Coal Gasification: Direct Applications and Syntheses of Chemicals and Fuels

A Research Needs Assessment

by the DOE Coal Gasification Research Needs (COGARN) Working Group

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COAL GASIF, ICATION: DIRECT APPLICATIONS AND SYNTHESES OF CHEMICALS AND FUELS*

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ABSTRACT

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The DOE Working Group for an Assessment of Coal-Gasification Research Needs (COGARN - coal gasification advanced research needs) has reviewed and evaluated U.S. programs dealing with coal gasification for a variety of applications. Cost evaluations and environmental-impact assessments formed important components of the deliberations. We have examined in some depth each of the following technologies: coal gasification for electricity generation in combined-cycle systems, coal gasification for the production of synthetic natural gas, coal gasifiers for direct electricity generation in fuel cells, and coal gasification for the production of synthesis gas as a first step in the manufacture of a wide variety of chemicals and fuels. Both catalytic and non-catalytic conversion processes were considered. In addition, we have constructed an orderly, long-range research agenda on coal science, pyrolysis, and partial combustion in order to support applied research and development relating to coal gasification over the long term.

The COGARN studies were performed in order to provide an independent assessment of research needs in fuel utilization that involves coal gasification as the dominant or an important component. The findings and research recommendations of COGARN are summarized in this publication.

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CHAPTER 1: SUMMARY OF RESEARCH RECOMMENDATIONS

The COGARN studies on coal gasification encompass the use of gasifiers for a wide variety of applications. Specifically included are all direct uses of the gases produced from coal, as well as conversions of product gases to chemicals and liquid fuels (indirect coal liquefaction). The research priorities summarized in this chapter were arrived at by COGARN members working as a group and therefore represent a consensus on research needs. These listed research needs were defined after a 12-month period of intensive review and study involving six separate full-day meetings at different locations, where discussions were held with many coal-gasification experts after presentations of on-going research by resident scientists and engineers. The fifty experts who provided valuable inputs are identified in the contributor listing of the Acknowledgments. While the scope of our deliberations was broad, it was not encyclopedic. In order to provide balance and perspective, we have solicited external reviews to this study (cf. Formal Reviews of the COGARN Report) with the expectation that the expert reviewers would provide independent comments and highlight important omissions and possible bias.

The gasifier is part of a complex process, of an integrated system, and it must accordingly be optimized as a unit operation within the context of the overall system. The proper perspective is total economic return. Coal gasification is always performed in connection with a downstream process. The primary emphasis may be on electricity generation, on syngas production for pipeline applications, or on syntheses of fuels and chemicals.

Neither the gasification system nor a research recommendation should be viewed as affecting a single unit process (e.g., the gasifier) but rather as impacting an integrated system that handles coal, contains a gasification

unit, and can ultimately produce an array of products for the fuel, chemical, gas, and electricity industries. The primary goal may involve one or more applications (e.g., electricity generation, electricity production with cogeneration of steam, production of multi-product slates of chemicals and fuels). The multi-product slates and opportunities for multiple applications make coal-gasification systems unique in the chemical process industries and offer important opportunities for cooperation in research between government and a variety of important US industries. This type of cooperative approach is required in order to assure a US competitive edge in domestic and international markets, particularly since potential foreign competitors appear to view coal-gasification systems from this same broad perspective.

In the absence of a quantitative procedure for optimizing process synthesis and because of the fact that experienced design engineers will remain, for some time to come, the most important element in the synthesis of a process flowsheet (compare Sec. 2.2), it appeared appropriate to ask members of the COGARN Working Group to identify primary areas for research emphasis in order to advance the art and science involved in the construction of improved coal-gasification systems. A random compendium of all of the three highest priority research tasks identified by COGARN members is summarized in the first column of Table ES-1 on pages 4A and 4B. This list was distributed to COGARN members with a request to identify the top four priority items. The selections made and their weighted preferences (with ten for first priority, five for second, two for third, and zero for fourth) are given in the last column of Table ES-1.

It will be noted that the entries in Table ES-1 are not listed according to the final weighted priority, which was arrived at according to the procedure described in the preceding paragraph. Thus, the initial random ordering of the first three choices made by individual COGARN members was retained deliberately in order to emphasize the fact that it is inappropriate to attach special significance to the listed numerical values because these numbers were arrived at by using the specified arbitrary weighting of 10, 5, 2, and 0 for the first four choices in the final list, respectively. Any different weighting of COGARN member priorities would have yielded different numbers for the final weighted priorities. The

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initial 33 different top three priority listings made by 11 COGARN members dealt with the 18 topical areas listed in Table ES-1, many of which represent first-priority choices for two or more COGARN members.

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Examination of the data listed in Table ES-1 shows that all of the listed research and development areas have their proponents, which is inevitable in view of the procedure used to obtain this list of entries from COGARN members with diverse interests and responsibilities. Selection of items (8), (11) and (18) for first or second priority reflects the COGARN members' predilection for an integrated systems approach in arriving at optimized gasification processes, while emphasis on items (2) and (10) indicates preoccupation with environmental controls that have become a major cost item in synfuels technologies, in general, and in coal gasification, in particular.

All of the items listed in Table ES-1 are important and merit support. If such topics as (6), (7), (12), and (14)-(17) are not adequately funded, there is little hope for innovation based on new scientific information. If item (2) goes unfunded, near-term systems cost reductions may be in jeopardy; special opportunities for savings are associated with items (1), (5), and (9). High load factors and low operating costs may result from success with item (13), while optimal process synthesis itself depends on advances of the type specified in connection with topics (3) and (4).

We may summarize the COGARN Working Group R&D recommendations as follows:

(i) Each of the topics (1) to (18) represents a vital research area in the advancement and improvement of cost-effective coal-gasification systems.

(ii) Priority assignments reflect the background and problem areas faced by individual investigators and cannot be made in an absolute sense and in a manner acceptable to a diverse group such as the COGARN members.

(iii) We recognize the overriding importance of item (11) if we are to proceed from the laboratory to commercial operation in an orderly fashion and in an advantageous manner in international competition.

(iv) R&D efforts merit support provided they (a) offer the promise of significant advances through innovative new approaches or (b) bring significant cost savings through incremental improvements in component

operation that benefit overall systems performance through reductions in capital, operation and maintenance costs. There are no entries in Table ES-1 that do not meet one of these two requirements.

In the Overview of Chapter 2, we return to the more traditional approach of component optimization by summarizing briefly the salient recommendations derived from the more detailed studies in Chapters 3 to 13. It should be recalled that this Summary of Research Recommendations and Chapter 2 represent assessments by the COGARN Working Group as a whole, while Chapters 3 to 14 contain the views of individual identified authors. Table ES-1. Summary of the three highest priority research and development recommendations for long-range emphasis identified by individual COGARN members.

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	Priority Research and Development Areas W P	eighted riority
. (1)	Continue fundamental research aimed at improved un- derstanding of the behavior of coals in gasifiers. This work should include a search for gasification catalysts and feed-preparation methods that improve gasifier performance and may reduce costs while in- creasing operating life; the selection and improve- ment of methods of coal feed for fixed-bed gasifiers require special attention.	4.0
(2)	Develop hot-gas clean-up techniques (for NH ₃ , alka- lis, heavy metals) and especially hot sulfur-removal systems and in-bed sulfur capture (including in-bed use of zinc ferrite, lime/limestone/dolomite) and ho filters.	7.7 t
(3)	Identify preferred gasifier configurations and per- form needed materials research to handle high-S and high-C1 coals in IGCC systems producing electricity and other products.	4.2
(4)	Develop and characterize slurry reactors to produce methanol and higher alcohols for fuels, together with electricity, from synthesis gas.	2.9
(5)	Develop mass-production techniques for oxygen from air separation at acceptable purity for gasification (~95%) in order to reduce oxygen-production costs.	6.0
(6)	Develop and test diagnostic techniques for improved measurements of (a) inflows of solids and liquids and (b) local reactor conditions in gasifiers and auxiliary systems to define rates and mechanisms of fouling and to improve scale-up procedures of solid- feed reactors.	6.9
(7)	Obtain expanded data for equilibria and kinetics involving sulfur compounds in alternate clean-up systems (including sulfur redox reactions in liquid aqueous and other solvents.)	3.4
(8)	Evaluate the integrated performance characteristics of advanced (pressurized) gasification technologies	4.3

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	Priority Research and Development Areas	Weighted Priority
	in combination with alternate downstream processing for both oxygen- and air-blown systems.]
(9)	Improve and validate scale-up procedures for coal gasifiers.	1.9
(10)	Develop a greatly expanded environmental data base for emissions, fates, and associated health hazards of trace constituents emanating (in gaseous, liquid and solid wastes) from coal-gasification systems.	6.9 5 1,
(11)	Determine limiting capacities of individual equip- ment (gasifiers, etc.) in demonstration coal gasi- fication facilities, such as Cool Water, Great Plains, etc., in order to obtain a needed data base for optimum design of future plants.	6.3
(12)	Develop chemical and physical understanding of coal conversion phenomena and their relations to (a) cha formation, (b) ash formation, (c) condensable pro- ducts chemistry, and (d) catalytic effects.	1- 4.6 ar
(13)	Develop comprehensive (numerical) models for gasi- fiers based on our best scientific knowledge of che ical and physical phenomena and validate and improv these models by performing appropriate laboratory a field measurements.	3.8 em- /e and
(14)	Characterize the properties of gasification residue including chemical analyses, leachability, and dis- posal methods.	es, 4.9 -
(15)	Define new and better syntheses (especially of ethanol from syngas) and determine the suitability of (to C_5 alcohols as fuels for transportation systems) with proper regard for costs, octane enhancement, toxicity, emissions, and distribution.	a- 2.2 71
(16)	Perform needed R&D to define opportunities for direct use of low H_2 to CO ratios in chemical synthes	3.0 ses.
(17)	Support needed research for total upgrading of Fischer-Tropsch products.	1.6
(18)	Investigate the applicability of knowledge-based ex	k− 3.6

pert systems, artificial intelligence and advanced computational methods to the design of improved systems involving integrated coal-gasification plants.

CHAPTER 2 OVERVIEW OF COAL-GASIFICATION R&D NEEDS

2.1. Introduction

Estimates of US coal resources and reserves indicate ready availability at current (~ 933×10^6 tons in 1985) and anticipated future production rates for several centuries, although prices in constant dollars are expected to rise from depressed 1985 levels of about \$20/ton fob utilization representing about 78% of total US generating capacity.

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Based on application of 1978 technology, world-wide coal reserves corresponded to about 3.04×10^{12} bbl of oil equivalent, with the US share of 28% of the total exceeding that of Europe (20%), the USSR (17%), China (16%), and other countries. Coals are characterized according to a variety of measures, with coal rank (roughly related to carbon content and heat of combustion) being a preferred measure in Western countries.

The direct utilization of coals currently dominates industrial and residential applications. This field has been examined in an antecedent study.¹ While direct utilization of coal has represented the lowest cost use and has therefore enjoyed the widest market penetration, the direct utilization of coals for electricity generation is being challenged by integrated coal-gasification combined cycle (IGCC) systems with gasification before combustion. When specified environmental standards must be met, IGCC systems may be competitive with or superior to direct coal use with required environmental control measures.*

The successful technologies that have been developed for coal gasification have opened up alternative markets that include not only gasifiers for IGCC systems but also gasifiers combined with fuel cells, gasification

* The Glossary should be consulted for definitions of abbreviations.

to produce methane as a substitute for natural gas, and gasification for the production of syngas followed by syntheses of chemicals and fuels. The processes, science and technologies involved in these coal-utilization schemes are reviewed and evaluated in this study. The compilation is not meant to be encyclopedic and the discussion of selected topics, as well as the omission of others, represents neither more nor less than the opportunity for COGARN review and study of an important, albeit limited, subset of a vast data and information base.

We have structured this report by beginning with accounts of gasification for electricity generation, SNG production, syntheses of fuels and chemicals, and fuel-cell applications. Next, we comment on gasification catalysts, coal feed, beneficiation, and solids processing. We conclude with potential applications of advanced diagnostics to coal gasifiers and the scientific underpinnings of the entire field, namely, coal conversion and coal properties as determinants in the design and development of coalgasification systems. The concluding chapter deals with costing of coalgasification systems as an example of our estimating capabilities for synfuels production.

While our discussions of coal-gasification systems and applications may stress developments of unit processes or unit-process components, the thesis of this study remains the necessity to view coal-gasifiers as components of integrated systems and improvements in unit-process performance as elements in integrated systems performance. The true measure of system-component improvement remains the improvement of system economics.

Reference for Section 2.1

 "Coal Combustion and Applications," a report prepared by the DOE Coal Combustion and Applications Working Group, Energy <u>9</u>, 361-418 (1984); see also Progr. Energy Combust. Sci. <u>10</u>, 87-144 (1984).

2.2. <u>Process Synthesis</u>

In accord with the primary approach to gasification identified in the Executive Summary, we place very great importance on viewing gasifiers

as components of integrated systems. The ultimate goal of a coal-conversion process is to produce a final product: power, chemical, fuels or any combination of these. Coal-conversion processes have in the past been discussed in terms of a sequence of unit operations, with attention focused on technical problems encountered in specific unit processes. This procedure reflects undue emphasis on specific unit operations that appear in existing flowsheets, rather than on process sythesis with primary identified goals. Experienced design engineers will remain, for some time to come, the most important element in the synthesis of a process flow sheet. , ` ; ;

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We note the growing use of computer-based design aids and even the beginnings of applications of artificial intelligence (AI) methods in the process synthesis of complex systems. Proponents of AI believe that its uses in synthesis and design in the process industries will become increasingly important during the next two decades. It is clearly desirable to include coal-conversion processes, in general, and coal-gasification systems, in particular, within the category of complex process systems for which powerful new tools will be needed in order to assure an orderly approach to systems optimization.

