive and weakly caking to non-caking. (Caking properties begin with bituminous coals which tend to be strongly caking and decreases with coal rank down to the lignites which tend to have little or no caking tendencies.) Eastern coals are mostly bituminous coals, have strong to moderate caking characteristics, and are less reactive. Table 4 gives a qualitative comparison of the two broad classes. For gasification purposes, the western coals are clearly more suitable. The eastern coals with their higher calorific contents are probably best utilized by direct combustion in power plants.

Table 3

ASTM Coal Classification by Rank

<u>Class and group</u>	<u>Fixed carbon^a</u> (%)	<u>Volatile matter^a</u> (%)	<u>Heating value^b</u> (Btu/lb)
I. Anthracitic			
1. Metaanthracite	> 98	< 2	
2. Anthracite	92-98	2-8	
3. Semianthracite	86-92	8-14	
II. Bituminous			
1. Low volatile	78-86	14-22	
2. Medium volatile	69-78	22-31	
3. High volatile A	< 69	> 31	> 14,000
4. High volatile B			13,000-14,000
5. High volatile C			10,500-13,000 ^c
III. Subbituminous			
1. Subbituminous A			10,500-11,500 ^c
2. Subbituminous B			9,500-10,500
3. Subbituminous C			8,300-9,500
IV. Lignitic			
1. Lignite A			6,300-8,300
2. Lignite B			< 6,300

^aCalculated on dry, mineral-matter-free coal; correction from ash to mineral matter made by means of Parr formula.

^bCalculated on mineral-matter-free coal with bed moisture content.

^cCoals with heating values between 10,500 and 11,500 Btu/lb are classed as high volatile C if they possess "agglutinating" properties or as subbituminous A if they do not.

Table 4

Qualitative Comparison of Eastern and Western Coals

	<u>Carbon</u>	<u>Oxygen</u>	<u>Sulfur</u>	<u>Volatiles</u>	<u>Moisture</u>	<u>Caking</u>	<u>Reactivity</u>	<u>Heating Value</u>	<u>Minemouth Cost</u>
Bituminous	Higher	Lower	Higher	Lower	Lower	Higher	Lower	Higher	Higher
Subbituminous									
Lignite	Lower	Higher	Lower	Higher	Higher	Lower	Higher	Lower	Lower

VI. Economics of Gasification Processes

In this section, we will examine plant investment costs for several coal gasification processes to delineate those areas which are the most capital intensive. The data is limited to that in Shinnar's report and to the C. F. Braun study of second generation coal gasification processes.¹⁶ Table 5 summarizes the data for the dry ash Lurgi, the BGC slagging Lurgi, and the Texaco gasification processes. The total direct investment costs per daily MM Btu of product gas are estimated at \$2845, \$1590, and \$2140, respectively. The high cost areas are steam plant, oxygen plant, and the gasifier itself. Acid gas removal (H_2S , CO_2) together with sulfur recovery is also another major item. The relative costs of these items depends, of course, on the particular process. The oxygen plant and waste heat boiler are high for the Texaco process while its low steam consumption and simple gasifier design lead to lower costs in these areas.

The data in Table 6 contains the C. F. Braun factored estimates for western coals gasified via four second generation processes with the dry ash Lurgi process taken as the base case. The processes are evaluated for the production of SNG, which was the primary motivation for their development. The costs were estimated (per MMBtu SNG) at \$2727 for Hygas, \$2777 for CO_2 Acceptor, \$3239 for Bigas, \$4688 for Synthane (dry feed), and \$3324 for dry ash Lurgi. The major costs are again incurred with gasification, acid gas removal, steam plant, and oxygen plant. Methanation and shift conversion were not included in Table 5.

Table 5

Breakdown of Capital Investment for Selected Processes

	<u>Dry Ash Lurgi</u>	<u>BGC Lurgi</u>	<u>Texaco</u>
Coal Handling and Prep.	0.0	10.1	9.3
Gasifier (Includes coal feed & ash removal)	20.8	17.1	8.4
Gas Cooling & Waste Heat Boiler	7.5	3.8	23.4
Gas Liquor Separation	2.3	1.9	--
Phenol Removal	1.8	1.9	--
NH ₃ Removal	2.3	2.2	2.3
Waste Water Treatment	3.2	1.6	--
H ₂ S Removal	3.5	3.1	3.7
Sulfur Plant	3.5	3.1	3.7
O ₂ Plant	13.3	22.6	34.1
Steam Boiler & Superheater	24.8	20.1	5.6
Offsites	8.9	12.6	9.3
	<u>100.0%</u>	<u>100.0%</u>	<u>100.0%</u>