One of the primary goals of research on process synthesis is to establish methodologies for determining optimal pathways from raw materials to final products. The current status of such techniques involves an interplay of heuristics, more formalized AI, and designer experience. Coalgasification development has generally emphasized optimization of obvious pathways through a process, rather than exploration of dramatic new routes to the final product.

Long-term advances in coal-gasification processes will undoubtedly rest on the development of process flowsheets that eliminate some of the currently-employed technology, i.e., some of the normal unit operations. Clearly, the most advanced techniques of process synthesis should be utilized in the development of novel flowsheets. The present state of the art in the discipline of process synthesis is unlikely to bring about major advances in ways of thinking about coal-gasification processes. However, process synthesis is a dynamic field of research and can be expected to move quickly. Coal gasification contains features that are uncommon in other process industries, while the latter have been providing technical

motivation for ongoing research. The nature of gas-cleanup requirements is a particularly cogent example of technological differences. The often unique features of the coal-gasification system may require emphases in process-synthesis research that would not be driven by other processindustry needs. It is therefore appropriate that some financial support be directed towards research in the area of process synthesis from those interested in the development of optimal coal-gasification flowsheets in order to ensure that new methodologies will be applied promptly and properly to coal-gasification systems.

2.3. Gasifiers for Electricity Generation

Coal gasifiers are easily incorporated into an integrated gasifier combined-cycle (IGCC) system producing electricity. From a utility perspective, this system has many advantages over traditional electricity-generation systems: low pollutant emissions, modular installment capability, relatively high energy-conversion efficiency and, in some cases, a lower net electricity cost.

Cool Water is a demonstration plant producing over 100 MWe of power. The successful operation of this plant has raised the level of confidence within the utility industry to the point where several large IGCC systems are being considered or planned. Utilities can expand or replace obsolete equipment by first installing turbines (with or without combined cycles) fired by NG and, at an appropriate time, installing coal-gasification units. This route avoids a full-scale commitment to both technology and capital investment and may therefore be a preferred strategy for utilities facing uncertain rates of return and capacity requirements.

Key research recommendations for improving entrained-flow gasifiers of the type used at Cool Water relate to the control of fouling and slagging and of corrosion and fatigue, high-temperature sulfur removal, gasifiers for low-rank coals, and low-cost gas separations and air enrichment. These are detailed in Sec. 3.4 The U-GAS system represents one of a number of alternate gasification schemes and is discussed in Sec. 3.3-3.

Our selection of gasifiers for detailed description is illustrative rather than exhaustive and does not represent a value judgement of

preferred technologies for IGCC applications.

2.4. Gasification for Syngas Production

The research and development needs associated with the long-range objectives of the gas industry in coal gasification cover a broad spectrum of activities, ranging from engineering studies to basic research. These needs include operational and economic data on large, integrated coalgasification plants, expanded engineering data bases, and the development of fundamentally-oriented information on the rate-controlling steps in the various process elements. While the gas industry needs are focused on coal gasification related to the production of high-Btu syngas or SNG, many of the process steps are generic and will be useful in a variety of coalgasification applications. Needs relate to engineering development, a technology data base and fundamental research. ć

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Engineering development requires: (i) large-scale operational and performance data on integrated coal-gasification plants such as the Cool Water integrated coal-gasification combined-cycle power-generation plant and the Great Plains coal-to-SNG plant; (ii) expanded engineering data bases for oxygen-blown, ash-agglomerating fluidized-bed gasifiers to optimize designs for specific processes or applications (high-pressure operations, fines collection and recycle, coal types, in-bed desulfurization); (iii) scale-up data for emerging technologies such as the direct methanation concept and the CNG advanced acid-gas removal concept; (iv) integrated performance evaluations of advanced gasification technologies such as the BGC/Lurgi slagging gasifier and the ash-agglomerating, fluidized-bed process with advanced downstream processing concepts such as direct methanation and CNG acid-gas removal processes; (v) development and validation of scale-up models with particular emphasis on coal gasifiers; (vi) exploratory studies to develop initial data bases for new or advanced process concepts for gasification and downstream processing; (vii) improved, high-temperature heat recovery systems; (viii) expanded environmental data bases for advanced technologies in the areas of trace-constituent production, fate, control, and disposal or treatment.

The technology data base requires: (i) development of metal alloys for high-temperature heat-recovery applications; (ii) development of improved ceramics for high-temperature applications (i.e., particulate filters, valves); (iii) expanded data bases on the erosion-corrosion behavior and resistance of metals and ceramics in coal-gasification environments; (iv) long-term corrosion data (for > 10,000 hr) in coal-gasification environments, i.e., in the presence of alkali metals, sulfidation, and chlorine compounds; (v) vapor-liquid equilibrium data at elevated pressures and temperatures for selected multicomponent systems involoving synthesis gas, steam, heavy oils (tars), light aromatics, phenolics, fatty acids, CH_4 , H_2S , CS₂, COS, mercaptans, NH₃, HC1, HCN, AsH₃, SeH₂, Hg, Zn, Pb, Cd; (vi) transport data (thermal conductivities, viscosities, diffusivities) for tars and slurries, especially in mixtures of solids with oils, tars and water; (vii) thermodynamic data (free energies of formation, heats of formation, entropies, specific heats) for all important constituents; (vii) vaporliquid equilibrium data in sour-water strippers for $H_0O/NH_3/CO_2/H_2S$ systems at 0 to 100 psig and 70 to 400°F; (ix) improved correlations for predicting mass-transfer coefficients and other engineering design parameters in multicomponent systems.

Basic research needs include: (i) improved understanding of the chemical processes associated with and controlling the fragmentation/gasification of coal; (ii) improved models for predicting vapor-liquid equilibria in multicomponent systems.

2.5. Gasification for Syntheses of Fuels and Chemicals

2.5-1. Overview

Chemicals constitute only about 7% of production from fossil fuels. However, manufacturing and marketing of high-value chemicals has a major impact on the US economy and our balance of trade. Although it is traditional to separate the fuels (utility, transportation and industrial) and chemical businesses, the production of synthesis gas (SG) is common to both the fuels and chemicals industries.

The distinction between fuels and many chemicals has become blurred for the following reasons: (i) Any utility plant based on SG will also be a potential source of SG for the production of chemicals and fuels. (ii) Any plant for the synthesis of chemicals from SG is a potential source of clean utility, transportation or industrial fuels. (iii) SASOL converts SG to more than 3 x 10^6 TPY of motor fuels but also produces more than 0.65 \times 10⁶ TPY of chemicals such as ethylene, ammonia, and polymers in the product slate. (iv) The Mobil methanol-to-gasoline (MTG) process has been commercialized in New Zealand with conversion of off-shore NG to over 4000 TPD of methanol, which is then converted to 14,500 BPD of high octane gasoline. Methanol may be used as a peaking or transportation fuel. In the MTO pro-cess, Mobil has converted methanol to C_2-C_4 olefins (chemicals, monomers) at high yields (56-81%) using a 100 BPD semi-works plant in the FRG, which was previously used for the fluidized MTG process. Mobil is also converting olefins from the MTO and FT processes into gasoline and diesel fuel with over 95wt% selectivity. All of the Mobil processes involve use of the shape-selective zeolite catalyst ZSM-5. In New Zealand, the MTG process has been used to obtain high yields of durene, which is unwanted in gasoline but is an excellent source of the valuable monomer pyromellitic anhydride. Gasoline made via the MTG process contains about 38wt% of BTX (benzene, toluene and xylenes); these compounds are petrochemical feedstocks and can be made in about 60wt% yield via ZSM-5 for use as chemicals. (v) SG is the primary source of H_2 , which is a fuel and is also used in making chemicals (ammonia, nylon) or fuels (hydrocracking, upgrading of heavy oils, hydrogenation of materials for fuels or for chemicals, potential use in direct liquefaction of coal, etc.). (vi) CO is an excellent fuel and is also used in carbonylation reactions to make chemicals [acetic acid, phosgene, methyl acetate (also a fuel), ethanol (a desirable fuel), etc.]. (vii) A medium-BTU gas mixture of CO and H_2 is an excellent clean fuel, that may be pipelined for over 100 miles. (viii) Tennessee Eastman makes methanol (a fuel, chemical) and acetic anhydride (a chemical). Surplus SG is available as an industrial or utility fuel via an IGCC plant. (ix) Northern Great Plains makes methane (a fuel) and methanol. (x) The Ube (Japan) Texaco gas-

ifier is used to make ammonia (a chemical); an IGCC plant is being considered for utility use. (xi) Japan and France have a 7000 BPD plant in Japan to make C_1-C_5 alcohols from SG. ENI (Italy) produces C_1-C_5 alcohols from SG for fuel use. (xii) Research is needed to synthesize ethanol directly from SG. Ethanol has usually been classified as a chemical but has also been used as an additive in transportation fuels (gasohol). The 1986 General Motors manual honors car guarantees with designated methanol and ethanol additives to gasoline.

The future prosperity of the utility industry may well depend on the flexible use of clean energy sources (i.e., IGCCs) as at Cool Water and Dow. The plant may use NG, petroleum or coal-gasification products interchangeably. As in the petroleum industry, the use of SG for electricity production will spawn plants for manufacturing transportation fuels and chemicals. Similarly, chemical plants using SG will spawn plants for power production.

The three main pathways for SG utilization are: (i) fuels and chemicals made directly (Table 2.5-1), (ii) fuels made via methanol by indirect syntheses (Table 2.5-2), and (iii) a long list of products from the reaction of SG or CO with another chemical, some of which are listed in Table 2.5-3.

Table 2.5-1. Principal fuels and chemicals made directly from SG.

ammonia, methanol, hydrogen, carbon monoxide, gasoline, diesel fuel, methane, isobutane, ethylene, C1-C5 alcohols, ethanol, ethylene glycol, C2-C4 olefins

Table 2.5-2. Principal fuels and chemicals made via methanol (indirect synthesis).

formaldehyde, acetic acid, gasoline, diesel fuel, methyl formate, methyl acetate, acetaldehyde, acetic anhydride, vinyl acetate, ethylene, propylene, ethanol, C1-C5 alcohols, propionic acid, benzene, toluene (BTX), xylenes, ethyl acetate, a methylating agent

methanol + isobutane	H+ >	methyl tert-butyl-ether
olefins + H ₂ + CO	CO ₂ (CO)8	aldehydes and alcohols
olefins + CO + H ₂	<u>H+</u>	highly branched acids
chlorine + CO	>	COC12 (phosgene)
methanol + HCl	>	chloromethanes
methanol + xNH3	>	methylamines
methanol	>	single cell protein
toluene + methanol		styrene
methyl propionate + HCHO	bases	methyl methacrylate
nitrobenzene + methanol + CO	>	isocyanates (urethanes)
terephthalic acid + methanol	>	dimethyl terephthalate

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Table 2.5-3. Some products from the reaction of SG or CO with a chemical not derived from SG.

2.5-2. <u>Research Recommendations</u>

The use of SG for fuels and chemicals is the wave of the future. By the year 2010, this country will be well on its way to an economy built largely on the use of clean fluid fuels, with coal gasification as a primary component. The acid-rain problem and transportation-fuel shortages may be solved by the use of SG. The following are research requirements: (i) Additional research is needed on the synthesis of ethanol from SG. Present selectivity to ethanol from SG is approaching 70%. Ethanol is used as an octane enhancer (gasohol has 10% of ethanol in gasoline); it is used neat in Brazil. Since the federal subsidy for fermentation ethanol may soon be removed, there is increased urgency for a better synthesis from SG. (ii) The direct production of C_2-C_5 alcohols also suffers from a lack of selectivity and poor understanding of conditions and catalysts needed for synthesis. The C_2-C_5 alcohols may be used directly as transportation fuels but are more

likely to be employed for blending with methanol as an octane enhancer or in the production of tertiary ethers (these are excellent octane enhancers). (iii) There is great uncertainty about the use of alcohol fuels, especially methanol and C_2-C_5 alcohols. Blending characteristics of these fuels in gasoline or the use of neat alcohols are not understood. Determination of the suitability of alcohols as transportation fuels or additives is needed, with emphasis on costs, octane enhancement, automobile compatibility, distribution problems, toxicity, and emissions. (iv) Methods for separating CO_2 in coal gasification with <10 ppm of H_2S are needed. Trillions of SCF of CO_2 are needed in enhanced oil recovery; it is also useful in supercritical extraction, refrigeration, carbonation, polymer production, etc. (v) CO₂ is the intermediate in the commercial synthesis of methanol using Cu/ZnO/Al $_2$ O $_3$ catalyst. Clarification of the role of CO $_2$ in methanol synthesis may lead to processes with reduced CO to H_2 ratios, with CO_2 replacing large amounts of CO. (vi) Studies should be conducted to identify major potential cost savings resulting from integration of the gasifier with down-stream processing. Thus, oxygen-purity requirements to minimize the cost of the overall process should be examined. (vii) Research is needed on the direct use of low H_2/CO SG in slurry FT processes. (viii) Improvements are needed in low-temperature, sulfur-tolerant water-gas-shift (WGS) efficiencies and economies to make either high H_2/CO SG or H_2 by minimizing excess steam requirements. (ix) FT reactor design, as in the slurry reactor, should be improved. (x) Continued exploration is needed on homogeneous and heterogeneous low-temperature/high-activity methanol synthesis catalysts. (xi) Work should be continued on the development of SG conversion catalysts that tolerate higher feed impurities (e.g. S compounds). (xii) Studies should be continued on the direct upgrading of the total vaporous FT-reactor effluents through improved catalyst design. (xiii) Improved FT catalysts are needed, especially catalysts with higher activity for FT and WGS and higher stability in producing lower light HC yields. (xiv) Investigations should be performed to obtain improved methods for upgrading FT wax via new catalysts and processes.

2.6. Gasifiers for Fuels Cells (FCs)

An overview of current and developing FCs is presented in Sec. 6.1 while Sec. 6.2 deals with special features of coal gasifiers for FC applications. The principal conclusions reached, insofar as the gasifier is concerned, are the following: (i) Site-specific emission requirements can be easily met and by-products must be properly eliminated. (ii) The plant configuration is modular and can be erected and on-stream within a 3-4 year period. (iii) The coal-gasifier-FC-system is expected to be economically competitive in the 100-150 MWe range. こうちょう さいたい おうごう とおう いたい

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The coal-gasifier unit should be a modular 20-50 MWe unit producing H_2 and CO. An atmospheric-pressure air-blown unit is acceptable but a pressurized gasifier would be preferable. The gasifier must be reliable for operation on a wide range of coals. It should produce H_2 -Co mixtures with high efficiency, yield minimal amounts of tar and oils in the raw-gas condensate, and become commercially available between the early and mid-1990s.

Since candidate gasification systems include units such as Shell, Texaco, Lurgi, KRW, KGN, MHI, and U-GAS, we recommend that the role of DOE, if any, be confined to cost-sharing with EPRI of an appropriate utilitydevelopment program. No long-range research to develop gasifiers specifically for FCs appears to be required.

2.7. Gasification Catalysts

Section 7.1-1 contains brief summaries of examples of current research on gasification catalysts used in the reactor itself for the temperature range 800 to 900°C.

Catalysis at much lower temperatures is also being investigated (cf. Sec. 7.1-2) and holds the promise of far greater cost reductions for capital equipment and operations. A currently pursued research area involves catalysts constructed by combining KOH, CsOH, NaOH, or LiOH with mixtures of transition-metal oxides. Significant conversions have been observed in the laboratory on time scales of hours at temperatures near

525°C and above. Empirical classification of efficiencies of transitionmetal oxides has shown, for example, that NiO is the most effective metal oxide tested thus far in combination with KOH and that the combination of KOH with NiO is far more effective than either KOH or NiO alone in the conversion of graphite according to the overall process 2C + 2KOH

 \rightarrow 2COK + H₂. A similar result was observed for gas production from Montana subbituminous coal. For coals, H₂-production rates are high initially and then decay with time. The mechanisms of catalysis for transition-metal oxides mixed with KOH are under active study. It has been found from XPS diagrams that the binding energies for NiO-KOH mixtures do not show the same resonances as NiO alone, whereas the KOH resonances are not materially changed. Fundamental work directed at finding low-T catalysts is clearly worth pursuing.

Section 7.2 deals with the development of the Exxon process for catalytic coal gasification (CCG) in the presence of 10 to 20% K. The work was carried through successfully to a PDU (1 mt/day) before termination. Long-term process and equipment performance data are needed on a large pilot plant before scale-up to commmercial plant sizes. Also needed are results for a variety of coals. Environmentally acceptable performance over a long period of time remains to be demonstrated. Required research areas include the following: (i) definitions of optimal coal-pretreatment conditions for different coals and catalysts; (ii) studies of rates and mechanisms of salt leaching from coal ash during counter-current washing for catalyst recovery and studies to reduce costs of the recycle system; (iii) identification of lower-cost, environmentally-benign, throw-away catalysts; (iv) identification of catalysts for operation at reduced T.

2.8. Gas Cleanup

Process designs for producing gaseous fuels or synthesis gas from the gasification of coal with steam and air/oxygen usually include one or more process units to treat the gas exiting from the primary reactor in order to bring the gas to the specifications imposed by its intended use.

These process functions are included in the gas clean-up system. The design may call for: (i) quench cooling (possibly with heat recovery); (ii) particulate removal (including removal of tars/oils); (iii) composition adjustment; (iv) acid-gas removal (usually with sulfur recovery).

These processing functions may be performed in various sequences and by using a wide variety of specific process configurations. For example, the quench/cooling step is often combined with particulate removal in a direct aqueous scrubbing step that also removes gaseous contaminants such as NH_3 , chlorides, sulfur-containing gases, and cyanides. Waste materials from the process units may be treated in a variety of processes or disposed of directly, depending on the gasification reactor, coal type, and discharge or waste-handling restrictions. The capital investment costs of these gascleanup systems generally represent 35% to more than 40% of the total capital cost of the gasification plant (exclusive of the end-use processes). . . .

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A summary of commercial and near commercial technologies is presented in Chapter 8. A review of this material leads to the important conclusion that the most probable source of significant economic advances in the gas-cleaning area results from elimination of one or more entire process units. Therefore, DOE research should emphasize approaches which are most likely to allow the elimination of process units or the combination and simplification of process units. The gas-cleanup functions most likely to yield benefits through elimination of units or significant simplification in the overall process are acid-gas removal and sulfur recovery.

The most common commercial design approach to acid-gas removal and sulfur recovery is a two- or three-step process in which acid gases (predominantly CO₂ and sulfur species) are adsorbed from the process gas and subsequently desorbed to produce a concentrated acid-gas waste stream. Sulfur is then removed from this waste stream until levels are reached that meet required environmental restrictions prior to gas discharge. Two approaches currently being investigated have the potential to eliminate at least one of these process steps: (i) hot-gas cleanup through the use of solid sorbents, with or without gasifier in-bed sulfur capture and (ii) liquid redox technologies that remove sulfur from the gas and convert it to elemental sulfur in the same unit.

2.8-1. Hot-Gas Cleanup and In-Bed Sulfur Capture

The use of solid sorbents to remove sulfur from the raw product gas formed in coal gasification provides the following process advantages: (i) delivery of the gas to the treatment system at temperatures in the 800-1200°F range may allow elimination of all or part of the quench/cooling processes and reduce or eliminate condensate normally produced during gas cooling, thus significantly reducing wastewater-treatment requirements and organic condensate handling and disposal, while retaining much of the thermal energy of the hot product gases, at increased thermal process efficiency; (ii) very high sulfur-capture efficiencies may result, which are relatively independent of the distribution of sulfur among the possible gas-phase sulfur species; (iii) sulfur will appear in concentrated solid form, which may be disposed of or reacted to regenerate the sorbent and produce a concentrated waste stream.

Research to date has led to identification of six key issues requiring resolution if hot-gas cleanup with solid sorbents is to be economically and technically viable. These are: (i) high-temperature particulate removal; (ii) reduced sorbent cost; (iii) increased sorbent durability during multiple regeneration cycles; (iv) improved sorbent capacity; (v) treatment or disposal of regeneration off-gases; (vi) disposal of spent sorbent.

Particulates entrained in the raw product gas will degrade the sorbent by obscuring its surface or plugging the gas paths through the reactor. Removal of particulates at high temperature has been accomplished with cyclones. However, the collection efficiency for cyclones is highly dependent on the aerodynamic efficiency for particles of different sizes and drops off rapidly for very small particles. Other approaches that are in the developmental stages involve the use of metal and ceramic filters, ceramic-based filters and high-temperature scrubbers.

Sorbent cost, durability and capacity are obviously closely coupled since less expensive sorbents may become economically viable, even with reduced durability during regeneration. An inexpensive sorbent might be acceptable as a nonregenerable sorbent which is disposed of after a single
use. The three most extensively characterized sorbent materials are activated carbon, calcium oxide (or carbonate) and zinc ferrite. Activated carbon exhibits limited capacity, must operate at relatively low temperatures and has limited durability. Calcium oxide is inexpensive and has high capacity, but its performance is highly dependent on the process-gas composition and it requires relatively long contact times. Zinc ferrite is relatively expensive but has high sorption capacity; its durability must be improved to compensate for its cost. 15.1

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Further investigation of the identified sorbents, as well as evaluation of alternate sorbent materials, sorbent-preparation techniques and sorbent-regeneration conditions may serve to overcome current technology limitations. In addition, phase diagrams of the primary compounds involved in the adsorption and desorption cycles for candidate sorbents should be obtained to provide a basis for the selection of optimal adsorption and regeneration conditions and definition of the optimum form of sorbent materials.

The potential for in-bed sulfur capture through the addition of solid reactants to the gasification reactor is closely related to hot-gas cleanup using solid sorbents. In-bed sorbents must be codisposable with the ash. Therefore, candidate materials must be inexpensive and produce an inert residue, i.e., they must be classified as nonhazardous under current and future RCRA regulations. Sulfur-capture efficiency is directly related to the temperature, residence time, and gas-composition profile experienced by the sorbent as it passes through the reactor. Thus, the configuration and operating conditions of the gasifier are major determining factors in sorbent performance. Both dolomite (a mixture of magnesium and calcium oxides) and lime have been tested as reagents for in-bed sulfur capture. Although other alkali oxides are potential candidates, most lead to significant problems with disposal or to high costs.

Investigations should include the development of reaction data defining both equilibrium compositions and kinetics as functions of gas composition and temperature in order to relate sulfur-capture potential to gasifier configuration and operation. Many of these data are available for lime and dolomite. Development of recovery techniques for reagents that

have higher sulfur capacity but are more expensive would greatly enhance the range of options that may become economically viable for in-bed sulfur capture.

2.8-2. Liquid Redox Processes

Absorption of reduced sulfur compounds in solution, followed by chemical oxidation of the sulfur to elemental sulfur in the solution, provides a one-step approach to the removal and recovery of sulfur from gasification-process gases. If the reagents can be oxidized to their original form, a closed-loop process may be operated. This approach has the following advantages: (i) a single process unit may be used for both removal and recovery; (ii) low reagent replacement-costs may result, depending on efficiency of reagent regeneration; (iii) high sorption efficiency is achieved using established liquid/gas contacting technology.

Commercial applications of the redox approach to sulfur removal and recovery involve aqueous solutions and operate at essentially atmospheric temperature and pressure. Low temperatures are maintained in order to minimize the rates of side reactions that produce non-regenerable compounds. There are reports on the impact of high-pressure operations but these are limited in scope, content and detail.

Experience with several liquid redox processes has led to identification of the following areas requiring further investigation and development: (i) absorber blockage; (ii) improving the quality of the sulfur product; (iii) study of the complex redox chemistry of sulfur with possible multiple oxidation states for the element; (iv) low sulfur-adsorption efficiency; (v) potential for side reactions that reduce the efficiency of elemental sulfur production and reagent recovery; (vi) high pumping and reagent costs; (vii) simplification of the complicated process control that is needed because of the occurrence of complex chemical equilibria and kinetics. Areas of recommended research include: (i) detailed investigation of sulfur redox chemistry; (ii) determination of the precipitation kinetics of elemental sulfur; (iii) investigation of sulfur reaction and reoxidation chemistry

of candidate redox agents or catalysts, including Va, Fe, Co, quinones, etc.; (iv) investigations of high-temperature and high-pressure operations; (v) investigations of alternate solvents for redox reactions of sulfur at higher temperatures and pressures than are possible in aqueous solutions.

2.9. Summary of Research Recommendations on Environmental Issues

Research recommendations related to the environmental control of coal-gasification processes are framed by several general questions regarding the methods and cost of meeting current and future environmental control requirements. These are: (i) Are adequate control technologies available to meet current environmental control requirements for surface⁻ coal-gasification facilities? Can the performance of such technology be predicted reliably to assure compliance with current requirements for air, water and solid waste emissions from commercial gasification processes? (ii) What are the anticipated trends in future environmental control requirements, and how will these affect future gasification technology in various applications? Are adequate technology and information available to handle potential future situations? (iii) What are the potentials for reducting the costs of environmental controls significantly through new process development and/or the development of improved control technology? What research is needed to pursue these opportunities?

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Each of the specified issues is addressed briefly in the following paragraphs.

2.9.1. Understanding Current Technology

Much of the environmental research on coal-gasification processes conducted over the past decade has been directed at characterizing the chemical compositions of gaseous, liquid and solid waste streams from various types of gasifiers. This procedure has aided the design of technology for air-pollution control and waste-water treatment, with the result that current environmental control requirements are generally met, albeit by often using empirical design criteria rather than fundamental understanding.

There are, however, some notable exceptions, which underscore the continuing need for more fundamental research on process factors related to environmental controls. Perhaps the most prominent example is the Great Plains gasification facility in North Dakota, which does not yet comply with SO_2 emission regulations because of the inexplicably poor performance of the commercial sulfur-removal unit (Stretford process). It is generally believed that the problem is related to trace compounds in the gas stream, which alter the chemistry and catalytic processes significantly, as compared to the less complex gas mixtures typically treated with this process. No solution has as yet been found.