Table 6
Breakdown of Capital Investment for Selected Processes

	<u>Hygas</u>	<u>CO₂ Acceptor</u>	<u>Bigas</u>	<u>Synthane</u>	<u>Lurgi</u>
Coal Storage	1.9	1.9	1.6	1.2	1.7
Coal Prep.	2.5	8.5	4.2	5.4	3.1
Coal Feed	3.8	3.9	2.1	6.9	23.0
Gasification & P.R.	6.6	27.8	5.4	4.1	↓
Raw Gas Quench	2.8	9.2	6.2	3.5	
Shift	4.5	--	4.0	4.4	
Acid Gas Removal	15.8	5.2	14.1	10.8	
Methanation	4.3	5.2	3.6	2.8	14.1
Sour Water Stripping Ammonia Removal	8.5	2.6	4.6	3.6	7.0
Sulfur Recovery	8.8	7.5	7.3	6.6	2.3
Solids Disposal	1.3	1.2	1.1	0.8	0.4
Product Gas Drying	0.1	0.1	0.1	0.1	0.1
Steam & Utility Systems	20.0	14.4	22.7	29.9	21.4
Plant Water System	2.5	2.6	3.1	1.7	2.6
Oxygen Plant	6.6	--	10.0	8.3	7.8
General	10.0	9.9	10.0	10.0	10.0

VII. Advantages and Disadvantages of Various Selected Processes

It is not our intention to quantitatively compare the many existing and proposed coal gasification processes. Instead, a qualitative assessment of several selected processes in terms of the discussions in Sections I-VI will be presented. The processes selected were chosen to be representative of the proven and emerging technologies. The only class not represented were the molten media schemes such as Atgas (molten iron) and Kellogg (molten salt) processes.

The proven technologies chosen were the Lurgi process, the Koppers-Totzek, and the Winkler. They also typify the three broad classes of gasifier: fixed bed (or more accurately, moving bed), entrained bed, and fluidized bed, respectively. Of the three, the Winkler is probably the weakest technology.

Of the emerging technologies, the BGC (British Gas Corporation) Lurgi slagger is a modification of the standard dry ash Lurgi designed for high temperature (slagging) operation. The volumetric throughput is greatly enhanced (estimated at 2 to 4 times) over that of the dry ash process. In addition, steam consumption is greatly decreased. The Shell-Koppers gasifier represents an attempt to eliminate the highly detrimental low pressure operation of the standard Koppers-Totzek process. The Texaco gasifier is an entrained flow gasifier of simple design which had previously seen considerable application for the production of synthesis gas from hydrocarbon feedstocks. It is currently under intensive development as a coal gasifier.

Many of the so-called second generation processes in the United States were designed with the idea of producing SNG directly in the

gasifier. Processes such as Hygas, Bigas, Synthane, and Hydrane are all examples of high pressure processes (1000 psi and greater) which attempt to promote direct carbon reduction with hydrogen via incorporation of hydrogasification zones within the gasifier or, in the case of Hydrane, utilize hydrogen as the gasifying medium. The interesting thing to note is that, with the exception of Hydrane which yields 68% CH₄ in the product gas, methane yields are in the 15 to 20% range which is not too much higher than the dry ash Lurgi process. The future of these processes is still in doubt, particularly when compared with BGC Lurgi, Texaco, or Shell-Koppers.

Of the remaining processes (Exxon catalytic, Cogas, and CO₂ acceptor), all have eliminated the need for an oxygen plant but by different methods. Exxon catalytic utilizes KOH to catalyze the water gas reaction so that the process can operate at lower temperatures and higher pressures (500 psi) thus promoting methane formation. The gasifier effluent is cleaned, acid gases are removed, and the gases cryogenically separated to a pure methane product and a CO, H₂, CH₄ recycle stream. Cogas supplies the endothermic heat of the water gas reaction by circulation of hot char between an air combustor and the gasifier. It can be shown, however, that such methods of indirect heating via external combustion with air probably lead not to savings but to increased capital costs due to the cost of air compressions, scrubbing, power recovery systems, etc. The CO₂ acceptor process supplies reaction heat by utilizing the heat of the lime-CO₂ reaction in the gasifier. This particular practice appears in an old British Patent (Krupp, Brit. Pat. 8426, 1892). The process has several advantages but is complicated by the need to keep the heat load in balance.