In contrast to Great Plains, sulfur removal and recovery systems at Cool Water have performed well on both high- and low-sulfur coals. Selexol for sulfur removal is followed by a modified SCOT plant and a Claus unit for sulfur recovery. Some gasifier trace compounds, which do not pose environmental or health hazards, are operational nuisances because they slowly contaminate the Selexol and SCOT solvents. Cool Water has only minimal wastewater-treatment facilities since the plant is located in an arid region where natural evaporation is effective for disposing of process blowdown water. This treatment and process-water system now perform well, after some stream rerouting during start-up. Most future commercial plants will not be located in an arid climate where natural evaporation is a practical method for process waste-water disposal.

Problems with environmental control-system performance often reflect a lack of understanding of process and chemistry details relating to environmental control-system design and performance. The following research recommendations are thus suggested: (i) Basic research is needed in order to obtain better understanding of process chemistry related to the control of gaseous pollutants. The chemistry of sulfur removal from complex gas mixtures, including the effects of trace compounds found in coal-gasification processes, are of particular concern. (ii) Fundamental research is also needed on gasification-process-water chemistry, particularly in the context of waste-water recycle systems which offer the potential for waste elimination. This research should provide a basic understanding

of the reactions of species and the fates of contaminants common to coal-gasification process condensates and waste waters.

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2.9-2. Future Environmental Requirements

During the past two decades, there has been a clear and continuing trend toward more stringent environmental control requirements for energy-conversion processes of all types. In recent years, environmental requirements have become more comprehensive in scope, covering emissions to all environmental media (air, water and land). At the same time, the level of sophistication with which potential pollutants are identified, measured, and regulated has also increased. While the nature of future environmental requirements inevitably remains speculative, several general trends are likely to affect coal-gasification processes. These include the following: (i) Control of traditional criteria air pollutants (those originally regulated by the 1970 Clean Air Act are SO_2 , particulate matter, NO_y , hydrocarbons and photochemical oxidants) will continue to be important. Recent trends in New Source Performance Standards (NSPS), such as those for combustion-related pollutants, have tended to become more stringent as control-technology capabilities have improved. In terms of future developments, the recent commercialization of technology to reduce emissions of NO_v greatly may compel further tightening of current NSPS requirements. (ii) Toxic air pollutants are likely to become more heavily regulated in response to concerns over their health and ecological impacts. In the context of coal-gasification processes, this development could affect emissions of heavy (trace) metals and organic compounds emitted in small quantities. (iii) Zero discharge of waste-water contaminants can be expected to continue to be the prevailing philosophy guiding regulatory requirements at the federal, state and local levels. This development could have significant implications for commercial coal-gasification facilities located in parts of the country where traditional methods such as solar evaporation ponds cannot be used. (iv) The disposal of solid as well as of liquid wastes will come under increasing scrutiny to make certain that waste materials, by-products,

and potential leachates are environmentally benign. Criteria defining hazardous and toxic substances are likely to evolve as new measurement techniques and research results become available.

Research recommendations derived from these observations include the following: (i) Sustained research is needed to characterize trace metals and other potentially hazardous or toxic emissions to air, water and land emanating from coal-gasification process streams, control technologies and fugitive sources such as cooling towers. (ii) Continued research is also needed in the areas of solid and liquid waste management, particularly the utilization of solid residues as by-products (rather than wastes). Better understanding is required of the fates of organic and inorganic contaminants in the environment (both near-source reactions and long-range transport should be explicated).

2.9-3. Advanced Control Technology

Environmental control systems currently account for a significant portion of total coal-gasification process costs. Therefore, high priority must be assigned to novel or advanced methods for reducing these costs while maintaining environmental quality standards.

The ability to eliminate or substantially simplify environmental control processes will depend, in part, on the gasifier design and, more substantially, on process application. Thus, processes producing gas to be used at room temperature invariably produce condensates requiring some degree of waste-water treatment in addition to gaseous pollutant removal, although gasifier types such as entrained beds produce inherently cleaner condensates than others (e.g., tar-producing fixed-bed gasifiers).

Gasifier applications for electric power generation offer the potential for significant simplification of environmental control systems by using hot-gas cleanup. Removal of pollutants at high temperatures, followed by combustion of the gaseous products, not only yields improved process efficiency but also eliminates several unit operations that are required for low-temperature processing (e.g., waste-water treatment). The ongoing DOE

research program on hot-gas cleanup offers an excellent opportunity for major improvements of this nature. The associated research recommendations are: (i) Current DOE research on hot-gas cleanup is important, generally well-focused, and deserving of strong continued support. Key research needs have been identified and are being pursued to develop viable means for particulate and sulfur removal at high temperatures using gas treatment and/or in-bed removal processes. (ii) Additional research is needed to ensure that NO_{χ} emissions with hot-gas cleanup systems can be controlled to the same degree that is achievable with current low-temperature coal-gasification systems and combustion-gas treatment devices.

2.10. Coal Beneficiation and Feed Preparation; Solids Processing

A cost item in the utilization of coal gasifiers is coal cleanup to meet applicable environmental regulations. One of the procedures that is widely employed for this purpose is pre-combustion cleanup or coal beneficiation, the purpose of which is to prepare as-mined coal and make it suitable for desired end uses. Coal preparation, cleaning and washing are required to meet environmental constraints at minimal costs and also to improve downstream equipment performance.

Beneficiation applied to gasification parallels its use in combustion. The cost of beneficiation may be balanced by savings in the gasifier or combustion equipment. In the same fashion, the size of the coal fed to the two types of processes must be properly selected to fit the peculiar needs of the specific gasifier or furnace. Technology for size reduction and size-classification is generally well developed, although a useful research area has been identified for counter-current, moving-bed gasifiers.

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2.10-1. Beneficiation

The process of coal beneficiation includes size reduction, size classification, removal of impurities, and drying. Table 2.10-1 contains a

summary of currently used commercial procedures for physical or mechanical coal cleaning.

The levels of coal cleaning vary from minimal to full at reduced yields and energy recovery; simultaneously, sulfur levels may be reduced. Costs vary from low to high as the level of cleaning is augmented.

A number of novel physical beneficiation processes have been or are under active development. We refer to Chapter 10 for a description of these techniques. Some of the beneficiation processes have reached developmental status.

Coal beneficiation may become competitive with combustion clean-up of coal and with post-combustion clean-up of effluents. The extent to which one or more of these techniques is employed in any particular gasification process depends on overall costs, including estimates for equipment failures and plant downtimes. While some preparation, cleaning and washing are used almost universally, applications of more sophisticated beneficiation procedures have generally not been judged to be cost-effective.

The development and assessment of the practical utility of coal-beneficiation procedures has been and continues to be of direct interest to DOE, especially in connection with direct coal-combustion technologies, and is viewed by the members of COGARN as a lower priority effort for coal-gasification technologies than for combustion systems.

Table 2.10-1.	Currently use	d procedures	for	physical	or
	mechanical co	al cleaning.			

Process	Techniques	
Size reduction	Rotary beakers, impact mills, single- and double-roll crushers	
Size classification	Vibrating screens, sieve bends, classifying cyclones	
Cleaning	Magnetic separation, concentrating tables, jigs, hydrocyclones, heavy- media cyclones, froth flotation	
Drying	Screens, filters, centrifuges, thermal dryers	

2.10-2. Feed Preparation

Occasionally, new approaches are proposed to surface comminution, such as the use of chemicals to loosen coal particles along their cleavage planes, new machines for preparing micron-sized coal, etc. However, no useful procedure has been found around the basic laws relating to energy requirements for comminution in commercial application. Similarly, improved classification equipment continues to reach the market, including screens and elutriators of various types. This development results from a general trend to use ever finer size fractions in newer gasification and combustion equipment.

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There is, however, one type of gasifier, historically the dominant system, which presents special R&D opportunities, namely, the moving-bed reactor. The apparatus requires passage of the upward-flowing gasifying medium (air, oxygen, steam, and CO_2) through the downward-moving bed of coal. To assure free and even flow and good contact requires special qualities of the solid feed. The ideal feed would have the following characteristics: (i) a preferred, coarse size which may range from 1/4" to 2" or more; (ii) a minimum strength, which remains in effect as the lumps move down through the reactor and are consumed by the reaction; (iii) absence of caking or softening as the temperature increases, thereby preventing melting of the solid and plugging of the reactor; (iv) good reactivity with steam and CO_2 at rates over the temperature range encountered in the gasifier; (v) ash behavior (softening/fusion) which allows the reactor to operate either in the dry or slagging mode, even in the highest temperature zone (bottom); (vi) in most situations, preferably no release of condensable heavy hydrocarbons or tars as the temperature is elevated. There are, unfortunately, no coals found in nature which fulfill this wishlist. It therefore remains a challenge to the engineer to devise a gasifier which can accommodate the properties of the coals which are available in practice.

There are two models of moving-bed gasifiers which may be viewed as extremes and span the range of approaches. First, there is the modern blast furnace. Here, the feed-preparation step (the coke oven) virtually

dominates the system, but the gasifier feed (coke) complies with every one of the listed needs except for reactivity, which is not important in slagging reactors because of the high temperatures involved (>2,700°F). As a result, the gasifier, which is the blast furnace, has been developed up to 55ft in diameter with 5-6,000 ton/day of coke-gasification capacity and stable, uninterrupted operation over 2-3 years. No other reactor comes even close to this performance. But the cost of feed preparation involved (the coking of coal) is prohibitively high.

The second model is the modern, high-pressure Lurgi gasifier, 15 to 16ft in diameter, which can accommodate unbeneficiated coal down to 1/4" size. The units have up to 1,000 ton/day capacity, depending on reactivity, and high ash-fusion temperatures. The same reactor will accept coals with a wide range of caking properties when using agitation in the critical temperature zone (600-1,200°F). By operating in a slagging mode, the range of coals is greatly extended to cover even strongly caking (greater than 25,000 Gieseler-degree) coals and coals with low ash-softening points.

All moving beds have the requirement that most of the feed must be of lump size and coarse. Since modern mining equipment tends increasingly to produce coal with less than 1/4" size, this requirement calls for feed preparation to increase size, such as pelletizing, briquetting, extrusion; these are relatively costly steps, although they are well developed and in wide commercial use.

The preceding statements suggest an area for R&D, which is best summarized as feed preparation for moving-bed gasifiers. These gasification systems have moved into the foreground as gasification regains the position it once had. Of particular interest here is work which deals specifically with the use of lime to control caking properties and reduce the evolution of tar while simultaneously increasing reactivity. In spite of progress already made, more fundamental research on coal properties and surface behavior may lead to further advances. The counter-currency of moving beds is unique among gasifiers and makes these thermally most efficient, with tremendous gasification potential, as has been shown for the blast furnace. Effective system utilization requires a substantial advance in the

feed-preparation area. R&D on this subject could have a major pay-off.

2.10-3. Gasification as a Solids-Processing Technology

Gasification of coal is, by definition, a solids processing operation. This operation requires intimate and efficient contact of solids with gas over a substantial pressure range and also involves major input of energy to the reactor at high temperatures.

It is important to recognize the unique problems associated with handling and converting (processing) solids. Physical and mechanical difficulties rather than process chemistry may be the determinant factors in gasifier performance. This is a significant observation regarding gasification and it is appropriate that the DOE R&D program reflects the special problems of solids processing.

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Applications of new or improved diagnostics are needed that will help the engineer to design better reactors, which will function smoothly and reliably. The needed measurements will assist the operator in monitoring solids behavior on-line and within the gasifiers.

2.11 Applications of Advanced Diagnostics to Coal-Gasification Systems

Two primary discoveries and developments have occurred during about the last 20 years that may be expected, in time, to change chemical process technologies, in general, and coal-gasification technologies, in particular, from applications of intuition-based art to quantitative science. These advances relate to (a) computers and numerical analyses and (b) advanced diagnostic techniques. The current status of diagnostics for coal-gasification systems is summarized in Chapter 11. The subject of numerical gasifier modeling is discussed in Chapter 12; it should be noted that this type of quantitative description almost always forms an integral component of current industrial development programs. The pacing items in obtaining improved numerical modeling relate to data inputs and verification of model assumptions. Modern diagnostic techniques play a key role in this

program.

Quantitative measurements for coal-gasification systems are required to improve our understanding of fundamental processes. Continuous monitoring of system operations is needed for on-line utility plants and other chemical process units utilizing coal gasifiers. Advanced diagnostics offer significant promise, including high spatial and temporal resolution and also the opportunity to probe highly-turbulent, multiphase flows. These techniques are non-intrusive and generally costly and challenging to apply. In fact, it is likely that successful field adaptation of any of the advanced techniques will require close long-term cooperation between instrument developers and system engineers dealing with such complex process technologies as coal gasifiers.

Existing advanced techniques have been shown to be useful for the measurement of essentially any desired parameter in combustion systems. In Chapter 11, Hardesty and Ottesen begin their overview on diagnostics by identifying the primary flow regimes in gasifiers and then describing these by identifying characteristics such as well-mixed gaseous regions, regions with minimal concentrations of particles, heavy particle loadings, strong gradients, highly turbulent flows, multiphase flows, etc. Each region presents special challenges for applications of diagnostics that support quantitative modeling and monitoring.

Among the advanced techniques that yield data with high spatial and temporal resolution and are likely to find wide field applications are the following: measurements of velocity components, temperatures, particulate loadings, atomization rates, species concentrations, rates of deposit build-up on walls and protruding surfaces, and others that are of special interest because they may influence successful operation or determine gasifier life.

Effective applications of sophisticated diagnostics to coal-processing units have been notably slow to materialize. There are two reasons for this slow progress: developers generally do not know what critical questions can be resolved by using advanced techniques and, even if the problems have been properly identified, they may be reluctant to utilize

costly procedures that have previously been employed successfully only by researchers working on idealized systems in clean laboratories.

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This issue could be profitably addressed by DOE, which has been funding the development of laser-diagnostic techniques for combustion applications for some years. What is required are first increased use of advanced diagnostics in laboratory systems of modest size. Subsequently, a user task group should be created, i.e., a group of well-trained people should devote their skills to instrumenting industrial plants and demonstrating incisive required measurements on these practical systems.

The view is often expressed that commercial instruments will be developed when they are needed. The fallacy with this argument in the present case is that users do not know what they need until they realize the very great value of improved diagnostics in process control and modelling. It is in this area that a DOE-sponsored program on technology transfer is most likely to be useful.

2.12 Fundamentals of Coal Conversion and Relation to Coal Properties

In order to develop reliable coal-conversion technology, it is important to have knowledge of the conversion behavior of coal and the relationship of conversion behavior to some measurable set of coal properties. Required are answers to such questions as the effects on gasifier performance of normal variations in organic and mineral properties of a coal from a single mine, of variations in coal particle size, and of switching coals. Unscheduled shutdowns of coal plants are often caused by unexpected and uncontrolled behavior of the coal. What will be the effect of instituting pollution-control strategies such as the injection of sorbents? Can slagging and fouling behavior be predicted from the coal mineral distribution and the process conditions? Can the concentration of tars and fines exiting the gasifier be predicted and controlled?

The design of new processes or scaling up is improved by the availability of good predictive capability. For example, to design a process for producing condensable products by mild gasification involving

incomplete reaction, knowledge of the product slate from devolatilization (condensables, char and gas species) and of the secondary reactions of the condensables is needed. The objective of work on fundamentals of coalconversion behavior should be the development of accurate predictive capabilities to put gasification technology on a sound engineering foundation. The steps toward achieving this goal are: (i) development of chemical and physical understanding of coal-conversion phenomena and their relation to coal properties; (ii) reduction of data and mechanisms to the form of engineering correlations and submodels; (iii) development of comprehensive computer-simulation codes for gasification processes incorporating the submodels.

Fundamentals of coal conversion involve coal characterization, gasification steps relating to the organic structure of coal, processes relating to the inorganic mineral matter, and the status and needs of computer modeling of gasifiers for monitoring, control and scale-up. Recommendations for research in these areas are listed in the following paragraphs.

2.12-1. Coal Characterization

While there are a number of standard characterization procedures for coal, they often do not provide information appropriate to advanced processes. Methods are needed to provide parameters from which coal behavior in gasification can be accurately predicted. (i) NMR and FTIR techniques promise to provide needed information on functional groups. The remaining problems are calibration, e.g., what percentages of carbons are seen and what are applicable absorption coefficients? Repeated parallel experiments on identical coal samples would help to resolve these issues. (ii) Validation is needed of methods for measuring coal viscosity at high heating rates and high temperatures. These measurements should be related to swelling and agglomeration phenomena observed under gasifier operating conditions. (iii) Standard pyrolysis tests need to be defined to provide extensive devolatilization data that are applicable to high heating rates at high temperatures. (iv) Work is required to define a reactivity test and methodol-

ogy to relate the test results to reactivity under gasifier operating conditions. (v) Work is required to define mineral characterization procedures and methodology to relate the test results to ash behavior under gasifier operating conditions.

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2.12-2. Fundamental Processes in Gasification and Partial Gasification

For gasification, the objective is to gasify coals of different rank in the shortest time at the lowest severity conditions, with small amounts of tars or fines exiting from the reactor. For mild gasification to produce co-products, the objective is high yields of quality products. These factors are controlled by heat transfer, pyrolysis rates, devolatilization processes, gasification of char, and secondary reactions of condensables and gases. Research needs for these areas follow.

There is a lack of data on the fundamental parameters involved in heat transfer (heat capacities, emissivities, heats of reaction, effects of volatile evolution on convective heat transfer). Heat-transfer calculations employing the measured parameters should be validated under typical gasification conditions by employing well instrumented laboratory-scale experiments, which allow coal-particle temperature measurements.

Accurate determinations are needed of the important chemicalkinetic rates in pyrolysis. In these experiments, coal-particle temperatures should be directly measured or accurately determined by indirect means. At high heating rates above 10,000°C/sec, attention must be given to temperature gradients within the particle. Experiments should be analyzed by using an agreed-upon standard model so that results can be directly compared. This model should provide rate expressions which are independent of heating rate or experimental geometry. The use of a small set of standard coal samples by several investigators should be encouraged.

Work should proceed towards finding an acceptable standard model to describe the devolatilization process. Experimental and theoretical work is especially needed on sulfur evolution, tar formation and char viscosity (including depolymerization, mass transport, and crosslinking processes),

and on the formation of chars (swelling, pore structure and reactivity).

There is a need to develop a better understanding of the chemical factors (i.e., functional-group composition, minerals) which influence intrinsic reactivity and how the observed reactivity is affected by physical factors (pore structure). For catalytic gasification, the dispersion of catalyst in the char is an important issue, along with interactions of added catalysts with minerals already present in the char. The elutriation of highly unreactive carbon in the form of fines from gasifiers is a problem which could benefit from a more fundamental understanding of gasification reactions.

There is a need for kinetic data and models of product evolution for the gas-phase cracking of tars from a range of coals. There is also a need for information on the kinetics of soot formation from tar. In addition, we require information on mechanisms and kinetics of secondary repolymerization reactions of tars which occur on surfaces inside and outside of the parent coal particle. This information is needed in order to understand the yields and quality of co-products generated in mild gasification.

Both mechanisms and rates should be determined for important mineral transformations in coals.

2.12-3. Transformation of Coal Mineral Matter

When the mineral constituents of coal are heated, they undergo thermal decomposition that is usually associated with weight loss. During these reactions, the mineral components of the ash (the major ones of which are compounds of silicon, aluminum, iron, and calcium) may form new eutectics with lower melting points and these new melts can mix with and dissolve in other molten mineral compounds. The practical significance of the behavior of the ash in gasification processes relates to (a) the desired trouble-free removal of ash or slag from the process and (b) ash deposition on heat-exchange surfaces downstream of the gasifier by semi-molten ash particles carried over by the product-gas stream.

The specific requirements for information on ash behavior vary with the particular conditions of the gasification process, e.g., in fluidized-bed gasifiers, a controlled amount of ash agglomeration may be favored but semi-molten ash particles can cause significant problems in process cyclones, with the recycling of carried-over, partially-gasified char particles into the fluidized bed. In slagging gasifiers, on the other hand, slag viscosity-temperature relationships must be known to ensure liquid-slag removal over a range of operating conditions. When the gasifier is coupled directly with a gas-turbine plant, the condensation of vapor phase alkali species in the gas turbine may cause corrosion. Ŀ,

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Traditionally, ash chemistry was used for coal mineral-matter characterization. In recent years, new analytical methods have become available, which are capable of yielding much more detailed and useful characterizations, including the types, amounts, size distributions, and structures of inorganic matter in coal. Theoretical and experimental studies are in progress under the sponsorship of DOE PETC, DOE METC, and EPRI to improve our understanding of the transformation of coal mineral matter under combustion conditions (high temperature oxidizing atmosphere) but little or no research effort is devoted to studies which pertain to conditions typical of those occurring in the various types of gasifiers.

It is recommended that fundamental studies of ash sintering, agglomeration, slagging, and partial vaporization be carried out under reducing conditions and in the temperature range typical of gasification processes. Furthermore, a data base on ash behavior should be created for the most important American coal types in gasification processes.

2.12-4. Mathematical Modeling of Gasification Processes

Development of coal-reaction process models should continue and should focus on entrained, fixed and fluidized beds in a coordinated manner. Work on gasification and combustion should be closely coordinated, since a given model generally has areas of applicability in both systems. Increased near-term emphasis should be given to model evaluation and application. On-going development and improvement of submodels, particularly those related to coal and residue properties, should be continued. Basic work should be pursued in such areas as turbulence-flame interactions and multi-phase flows.

Support should be provided for selected, well instrumented and flexible laboratory-scale experiments that can be employed to validate selected aspects of the comprehensive codes.

CHAPTER 3: GASIFICATION FOR ELECTRICITY GENERATION

3.1. Integrated Coal-Gasification Combined Cycles (IGCC)

3.1-1. Introduction

Because of the huge US coal reserves (estimated to last at least 200-300 years), the preferred use of the cheapest available energy source, the stalemate faced by the nuclear industry, and the uncertainty of future natural gas (NG) prices, it is likely that coal will continue to be the major fuel for electric utilities in the future.

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Integrated coal-gasification combined cycle (IGCC) systems offer many advantages over conventional pulverized-coal combustors. These advantages include higher energy-conversion efficiency, reduced pollutant emissions, lower financial risks associated with staged capacity additions, and the relatively small modular unit size used, as well as the ability to accept a variety of feedstocks.

An IGCC power plant involves the coupling of a coal-gasification system producing a clean fuel gas to combustion and steam turbines that generate electric power. A schematic diagram of a unit of this type is illustrated in Fig. 3.1-1. To illustrate the important features of an IGCC, the Cool Water Coal Gasification Program (CWCGP), which is an actually operating IGCC plant, will be described in Sec. 3.2.

Sections 3.1 and 3.2 were written by S.B. Albert, S.S. Penner and D.F. Weisenhahn; Sec. 3.3-3 by P.B. Tarman, and the remaining subsections of Sec 3.3, as well as Sec. 3.4 by S.S. Penner and D.F. Wiesenhahn with the advice and inputs from correpondents identified in the subsections.

3.1.2. IGCC System Status**

Development of a number of advanced coal-gasification systems has been progressing at a rapid pace (compare Table 3.1-1). Uncertainty regarding conventional fuels (NG and oil), environmental regulations that represent increasingly tight standards, and uncertainties regarding nuclear power deployment in a number of countries have spurred commercial developments of coal-gasification systems for diverse applications such as (a) electricity generation, (b) fertilizer, hydrogen and organic chemicals production, and (c) generation of hot water for district heating, etc.

Coal-gasification systems may be classified according to the type of gasifier used in which coal is contacted and reacted with an oxidant (air or oxygen) to produce the desired fuel gas. If the system is blown with air, the fuel gas is low-Btu gas; if the system is blown with oxygen, the fuel gas is medium-Btu gas. Three types of contacting devices are moving beds, fluidized beds, and entrained flows.

In moving beds, a descending bed of coal, usually of 1/8 to 1 inch in coal, is fed by a pressurized lockhopper system to the top of a shaft. Reactant gaseous oxygen (or air) and steam enter the bottom of the vessel. As coal descends, it is devolatilized; then, pyrolysis reactions occur and finally carbon is gasified. The raw product gas contains tars and oils, which need to be condensed and removed. The ash may be withdrawn as a dry solid or as molten slag. In some moving-bed versions, tars, oils, and coal fines are recycled to extinction.

In fluidized-bed reactors, coal is ground to produce a fluid-bed grind (ca 8 mesh or less). The oxidant gas (and some steam) are introduced through a perforated deck or grind at the bottom of a vessel. The flow rate of the reactants is high enough to suspend the coal particulates but not blow them out of the vessel. A uniform temperature is obtained as the result of the mixing that occurs. Depending on the temperature, tars and oils can be avoided but fines carryover and ash slagging limit conversion of some coals to 80-90% of the carbon. In order to overcome this limitation, the carbon-containing ash may be processed in an additional vessel or the unconverted carbon can be recycled to the gasifier.

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This section is reproduced from Ref. 1.

In entrained-flow systems, a relatively fine grind of coal (ca 75% through 200 mesh) is fed either as a dry solid or as a water and coal mixture to a short-residence time reactor. Contacting with the oxidant is achieved by means of a nozzle arrangement. At the high velocities and temperatures used in entrained systems (2000 to 3000° F), no tars or oils are produced. Carbon burn-out is nearly complete and the product gas is essentially a mixture of CO and H₂.

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In the US and abroad, advanced coal-gasification technologies have been under development for the last decade. Several technologies have been supported by EPRI: (i) Texaco technology represents an entrained system that features a coal-water slurry feeding the pressurized, oxygen-blown gasifier. It is the farthest advanced in that three commercial or demonstration plants are in operation. Two of these plants are located in the US and one in Japan. A plant in the FRG will start up in late 1986 to produce organic chemicals and hot water for district heating. Projects have also been announced for China and Sweden. (ii) The Shell coal-gasification unit is under construction at 250/400 TPD



Fig. 3.1-1. Schematic drawing showing a generic IGCC system.