Information pertinent to each of these processes is outlined in Table 7. A qualitative assessment of each of the processes follows.

Dry Ash Lurgi

Advantages:

1. Proven technology.
2. Pressure of 300 to 450 psi is in the optimal range.
3. Methane in raw gas of 8 to 14% is good for fuel gas production.
4. H_2/CO ratio of 2/1 minimizes or eliminates shift.
5. High coal conversion ~99%.

Disadvantages:

1. High steam consumption mainly due to the need to prevent slagging. The excess steam is used to cool the combustion zone. This high consumption results in lowered net thermal efficiencies.

2. By products of tars and oils (100 lb/ton of coal) and aqueous liquors (5200 lb/ton of coal) present a disposal problem.

3. Caking coals require pretreatment.

4. Sizing requirement of 18 in.-1-1/2 in. means that 15 to 40% of mined coal is too small for fixed bed gasification.

5. Methane content of 8 to 14% is detrimental for synthesis gas processes.

6. High CO_2 content (30%) in product gas.

Koppers-Totzek

Advantages:

1. Proven technology.
2. Slagging operation allows for lower steam consumption.
3. No by-product tars or oils.

Table 7

Process Data for Selected Coal Gasification Processes^{17,18}

Process	DA Lurgi	Koppers-Totzek	Winkler	BGC Lurgi	Texaco	Shell-Koppers
Type	Fixed Bed	Entrained Flow	Fluid Bed	Fixed Bed	Entrained Flow (coal-water slurry)	Entrained Flow
Gasifying medium	Steam	Steam	Steam	Steam	Steam	Steam
Heating method	air/O ₂	air/O ₂	air/O ₂	O ₂	O ₂	O ₂
Mode	dry ash	slagging	dry ash	slagging	slagging	slagging
Temp.	C.Z. ⁺ -1800°-2500°F G.Z. ⁺⁺ -1200°-1500°F Out-700°-1000°F	C.Z.-3500°F Out-2700°F	1500-1800 depending on coal type	Out 800-1000°F	Above ash fusion temp.	Above ash fusion temp.
Pressure	300-450	20	30	300-450	300-1200	450
Steam/O ₂	6-8	0.8	1.5	1.3	1.6	
O ₂ /coal	0.45	0.94	0.76	0.54	0.95	
CGE [*]	78	71	75	90	75	
NTE ^{**}	67	58	57	77	72	
By-products	Tars Tar Oil	None	None	Tars Tar Oil	None	None
Special treatment of caking coals	yes	no	yes	yes	no	no
Coal sizing	1/8"-1-1/2"	70-90% > 200 mesh	0 x 3/8"	1/8"-1-1/2"	pulverized	70-90% > 200 mesh
Methane (water-free basis)	8-14%	0	1-2%	6-8%	0	0
H ₂ /CO	2/1	6/10	1/1	1/2	2/3	6/10
Raw Gas Composition						
H ₂	21 40	29 34	26 39	29 31	29 35	32
CO	9 17	46 53	24 36	54 57	42 52	55
CH ₄	5 9	0 0	1 1	7 7	0 0	0
CO ₂	16 30	9 10	15 22	2 2	8 10	11
H ₂ O	47 --	14 --	33 --	6 --	18 --	--

⁺ C.Z. = Combustion Zone^{**}NTE = Net Thermal Efficiency⁺⁺ G.Z. = Gasification Zone^{*}CGE = Cold Gas Efficiency

Table 7. Continued

Process	Bigas		Hygas		Synthane		Hydrane	
Type	Entrained flow (coal-water slurry)		Single Vessel Multistage fluidized Bed (coal-water slurry feed)		Fluid Bed		Free fall dilute phase with fluid bed	
Gasifying medium	steam		steam		steam		H ₂	
Heating method	O ₂		O ₂		O ₂ /air			
Mode	slagging		dry ash		dry ash		dry ash	
Temp.	Stage 1 2700°F Stage 2 2200°F Out - 1700°F		Slurry Dryer 600°F Stage I 1200°F Stage II 1700°F C.Z. 1850°F		Fluid Bed 1800°F Outlet 1400°F		Fluid Bed 1800°F Outlet 1250°F	
Pressure	Medium 300-500	High 1000-1300	1150		1000		1000	
Steam/O ₂	1.6	2.5	7.3		3.7		--	
O ₂ /coal	0.57	0.49	0.25		0.34		--	
CGE	85	89	88		85		[1]	
NTE	80	78	78		73		[1]	
By products	none		light oils(BTX)		tars, oils char contains 50-70%C		char contains 85% C	
Special treatment of caking coals	probably none		yes		yes		no	
Coal sizing	70% through 200 mesh		-10 mesh		-20 mesh		70%-200 mesh	
Methane (water free basis)	9	15	16		20		68	
H ₂ /CO	7/10	8/10	1/1		1/1		3/1 ^[2]	
Raw Gas Composition								
H ₂	30	33	20.5	27	15	30	14	20.5
CO	43	47	26.5	36	13	26	15	22
CH ₄	8	9	11	15	8	16	13.5	20
CO ₂	8	9	16	21	12	24	23	34
H ₂ O	9	--	25.5	--	50.5	--	32	--

[1] No good estimates are available.

[2] Polishing methanator is used to generate more methane.

Table 7. Continued

	Cogas ^[3]		CO ₂ Acceptor	Exxon Catalytic
Process				
Type	Fluid Bed		Fluid Bed	Fluid Bed
Gasifying medium	Steam		Steam	Steam
Heating method	Hot char circulation		Exothermic Chemical Reaction $\text{CaO} + \text{CO}_2 \rightarrow \text{CaO}_3$	Steam $2\text{C} + 2\text{H}_2\text{O} = \text{CH}_4 + \text{CO}_2$ for which $\Delta H_R \approx 0$
Mode	Dry Ash		Dry Ash	Dry Ash
Temp.	Gasifier 1600°F Combustor 3500°F		Gasifier 1500°F Regenerator 1850°F	1300°F
Pressure	15-45		150	500
Steam/O ₂	--		--	--
O ₂ /coal	--		--	--
CGE				
NTE				
By products	1 bbl/ton #4 fuel oil		none	none
Special treatment of caking coals	none		Non-caking only	none
Coal sizing	0 x 1/8"		-8 + 100 mesh	- 8 mesh
Methane (water-free basis)	4		14	100
H ₂ /CO	2/1		3/1	0
Raw Gas Composition				
H ₂	58		59	
CO	31		16	
CH ₄	4		14	100 ^[4]
CO ₂	7		9	

[3] Cogas was developed for the gasification of char from the COED process, a multistage fluid bed pyrolysis for the production of low sulfur fuel oil (#4 equivalent).

[4] The gasifier effluent is CO, 6.3%; H₂, 22.5%; CO₂, 14.8%; CH₄, 22.9%; H₂O, 33.5%. After CO₂ and H₂O removal, there remains CO, 12.2%; H₂, 43.5%; CH₄, 44.3%. These gases are separated cryogenically into a product stream of pure methane (34%) and a recycle stream (66%) of composition, CO, 19%; H₂, 70%; CH₄, 11%.

4. Accepts caking coals without pretreatment.
5. Absence of methane is advantageous for synthesis gas production.
6. High coal conversion $\sim 96\%$.

Disadvantages:

1. Atmospheric pressure operation leads to pressure mismatch for most subsequent synthesis gas processes and pipelining. Compression costs lead to large losses in net thermal efficiency.
2. Very high temperature operation leads to high oxygen consumption requiring large oxygen plants and further losses in net thermal efficiency.
3. High CO/H_2 ratio of 6/10 will require shifting for most synthesis gas processes.
4. Lack of methane is detrimental for fuel gas production.

Winkler

Advantages:

1. Proven technology.
2. No by-product tars or oils.
3. Ability to handle small particles and fines.
4. Good temperature control.
5. Safety--the high inventory of fuel in the reactor minimizes the chances of oxygen breakthrough in the event of fuel interruption.

Disadvantages:

1. Atmospheric pressure operation leads to pressure mismatch for most subsequent synthesis gas processes and pipelining. Compression costs lead to large losses in net thermal efficiency.
2. High oxygen demand leads to further loss in net thermal efficiency and large oxygen plant.

3. Coal conversion is low ~86%.
4. Certain bituminous coals (free swelling index > 4) require pretreatment.
5. High CO₂ content (22%) in product gas.

BGC Lurgi Slagger

Advantages:

1. Pressure of 300 to 450 psi is in the optimal range.
2. Methane in raw gas of 6 to 8% is good for fuel gas production.
3. Favorable H₂O/O₂ ratio of 1.3 due to slagging operation leads to high thermal efficiencies.
4. Moderate oxygen consumption.
5. Low CO₂ content (2%) in product gas.
6. Coal conversion is ~ 100%.