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Manufacturer	Operating Plants			
Texaco	Cool Water: 2×1000 TPD; 117 MW ; Ube: 4×500 TPD; Tennessee Eastman: 2×900 TPD; Ruhrchemie: 1×600 TPD			
Shell	250 TPD pilot plant in TX			
Dow	160 MW _e IGCC at Plaquemine, LA; $1 \times 2,500$ TPD gasifiers			
BGC/Lurgi	600 TPD at Westfield, Scotland			
Allis-Chalmers	600 TPD at Wood River			
KRW	35 TPD at Waltz Mills; 500 TPD in China (1989 start-up)			
IGT	40 TPD at Chicago; 200 TPD proposed for France			

Table 3.1-1. Status of selected coal-gasification technologies.

pilot-plant scale at their research center in Deer Park, Texas, and is expected to lead to commercial designs in the late 1980s. The Shell process features a dry-feed, entrained gasifier system that operates at elevated temperature and pressure. Current studies with US electricity companies are defining commercial opportunities. (iii) The British Gas Corporation and Lurgi GmbH have jointly developed a slagging, moving-bed gasifier system. A commercial gasifier prototype (600 TPD) will be started up at Westfield, Scotland, in early 1986. Virginia Power is considering installation of a coal-gasification system for a 200-MW_e IGCC power plant based on the BGC/Lurgi technology. (iv) An air-blown, rotary, ported kiln (similar to a moving-bed device) is under development by Allis Chalmers Corporation. A 600 TPD prototype is located at an Illinois Power Co. power station. (v) The Dow Chemical Company is installing a 160-MW_e IGCC plant in Louisiana that will produce electricity and synthesis gas for industrial chemicals. Details of the system are proprietary, but it features a coal-water-slurry-fed entrained gasifier. Price supports of \$620 million from the Synthetic Fuels Corporation have been obtained for the project.

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Other gasification-systems technologies have been evolving, including the Kellogg-Rust-Westinghouse gasifier and the Institute of Gas Technology U-GAS system. These are representative of ash-agglomerating fluid-bed systems. Advanced fluid-bed systems are also being developed in Japan. A Winkler demonstration fluid-bed system operating at elevated temperature and pressure is being started up in the FRG by Rheinische Braunkohle. The Winkler system will handle 700 TPD of coal to produce industrial chemicals and electric power.

Other projects that are at the pilot-plant stage of development include a 50 TPD pressurized pilot plant by GKT-Krupp. The Vereinigte Elektrizitatswerke Westfalen (VEW) has started up a 250 TPD pressurized pilot plant that partially converts coal (60% conversion) to low-Btu gas for power generation. Lurgi has gasified lignite in an atmospheric-pressure, circulating fluid bed in their 15 TPD pilot plant in Frankfurt, FRG.

In Japan, several pilot-plant programs are also underway, including development of a molten-iron gasification system. A 250 TPD pilot plant is under construction in Sweden by Sumitomo-KHD; in this unit, sulfur is captured in the slag.

Development of advanced combustion turbines is also proceeding rapidly. The efficiency of combined-cycle equipment is increasing because of the ability to operate at higher firing temperatures. In utility applications, firing temperatures of 2,000°F are conventionally used and higher temperatures of 2,300°F may be expected before 1990. Developments in the areas of reheat, materials, and advanced cooling methods promise additional improvements in efficiency in the 1990s.

Table 3.1-2. Future goals for 500-600 MW_e IGCC plants; reproduced from Ref. 3. Comparisons refer to conventional coal-fired plants as baseline.

About 10% higher efficiency, i.e., heat rates of 9000-9100 Btu/kWh, corresponding to 37.5-37.9% efficiency.

Lower pollutant emissions, 33% less water consumption, reduced wastewater treatment and formation of non-hazardous, useful by-products.

A 15% reduction in levelized electricity costs.

More rapid and cheaper construction of smaller modular units.

3.1-3. Advantages of IGCCs

High efficiencies are obtained in combined-cycle operation because efficient combustion turbines are combined with steam turbines. The gas turbine converts high temperature (~ 2300° F) heat efficiently while the steam turbine utilizes low-temperature heat efficiently in the form of steam (~ 1050° F). Figure 3.1-1 shows a schematic drawing of a generic IGCC system.

Low pollutant-emission levels result from the combustion of a clean fuel. Pollutants are removed before combustion by using gas-purification systems tested in other industries. Combined-cycle systems yield very low emissions when NG is burned. Water consumption of IGCC systems is also substantially lower (~ 33%) than for pulverized-coal combustors. Thus, coal-gasification systems are environmentally superior to other alternate coal-utlization technologies and will meet rigorous environmental standards for S and NO_v, as well as particulates.

Compared to conventional coal-combustion plants, IGCCs have both lower capital and lower operating costs,² resulting in lower net electricity costs to consumers. Compared to conventional or combined-cycle systems burning NG, the econonic benefits based on current costs (ca \$2/million Btu) are not so clear.² When NG prices are very low, as at present, it is the preferred fuel for power generation.

Because of its modular design, an IGCC system may be phased in at different stages of plant construction, as is illustrated in Fig. 3.1-2. Each stage has a short construction time. The use of small capacity additions eliminates the need for large, high-risk capital investments. This aspect of IGCC units is especially attractive to utilities with uncertain future demand requirements. The last step (addition of the gasifier) may be delayed until fuel prices make this addition economically attractive.

A properly designed IGCC system will have the flexibility of accepting many different types of feedstocks, including such low-rank coals as lignites, as well as petroleum coke. Additionally, gasification systems may be configured to produce other industrial chemical products, which adds a desirable degree of flexibility.



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Fig. 3.1-2. Four installation stages of a phase-in IGCC system; reproduced from Ref. 2. The existing capacity is designated

3.1-4. Future Utilization of IGCCs

Table 3.1-2 is a summary of future goals for $500-600 \text{ MW}_{e}$ IGCC plants. Research needs relate especially to studies designed to reduce capital and operating costs.

Among existing coal technologies for electricity generation, the IGCC may well represent a superior choice. The most serious limitation for IGCC use is its cost when compared with the use of NG and petroleum at currently low prices in conventional electricity generation units. Continuing research to reduce system costs is recommended.

References for Section 3.1

- D.F. Spencer, S.B. Alpert and M.J. Gluckman, "Integrated Coal Gasification Combined Cycles (IGCC) an Emerging Commercial Option for the Power Industry," paper presented at a 1985 ACS meeting, EPRI, Palo Alto, CA (1986).
- D.F. Spencer, "The Commercial Implications of the Cool Water Project for the Electric Power Industry," EPRI, Palo Alto, CA (1986), unpublished.
- W.N. Clark, "Remarks at Alternative Coal Tests Press Briefing," Cool Water Coal Gasification Plant, Daggett, CA (April 4, 1986).

3.2. The Cool Water IGCC

3.2-1. <u>General Features</u>

The Cool Water Coal Gasification Program (CWCGP) utilizes a 100 MW_e IGCC plant located in Daggett, CA. It has a coal capacity of 1000 TPD and is located adjacent to a 600 MW_e NG-fired plant of the Southern California Edison Co. Construction was started on December 15, 1981, and first electricity production occurred on May 20, 1984. The CWCGP was completed ahead of schedule and below budget.¹ The total capital cost was \$263 million.

There are six participants, each contributing a minimum of \$25 million: Texaco Inc. (\$45 million), Southern California Edison Co. (\$25 million, EPRI (\$69 million), Bechtel (\$30 million), General Electric Co.

(\$30 million), and the Japanese Cool Water Program Partnership (\$30 million). Additional \$5 million contributions came from the Empire State Energy Research Corp. and the Sohio Alternate Energy Dev. Co.; there was also a \$24 million loan.

3.2-2. Process Description

The CWCGP is shown schematically in Fig. 3.2-1. More detailed diagrams can be found in Ref. 2.

Coal is brought by rail cars, stored in two large storage silos (1), and transferred to be ground and slurried (2). A 60/40% coal-water slurry is normally used. The slurry is reacted with 0_2 in the gasifier (3). Oxygen is supplied from an over-the-fence plant (4). A Texaco gasifier is used (compare Sec. 3.3-1). If the gasifier operates in the heat-recovery mode, the hot gases are collected in a heat exchanger and high pressure steam (~ 100 atm) is raised.

Slag is removed with a lockhopper system (5); ash and water from the gasifier are separated (6). Some solids are recycled back to the grinding and slurrying processes (2). Solid slag is presently stored in speciallylined landfills. Recently, however, the EPA and the State of California Health Department have determined that this slag is non-hazardous. Studies of markets for concrete or asphalt applications are being undertaken. The product gases are scrubbed to remove particulates (3) and are then transferred to the syngas cooler (7) and the sulfur removal unit (8). Sulfur-compounds (H_2S and COS) are sent to the sulfur recovery unit (9), where the sulfur is converted to elemental form and sold (currently at \$100/ton). Sulfur removal is accomplished by the Selexol process; sulfur recovery from H_2S and COS is implemented by using the Claus system. Waste acid-gases from the Claus unit are cleaned by the SCOT process.

The clean syngas is saturated (10) to control NO_x emissions prior to combustion and power generation in the General Electric combustion turbine (1). The combustion-turbine exhaust gases are sent to the Heat Recovery Steam Generator HRSG (12), and vented to the atmosphere. In the HRSG, heat from the hot combustion gases is used to make steam. This steam is combined with the steam made by cooling of the syngas (3) (if applicable) and is then passed through the steam turbine (13). At Cool Water, the





combustion turbine generates 65 MW and the steam turbine 55 MW for a total capacity of 120MW.

Boiler feedwater (14) for the steam turbine is supplied from the adjacent Southern California Edison plant. Well water (15) is used for slag processing (5). Waste-water is treated (16) and sent to on-site evaporation ponds.

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3.2-3. Performance Results

Some of the design goals and actually achieved performances are listed in Table 3.2.-1.

Three representative coals have been gasified so far. The plant has met all of the design goals. The performance of the CWCGP is very good for the coals that have been tested. Illinois No. 6 and the Pittsburgh No. 8 coals with sulfur contents of 3.1 and 2.9wt%, respectively, have been handled. Plans call for the testing of additional coals, including an Australian coal.

Because of the high carbon-conversion efficiency, the carbon recycling system illustrated in Fig. 3.2-1 has not been used. Refractory wear in the gasifier has exceeded expectations. Minor problems encountered were wear and plugging of the slag-handling system, difficulty in keeping the lockhopper valves operating smoothly, and fine slag particles remaining in the gas-scrubbing system.¹ All of these problems were resolved by making minor modifications in plant operation or design

Pollutant-emission results are given in Table 3.2-2. Actual emission levels were always well below requirements, even with high-sulfur Eastern coals. The environmental requirements listed in Table 3.2-2 are the strictest for any coal-burning power plant in the US.

Both modes of gasifier operation have been utilized: gasifier heat recovery and direct quenching (compare Sec. 3.3-1). Capacity factors have met targets expected for the first 2 years of operation and have been generally equal to or superior to targeted goals. It is expected that a multi-purpose IGCC will have a capacity factor greater than 80%.

Performance Parameter	Design [†]	Actual Performance		
Coal type	SUFCO	SUFCO	Illinois No. 6	Pittsburgh No. 8
Sulfur content (wt%)	0.48	0.4	3.1	2.9
HHV (Btu/lb)	12, 300	12,300	12,800	13,700
Coal-feed rate (TPD)	1000	1000	1000	1000
Oxygen consumption (TPD)	962	908	885	97 9
Gross power production (MW _e)	114	116	120	125
Byproduct sulfur produced (TPD)	4.6	3.8	30	27
Coal/water slurry concentration (wt% solids)	60	60	64	62
Carbon conversion (%)	98.3	98.3	96.6	99.1
Gasifier/syngas cooler efficiency (%)	90.3	91.5	88.5	91.6
Gasifier refractory life (yr)	1.0	2,6	1.1	\$
Overall heat rate (Btu/kWh) \S	11,500	11,300	12,000	11,600
Efficiency (%)	29.7	30,2	28.4	29.4

Table 3.2-1.	Design and actual performance for the CWCGP; reproduced
	from Ref. 4.

[†] Design parameters based on SUFCO coal.

[‡] Data not yet available.

[§] The heat rates were not optimized and are expected to be reduced by ~2,500 Btu/kWh in future plants.

Coal Type	Pollutant	Permit & Regulation Limits (a)	1985 EPA Test	Preliminary Test Results	Federal NSPS (b)
SUFCO (0.5% S)	so ₂ No _x co	0.033 0.13 0.07	0.018 0.07 0.004		0.24 (c) 0.6 NS (e)
Illinois No. 6 (3.0% S)	SO _Z NO _X CO Particulates	0.16 0.13 0.07 0.01		0.076 0.094 0.004 0.009	0.6 (d) 0.6 NS 0.03
Pittsburgh No. 8 (2.9% S)	so ₂ No _x Co	0.16 0.13 0.07		0.086 0.09 0.004	0.6 (d) 0.6 NS

Table 3.2-2. Allowed pollutant levels and actual CWCGP pollutant emissions measured at the HRSG. All units are lbs/ 10^6 Btu; from Ref. 4.

(a) Emission requirements for the HRSG Stack from limiting permit and regulatory emission criteria.

(b) New Source Performance Standards for a coal-fired power burning equivalent coal as CWCGP.

(c) $0.8 \text{ lb}/10^6$ Btu uncontrolled emissions $\times 0.30$ for controlled emissions.

(d) Emissions controlled to 0.6 lb/10⁶ Btu.

(e) NS: No standard.

References for Section 3.2

- 1. D.F. Spencer, S.B. Alpert and H.H. Gilman, Science 232, 609 (1986).
- Electric Power Research Institute, "Cool Water Coal Gasification Program - First Annual Report," Report No. EPRI AP-2487, Palo Alto, CA. (1982).
- 3. Ref. 2 of Sec. 3.1.
- 4. Ref. 3 of Sec. 3.1.