Disadvantages:

1. By product tars and oils need to be upgraded or disposed. Aqueous liquors, while far less than those from dry ash Lurgi (because of far lower steam requirements), still require treatment.
2. Caking coals will probably require the addition of a flux (15% blast furnace slag) for gasification.
3. Sizing requirement of 1/8 in. x 1-1/2 in. means that 15 to 40% of mined coal is too small for fixed bed gasification.
4. Methane content of 6 to 8% is detrimental for synthesis gas processes.
5. H₂/CO ratio of 1/2 requires shift conversion for most synthesis gas processing.

Texaco

Advantages:

1. Pressure of 450 psi is in the optimal range.
2. No by-product tars or oils.
3. No methane in product gas is beneficial for synthesis gas.
4. No waste, phenols, or aqueous liquors for treatment.
5. Net thermal efficiency is between dry ash Lurgi and slagging

Lurgi.

6. Accepts all coals, as well as tars and by-products from other gasifiers.

7. High coal conversion ~ 100%.

Disadvantages:

1. High temperature operation and slurry feed result in high oxygen demand which decreases net thermal efficiency and requires large oxygen plant.

2. Lack of methane is detrimental for fuel gas production.

3. High CO/H₂ ratio of 3/2 will require shifting for most synthesis gas processes.

Shell-Koppers

This gasification process should be quite similar to the Texaco system.

The gasifier will be a four-headed Koppers-Totzek designed for operation at 450 psi. The objective is to eliminate the most detrimental feature of the standard Koppers-Totzek process, atmospheric pressure operation.

The throughput of the gasifier is expected to increase by a factor of

six. The advantages and disadvantages listed for Texaco will probably apply here. This is potentially a very attractive process since, like the BGC slagger, it is based upon an already proven technology.

Bigas

Advantages:

1. For medium pressure operation (300 to 500 psi), pressure is in optimal range.
2. No by-product tars or oils.
3. Lower oxygen demand than Texaco but comparable to slagging Lurgi.
4. Methane in product gas (9%) is beneficial for fuel gas production.
5. Accepts all coals.
6. High coal conversions.

Disadvantages:

1. Methane content is detrimental for synthesis gas.
2. High pressure operation (1000 psi) leads to nominal gains in methane at greatly increased vessel costs.
3. High CO/H₂ ratios will require shifting for most synthesis gas processes.

Hygas

Advantages:

1. By products are predominately light oils (BTX) ~ 54 to 57 lbs/ton of dry coal.
2. Small oxygen demand leads to decreased O₂ plant costs.
3. High methane is advantageous for fuel gas.
4. High thermal efficiencies in spite of high H₂O/O₂ ratio.

Disadvantages:

1. High steam/O₂ ratio (17.3) leading to reduced thermal efficiencies.
2. High pressure (1160 psi) leading to increased vessel costs and surprising little CH₄ production (16%).

3. Complicated vessel design incorporating slurry dryer, two hydro-gasification fluidized beds, and a combustion zone with associated internals for transfer of solids.

4. Carbon conversion is low (61 to 71%).

5. Caking coals require pretreatment.

Synthane

Advantages:

1. High methane (15%) is advantageous for fuel gas.

2. Small oxygen demand leads to decreased O_2 plant costs.

Disadvantages:

1. High pressure operation (1000 psi) leads to increased vessel costs while increasing methane to only 15%.

2. Methane content is detrimental to synthesis gas processes.

3. Caking coals require pretreatment.

4. Carbon conversions are low ~ 65%.

5. By-product tars amount to 94 lb/ton coal.

Hydrane

Advantages:

1. -High methane content (68%) in the raw gas requiring a small methanation plant for conversion to SNG.

2. Process accepts all coals.

3. By-product oils (mainly BTX) at 26 lb/ton of coal.

Disadvantages:

1. Hydrogen must be made via gasification, electrolysis, etc. The process requires 160 lbs H_2 /ton of coal. If made by gasification, then oxygen and steam plants will also be required.

2. High pressure process (1000 psi) leads to increase vessel costs and coal feeding problems.

3. Carbon conversions are low. Char from gasifier contains up to 85% C which is gasified to make H_2 .

Cogas

Advantages:

1. No oxygen plant. Hot char circulation provides reaction heat.
2. Integrated process which removes volatiles through pyrolysis process (such as COED) and then gasifies resulting char.
3. Favorable H_2/CO ratio of 2/1 for most synthesis gas processes. Methane content, while low (4%), could be a problem.

Disadvantages:

1. Low pressure of 15 to 45 psi will require further compression leading to decrease in net thermal efficiency.
2. Yields from the pyrolysis step are quite low (1 bbl/ton from COED). The extra investment for all this processing may not be justifiable.

CO_2 Acceptor

Advantages:

1. No oxygen plant. Reaction heat supplied by exothermic combination of CO_2 with CaO .
2. No by-product tars.
3. Gas produced has high methane content and the remaining H_2/CO ratio is about 3 which is ideal for subsequent catalytic methanation without prior shift conversion.
4. In-situ CO_2 removal enhances both the shift and methanation reactions.

Disadvantages:

1. Process is limited to highly reactive western coals (lignites and subbituminous) because gasifier must operate at 1600°F or less due to dolomite acceptor.
2. Process is mainly directed toward fuel gas and not toward synthesis gas.
3. Potential operating difficulties may arise because of the need to balance material flows between three fluidized beds.
4. Regeneration of CaCO_3 is expensive.

Exxon Catalytic

Advantages:

1. SNG (methane) is made in a single vessel without any subsequent downstream processing.
2. No oxygen plant.
3. Minimal heat requirements since reaction is almost thermally neutral.
4. Accepts all coals since catalyst (KOH) prevents caking.
5. Low gasification temperature (1250° to 1300°F).
6. Reactor is simple without complicated internals.
7. No by-product tars and oils.

Disadvantages:

1. SNG production only.
2. Catalyst must be recovered and recycled.
3. Process is still in very early development stage.

VIII. Conclusions

From an engineering viewpoint, generating innovative ideas which will lead to considerable economic advantage for coal gasification is quite difficult. Coal gasification has been commercially practiced for over 150 years and is a mature technology today. By its very nature coal gasification is an energy intensive process. The "coal molecule" consists of a number of polyaromatic and polyhydroaromatic structures linked together by alkyl chains of varying lengths and includes ether, carboxyl, sulfide, and desulfide linkages. The gasification of coal results in the breaking of a large number of bonds, i.e. a complete disruption of the coal matrix. The resulting product is a gas composed of simple molecules (CO , H_2 , CO_2 , CH_4) which can be burned as a fuel gas or used to synthesize more complex molecules. The very notion of gasification is one in which the chemical complexity of coal is circumvented by destroying the structure and starting over with a simple material. This is in direct contrast with coal liquefaction which attempts to preserve much of the coal structure by concentrating on the disruption of the coal matrix by selectively breaking the bonds which link the aromatic pieces together. This concept is more attractive from a rational viewpoint, but coal liquefaction has technical and economic problems which may negate this primary advantage. Nevertheless, the basic stoichiometric, kinetic, and thermodynamic constraints on coal gasification are rather severe and dictate that the process is inherently expensive.

Another problem with coal gasification is that the term is generally applied to all processing (and expenses incurred) from coal storage and

preparation to the delivery of a clean product gas. This includes many items which really have nothing to do with gasification per se but are associated with the total processing required for handling a difficult material like coal. Thus, when it is stated that for a coal to gasoline plant 80% of the investment cost is for coal gasification, there would be significant changes in cost distribution if a raw product gas rather than a clean synthesis gas were delivered to the methanol plant.

The technology of coal gasification seems to have reached the point where future gains will be marginal rather than substantial. It is also not clear that more basic understanding of coal gasification from a chemical viewpoint would enable the development of much less expensive gasification processes. But it seems that without such basic understanding, we have progressed about as far as we can.

There are many areas in which further research and development in support of coal gasification should be pursued. These include materials research, modelling and scaleup of coal gasifiers, instrumentation, and diagnostic procedures, etc. Such improvements lie beyond the scope of this report. We feel the following areas could yield substantial benefits:

1. Development of gasifiers and processes which minimize steam and/or oxygen consumption.
2. Development of new and cheaper acid gas removal systems.
3. Development of an efficient staged fluidized bed gasifier.
4. Study of basic coal chemistry with emphasis on the kinetics and mechanism of gasification.
5. Study of coal pyrolysis kinetics and mechanism.

6. Study of the low temperature, catalyzed carbon-steam reaction.
7. Study of free radical reactions which are important in coal gasification. What radicals are important, how are they generated, etc.
8. Development of synthesis gas conversion processes that utilize high CO content synthesis gas. This includes new Fischer-Tropsch catalysts, Klbel-Englehardt ($\text{CO} + \text{H}_2\text{O}$) and modified Klbel-Englehardt ($\text{CO} + \text{H}_2 + \text{H}_2\text{O}$) syntheses.

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