3.3. Selected Gasifiers for IGCC Plants

The following coal-gasification systems represent important developments in gasification technology. The systems are designed to handle a wide variety of coals and to be useful in both combined-cycle gasification systems for electricity generation or for the production of pipline-quality SNG.

3.3-1. The Texaco Coal-Gasification Process (TCGP)

3.3-1A. Introduction

The Texaco Coal Gasification Process (TCGP) has the following design features: (a) a pressurized reaction vessel; (b) a downward loading, entrained flow, slagging reactor; (c) air-or 0_2 -blown gasification; (d) high operating temperatures; (e) flexible feeds of fuels and output products; (f) system coupling for cogeneration (i.e., using the excess heat produced in the gasifier to generate electricity).

The development schedule for the TCGP is summarized in Table 3.3-1.

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3.3-1B. <u>Process Description</u>

Two configurations of the TCGP are shown in Fig. 3.3-1, depicting two different gas-cooling methods. The TCGP is designed to operate at

^{*} The radiant section is necessary to cool the gases below the sticking temperature of the slag before entering the convective cooler.

pressures between 20 and 80 atm and at temperatures between 1200 and 1500°C.

Owner	Type of Plant	Location	Coal Capacity, TPD	Start- Up	Gas Cooling	Product
Texaco, Inc.	pilot	California	15	1973	direct quench (d.q.)	-
Texaco, Inc.	pilot	California	15	1978	d.q./heat recovery	-
Texaco, Inc.	pilot	California	15	1981	d.q.	-
RAG/RCH	demon- stration	W.Germany	165	1978	heat recovery	oxo-chemicals
Dow Chemical	demon- stration	Louisiana	400	1979	-	synthesis gas for electric power
TVA	demon- stration	Alabama	190	1982	d.q.	ammonia
Tennessee- Eastman	com- mercial	Tennessee	900	1983	d.q.	acetic anhydride
Southern Calif. Edison Co., etc. (Cool Water)	com- mercial	California	1,000	1984	heat recovery or d.q.	synthesis gas for electric power
Ube	com- mercial	Japan	1,650	1984	d.q.	ammonia
SAR	com- mercial	W. Germany	800	1986	d.q./heat recovery	oxo-chemical/ ^H 2

Table 3.3-1. Development of the TCGP; taken from Ref. 1.

The coal is wet-ground (1) and slurried with oil or water (2). If (molten) coal-liquefaction residues are used, these steps are omitted. Typical slurry feeds have between 60 and 70wt% of solids. The slurry is mixed with O_2 or air in the gasifier-burner (3). For gasification of an oil slurry, steam or another temperature moderator is added to the burner stream; water serves this purpose for water slurries. By properly adjusting the O_2 /slurry ratio, temperatures are maintained above ash-fluid temperatures.

After leaving the gasifier (burner), the gases are cooled (4), either by direct contact with quenching water [Fig. 3.3-1(a)] or by passing through a radiative cooler ^{*} and then a convective cooler [Fig. 3.3-1(b)]. In the latter case, heat is recovered from these gases (and from the gasifier) in the form of high-pressure steam, which can be used to generate electric power. The former method is preferred when the output is NH₃ or



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Fig. 3.3-1. The process diagram for the TCGP is shown for two gas-cooling modes: (a) direct quench and (b) waste-heat recovery; reproduced, with minor modification, from Ref. 1.

 H_2 , since the required shift reactor is easily integrated in the quench mode; also, heat transfer from the gases to the quenching water produces steam, which is used downstream to increase the H_2 yield.

After cooling, the gases enter a water scrubber (5), where char and fly-ash are removed from the product gas. If necessary, the product gases also undergo sulfur cleanup (not shown) using commercially available technology. The scrubbing water is sent to the clarifier (6) and is then recycled to the particulate scrubber (5), thus forming a closed loop. Some of the recycled water is purged to prevent scaling and to control the level of dissolved solids. A small amount of make-up water is needed. Most of the ash from the gasifier (3) is removed as a quenched slag through a water-sealed depressurizing lockhopper system (7) and is then sent to the slag-collection sump (8). Fines from the slag separator (9) are pumped to the clarifier (6) for recycle or disposal while the coarse slag from the separator is removed.

The product gases leaving the particulate scrubber (5) contain H_2 , CO, CO₂, H₂O, and traces of Ar, N₂, CH₄, H₂S, and COS. The amounts of the two sulfur pollutants present depend on the sulfur contents of the feed fuels². There is no detectable amount of NO_x formed,² and it is stated that no SO_x is produced.¹ Generally, very low pollutant levels result from the TCGP in both the gaseous and wastewater streams. A detailed analysis of all pollutant levels is given in Ref. 2. The observed excellent gasifier performance is attributed to the high reaction temperatures² and the highly-reducing environment used in the process.¹

A number of different products have been prepared in commercial plants (compare Table 3.3-1). These include H_2 , NH_3 , fuel gas for electricity generation, and synthesis gas (CO and H_2) for the production of methanol or other oxo-products.

Many different types of fuels have been successfully gasified in the TCGP. According to Texaco, any carbonaceous material that may be formed into a pumpable, concentrated slurry can be gasified. A summary of the types of coals, cokes and liquefaction residues that have been gasified in the Texaco pilot plants is given in Table 3.3-2. Free-swelling indices ranging between 0 and 8 have been handled at the RAG/RCH plant in FRG.¹ In Ref. 3, the conversion of petroleum coke to synthesis gas in a 30 TPD plant in Ube City, Japan, is described in detail. This plant has been operating since 1982.

Table 3.3-2. Examples of feedstocks gasified in the Texaco Montebello plants. 1000

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- Coals: anthracites, semi-anthracites, bituminous and subbituminous coals, and lignites.
- Petroleum cokes: fluid, delayed, calcined, fluid from tarsands bitumens.
- Coal liquefaction residues: formed from solvent refined coal (SRC I and II), H-coal, and in the Exxon donor solvent (EDS) process.

Others: Lurgi tar/oil.

3.3-2. The Shell Coal-Gasification Process (SCGP)

3.3-2A. Introduction

The past and current development schedules of the SCGP are summarized in Table 3.3-3. The SCGP is described as a "highly efficient

Date	Scale of Operation	Location	
1972	development initiation		
1976 (start-up)	6 TPD pilot plant	Amsterdam, Holland	
1978 (start-up)	150 TPD experimental unit	Harburg, FRG	
1987	SCGP-1 (~1/5 of commercial size): 250 TPD of high- S bituminous coal, ~400 TPD of wet, high-ash lignites	near Houston, TX	

Table 3.3-3. Milestones in the SCGP development.

* This is a brief summary of technical material provided by Heitz and Nager.⁴ It has been reviewed and approved for accuracy by M. Nager (Shell Oil Company) to whom we are greatly indebted for advice and assistance.

process with demonstrated feedstock flexiblity from lignites to coke."⁴ The SCGP-1 demonstration unit is expected to be completed during the fourth quarter of 1986, with plant start-up scheduled for the first half of 1987.⁴ It is being developed by several Shell Oil units, in collaboration with EPRI and Lummus Crest (a Combustion Engineering subsidiary). The initial application of this technology is expected to be to electric power generation.

An evaluation of the 6 TPD SCGP in Amsterdam is given in Ref. 5. Two coals were tested: Illinois No. 5 and a Texas lignite. Further information on the SCGP, including an economic assessment of an IGCC system utilizing the Shell gasifier, may be found in Ref. 6.

3.3-2B. <u>Process Description</u>

The process diagram for the 6 TPD process-development unit is reproduced in Fig. 3.3-2 from Ref. 5. Pulverized coal is sieved over a vibrating screen with 1 mm openings to remove the coarse materials. It is then pressurized in a lockhopper system (1) and is pneumatically transported from the feed vessel (2) to the reactor (3), which consists of two oppositely-fired burners.

Temperatures in the reactor are sufficiently high to melt the coal ash and produce a liquid slag. A dense, non-leachable slag is formed as the liquid slag leaves the reactor through the slag tap and falls into a water bath 4.

The reactor product gas and fly slag (which is comprised mostly of residual carbon and partially molten ash) is quenched (5) with recycled product gas to about 350°C. Primary separation of fly slag from product gas occurs in a cyclone (6). Further separation is accomplished in the venturi scrubber (7), the separator vessel (8), and the packed-bed scrubber (9). The product gas is now free of solids (<1 mg of solids/Nm³). Some of this gas leaves the plant as high-pressure product gas (10), while some is recycled to the quench section (5). Before this recycle gas reaches the quench section, it passes through a condenser (11), separator vessel (12), recycle-gas compressor (13), and buffer vessel (14).


Fig. 3.3-2. The process diagram for the 6-TPD SCGP is shown.⁵

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Boiler feed-water (15) enters the system through the separator (8) and the packed-bed scrubber (9). Water from the recycle-gas clean-up section (16) is also admitted to the packed-bed scrubber. The water is finally passed through the sour-water stripper (17), where low-pressure gas (18) and steam (19) are produced.

The 250 TPD SCGP-1 has been described⁴ as substantially different from the 6-TPD pilot plant, with improvements derived from results of continuing research at the Shell Research Laboratory in Amsterdam and the 150 TPD Harburg plant.

In the pilot plant, nitrogen is typically employed to transport coal to the gasifier. However, recycle product gas may also be used when a product gas essentially free of nitrogen is desired. Typical gas concentrations are given in Table 3.3-4 and indicate that N_2 comprises around 14 or 15% of the product gas. In larger-scale systems, a denser flow of solids can be handled, thus reducing the carrier-gas flow-rate. These product gases have high CO and H₂ but low CO₂ and CH₄ concentrations. This desirable feature is attributed to the dry feed and high temperature in the Shell gasifier. The gas composition on a dry, nitrogen-free basis expected from the SCGP-1 is given in Table 3.3-5 for comparison. Trace components for both processes are similar and compounds such as naphtha, phenols, tars, and other HCs do not survive the gasifier.

Other design improvements are aimed at potential economies of scale, improved stream factors and careful component optimization.

According to Heitz and Nager,⁴ it is expected that units processing 2500 TPD or more will be shop-fabricated and transportable by rail in the US. The SCGP-1 will be used to confirm equipment life and to provide needed information for commercial designs. Key components for evaluation include the feed system, gasifier, and syngas cooling system. Environmental data will be obtained for feedstocks designated by the participants, with the acid-gas removal system designed to meet applicable strict environmental control legislation. A gas-treating slip-stream unit will be operated to test cleanup options.

Computerized data-acquisition and handling systems are being installed.

For further details and information on project management and related topics, we refer to Heitz and Nager.⁴

	Coal Type			
Component	Illinois No. 5	Texas Lignite		
H ₂	26.78	26.49		
co	52.24	52.43		
CO2	5.14	6.61		
CH ₄	0.02	0.13		
H ₂ S	0.77	0.27		
N ₂	14.98	14.01		
H ₂ O [†]	7.38	9.35		

Table 3.3-4. Representative product-gas compositions (in vol%) obtained at the SCGP in Amsterdam; from Ref. 5.

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[†] Vol% on a dry-gas basis.

Table 3.3-5.	Typical treated product-gas composition anticipated
	for the SCGP-1; reproduced from Ref. 4.

Component	% by volume (N ₂ -free)		
H ₂	30		
CO	69		
CO2	< 0.1		
H ₂ S	< 0.01		
COS	< 0.01		
HCN	< 0.001		
NH ₃	< 0.001		
HCI	< 0.001		
HF	< 0.001		
CH ₄	0.03		
H ₂ O	0.6		
Ar	0.2		

3.3-3. The U-GAS Process *

3.3-3A. Introduction

The Institute of Gas Technology (IGT) has developed the U-GAS process to produce gas from coal in an efficient economic, and environmentally acceptable manner. The product gas from the process may be used to produce low-Btu gas, medium-Btu gas, and substitute NG for use as fuels, or chemical products such as ammonia, methanol, hydrogen, and oxo-chemicals, or electricity generated by a combined cycle or a fuel cell. The three main goals for developing a new gasification process have been economical handling of large volumes of gas throughput, high carbon conversion of coal to gas without producing tar or oil by-products, and minimum damage to the environment.

The U-GAS process has been developed in a multiphase program over a period of 8 years and has utilized skills and expertise evolving from earlier coal-gasification projects at IGT that date back to 1950. The process has been extensively tested in a pilot plant to establish process feasibility and provide a large data base for scale-up and design of the first commercial plant. The U-GAS process is considered to be one of the more flexible, efficient, and economical coal-gasification technologies developed in the US during the last decade. The U-GAS technology is currently available for licensing from GDC, Inc., a wholly owned subsidiary of IGT.

3.3-3B. <u>Process Description</u>

The U-GAS process accomplishes four important functions in a single-stage, fluidized-bed gasifier (Fig. 3.3-3): it decakes coal, devolatilizes coal, gasifies coal, and agglomerates and separates ash from

^{*} Prepared by P.B. Tarman, Vice President, Research and Development, IGT, 3424 South State St., Chicago, IL 60616.

char. Other characteristics of the process are shown in Table 3.3-6. In the process, coal (1/4 inch x 0) is dried only to the extent required for handling purposes. It is pneumatically injected into the gasifier through a lockhopper system. Within the fluidized bed, coal reacts with steam and oxygen (air can be substituted for oxygen) at a temperature of 1750 to 2000°F. The temperature of the bed depends on the type of coal feed and is controlled to maintain nonslagging conditions for ash. The operating pressure of the process depends on the ultimate use of product gas and may vary between 50 and 350 psi. The pressure must be optimized for a

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Fig. 3.3-3. Schematic diagram of the U-GAS fluidized-bed gasifier.

Table 3.3-6. U-GAS process characteristics.

High conversion of coal to gas using an ash-agglomerating technique; capability to gasify all ranks of coal; ability to accept fines in the coal feed; simple design, safe and reliable operation; easy to control, ability to withstand upsets; product gas virtually free of tar and oils; no environmental problems; operation at lower temperature than are used with slagging gasifiers; large turndown capability; large unit capacity.

particular system; for production of an industrial fuel, a minimum pressure of 80 to 100 psi is desirable. At the specified conditions, coal is gasified rapidly, producing a mixture of H_2 , CO and CO₂, and small amounts of CH_4 . Because reducing conditions are always maintained in the bed, nearly all of the sulfur present in coal is converted to H_2S . Simultaneously with coal gasification, the ash is agglomerated into spherical particles and separated from the bed. A portion of the fluidizing gas enters the gasifier through a sloping grid. The remaining gas flows upward at high velocity through the ash-agglomerating device and forms a relatively hot zone within the fluidized bed. High-ash-content particles agglomerate under these conditions and grow into larger and heavier particles. Agglomerates grow in size until they can be selectively separated and discharged from the bed into water-filled ash hoppers, from which they are withdrawn as a slurry. In this manner, the fluidized bed achieves the same low level of carbon losses in the discharge ash that is generally associated with ash-slagging gasifiers.

Coal fines elutriated from the fluidized bed are collected in two external cyclones. Fines from the first cyclone are returned to the bed, and fines from the second cyclone are returned to the ash-agglomerating zone, where they are gasified and the ash is agglomerated with bed ash. The raw product gas is virtually free of tar and oils, thus simplifying the ensuing heat recovery and purification steps.

3.3-3C. Pilot-Plant Description

Most of the U-GAS process development work has been accomplished on a pilot plant put into operation in 1974. A chronological listing of pilot-plant development is given in Table 3.3-7. The development program has been funded by the US DoE and the American Gas Association. The pilot plant is located at IGT's test facilities in southwest Chicago. It consists of a gasifier and all required peripheral equipment with utilities and other support services. Most of the equipment is contained in an enclosed structure that is about 100 ft. high. 41, 1

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The pilot plant consists of a drying and screening system, feedstorage silos, a lockhopper system for feeding coal at rates up to 3000 lb/hr., a refractory-lined fluidized-bed reactor with a special agglomerate with-

Date(s)	Number of Tests	Function
1974	9	Equipment shakedown
1974-1975	53	Process-feasibility studies
1975	13	Testing of highly-reactive small-size feed
1977	4	Shakedown of the modified pilot plant
1977	7	Testing of highly-reactive feedstock
1977	6	First bituminous coal tests
1978	8	Testing of unwashed high-ash feedstock
1978-1982	25	Demonstration/commercial plant design data
1980	3	Testing of highly-caking feedstock
1981	3	Coal-verification test with different feedstocks for different clients
1983	2	Coal-verification tests with ROM French coal
1984	1	Coal-verification tests with ROM Utah Coal (air and enriched-air gasification)
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Table 3.3-7. Test history of the U-GAS pilot plant.

drawal system in its base, a product gas quench system, a cyclone system for removal and recycle of elutriated fines, a product-gas scrubber, a productgas incinerator, and a lockhopper ash-removal system. The pilot plant flow diagram is shown in Fig 3.3-4. The gasifier is a mild-steel, refractoryline vessel with an inside diameter of 3 ft and a height of about 30 ft. The pilot plant is thoroughly instrumented to provide necessary operating information and data for the calculation of accurate mass and energy balances. A computer system for automatic data acquisition provides on-line process flows, balances, critical variable trend plots, and operating data summaries at regular intervals. The pilot plant contains special sampling systems for complete characterization of the raw product gas, water effluents, and coal fines necessary for gas-purification and wastewater systems.

3.3-3D. Process Development

Over the last 7 years, IGT has conducted an extensive, multidisciplinary program to develop important aspects of the U-GAS technology and to obtain information for the design of a commercial plant. The program has included the following steps:

(i). Operations of the U-GAS pilot plant to demonstrate process feasibility, including ash agglomeration and fines recycle. The pilot plant has also yielded data on the process, mechanical and operational design of a commercial plant. A detailed mechanical design of the gasifier has been on-going while the pilot plant has been operational. This procedure has been of great benefit in identifying design data gaps that could be obtained from the operating pilot plant.

(ii). Scale-up studies on large, cold-flow model. The basic concerns in scaling up from a pilot plant to commercial scale are centered around the grid and venturi region of the gasifier. A semi-circular cold-flow model and a pressurized cold-flow model have been operated to understand the hydrodynamics of the grid/venturi region, determine the mechanical configuration of the scaled-up grid-venturi, and select the dimensions of the venturi to discharge the necessary quantity of ash agglomerates. An X-ray cinestudy has been conducted to examine visually



Fig. 3.3-4. Schematic of the process flow in the U-GAS pilot plant.

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solids circulation, jet penetration, and bubble dynamics in the grid/venturi zones of different mechanical configurations. Numerical simulation and engineering calculations have been carried out to compare the thermal and hydrodynamic similarities between the pilot and commercial plants and to select appropriate design parameters.

(iii). Ash chemistry studies and bench-scale experiments. Extensive ash-chemistry studies have been conducted to understand and develop mechanistic models of ash agglomeration and ash adhesion. Bench-scale experiments have been carried out to determine the main operating variables affecting the formation of ash agglomerates. Steam-oxygen gasification and high-pressure fluidization knowledge and skills have been developed in various other coal-gasification projects at IGT dating back to 1950. A computer model of the U-GAS gasification system has also been developed to predict the performance of the gasifier at different operating conditions and with different coals.

(iv). Environmental characterization of the process. During the pilot-plant operation, extensive sampling and analysis have been conducted to obtain information for complete environmental characterization of the process. The raw product-gas samples have been collected in a specially developed sampling train to trap all impurities present in the gas. These analyses have yielded the needed data for design of the downstream gas-purification equipment. The water-discharge stream for the venturiscrubber system has been analyzed for information on design of wastewatertreatment facilities. All solid streams entering and leaving the gasifier have been analyzed for trace metals to obtain a material balance and determine the fate of trace metals present in the coal feed. Ash agglomerates and other solid discharges have undergone leaching tests to assess compliance with regulations. No environmental problem has been encountered in the design of the commercial plant, as evidenced by approval of the Environmental Impact Statement by all US, state, and local regulatory agencies.

Based on successful development of all aspects of the U-GAS technology, the process is ready for commercialization. Independent evaluations by several large engineering and petroleum companies support this conclusion.

3.3-3E. Pilot-Plant Operations

The U-GAS pilot plant has been the primary unit in which the process development has been conducted. A total of 10,000 hrs of operating time has been logged in the pilot plant, during which period over 120 tests have been conducted with about 3500 tons of various coals. Several test runs have lasted over 2 weeks, thereby providing long, steady-state operating periods with excellent mass and energy-balance closures. いため、そこので、このであるというで、たいという

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The pilot-plant development has been carried out in a multiphased program starting in 1974. As is typical in pilot-plant developments, both mechanical and process problems were encountered. One by one, solutions were found for each of these. By the end of the development program, all important aspects of the process (raw coal feed, stable ash agglomeration, and fines recycle) were both routinely and repeatedly achieved in several tests. A detailed description of the pilot-plant development is given in IGT reports. In phase I, process feasibility was demonstrated using metallurgical coke and char as feed. For phase II, the pilot plant was modified to feed coals, and trial tests were made with subbituminous and bituminous coals. During phase III, process feasibility was proved using high-sulfur-content, caking bituminous coal as feed and data were developed for scale-up and design of a commercial plant. In phase IV, environmental data were collected and the reactor dynamic response was investigated.

The major achievements in the pilot plant have been as follows: (i) Process feasibility has been verified in a series of tests of extended duration. (ii) The application of the technique of ash agglomeration and fines recycle has been perfected, and an overall coal-utilization efficiency of over 98% has been achieved. (iii) The process has been shown to have a wide operating window, thus providing flexibility to gasify a wide variety of feedstocks. (iv) The tests have produced a strong data base for scale-up and design of the first commercial plant. (v) Data related to environmental aspects of the process, particularly raw gas and wastewater characteristics, have been obtained. These data show that there are virtually no tars or oils produced in the process. (vi) Commercially available refractories and metallurgical products have performed quite satisfactorily in the gasifier. Mechanical information has been obtained for designing gasifier internals, critical hardware, valves, cyclones, etc., which are important for reliable operation.

3.3-3F. Feedstocks

A wide variety of feedstocks have been used in the pilot plant to determine process sensitivity to variables such as ash content, ash properties, particle size, reactivity, free swelling index, and volatile matter. Eight types of different coals and three types of chars have been tested in the pilot plant (cf. Table 3.3-8). The feedstocks for testing have been selected to cover a wide range of important coal properties that could have significant effects on gasification and ash agglomeration. The range of feedstock properties is shown in Table 3.3-9.

All feedstocks except chars are 1/4 inch x 0 in size and are fed to the gasifier without any removal of fines. The coals are also directly fed into the gasifier fluidized bed without any pretreatment, regardless of their caking tendencies (free swelling index). Also, for western Kentucky coals, both washed and unwashed coals have been successfully tested to determine the effects of the large quantity of clay and shale that is present in unwashed underground-mined coals.

Lignites have not been tested in the pilot plant because of funding limitations, but the Wyoming subbituminous coal has reactivity, moisture, and volatile matter content very similar to lignites. Therefore, lignites should not pose any problems in the U-GAS process. Specifically, ash properties are more significant in the U-GAS process than coal reactivity, and the range of coals tested in the pilot plant covers almost all lignite-ash compositions.

3.3-3G. Utah Bituminous Coal Test

A test was carried out with Utah bituminous coal in the U-GAS pilot plant. ANR was interested in evaluating the performance of the U-GAS process to produce low-Btu gas and to provide data for the design of a commercial plant. The test called for 7 days of operation at 5 different set-points.

The test was successful in achieving all of ANR's predetermined test objectives. These objectives were (i) to prove the feasibility of producing low-Btu gas by gasifying the coal with air and steam, (ii) to maximize coal-conversion efficiency, (iii) to gasify coal with enriched air,

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Western Kentucky No. 9 bituminous coal (both washed and unwashed) Western Kentucky No. 11 bituminous coal Illinois No. 6 bituminous coal Pittsburgh No. 8 bituminous coal Australian bituminous coal Polish bituminous coal French bituminous (unwashed) coal Utah bituminous (unwashed) coal Utah bituminous (unwashed) coal Montana subbituminous coal Montana subbituminous coal Metallurgical coke Western Kentucky coal char Illinois No. 6 coal char

Table 3.3-9. Range of U-GAS gasifier feedstock properties.

Property	Value		
Moisture, % Volatile Matter. %	1 to 32 [†] 3 to 43 [‡]		
Ash, %	6 to 35		
Sulfur, %	0.5 to 4.6		
Free Swelling Index	0 to 8		
Ash-Softening Temperature, °F	1980 to 2490		
°C	1080 to 1370		
Gross Heating Value, Btu/lb	7,580 to 12,650 [†]		
kJ/kg	17,631 to 29,424		
[†] As received; [‡] dry basis.			

(iv) to investigate gasifier turndown, (v) to test gas desulfurization using limestone, (vi) to evaluate a high-temperature coal-dust filter, (vii) to test combustion characteristics of the low-Btu product gas, and (viii) to obtain data for the design of a commercial plant.

The pilot plant was operated for 6 days during which time 58 tons of Utah coal were gasified. Steady-state, ash-balanced operations were maintained for 6 different set-point operating conditions. The coal-conversion efficiency was 93 to 99% during the various set-points of operating conditions. The test was voluntarily terminated when all of the test objectives were completed. A summary of the pilot plant test results from one of the set-points is shown in Fig. 3.3-5.

Gasification was carried out with air and steam and enriched air (34% oxygen) and steam. The heating value of the low-Btu gas was varied from 75 to 171 Btu/SCF. The heating value of the low-Btu gas was lower than is expected in a commercial plant because of (i) high heat losses relative to the reactor coal feed capacity and (ii) excessive cooling of recycled fines in the primary water-jacketed cyclone.

During one of the set points, the capability of the gasifier for turndown was demonstrated by reducing the gas-production rate by half. The ability of banking the gasifier was demonstrated also during some mechanical failures encountered during the test. For example, the coal-feed system was shut down for almost 10 hours to repair the variable speed feed mechanism. During this period, the gasifier was maintained in a hot, standby position and restarted without any problems after repairs were completed. During typical plant upsets, the gasifier was made to respond in a controlled and logical fashion, without major interruptions in gas production.

The test demonstrated total fines recycle, which is necessary to achieve high coal-conversion efficiency. The fines from the primary cyclone were recycled during all six set-points and the fines from the secondary cyclone were recycled during five of the six set-points. Secondary fines recycle was achieved under smooth and controlled conditions and was shown to be easily initiated and controlled. Any intermittent interruptions in the recycle of the secondary fines did not cause operating upsets or reduction in gas production.

As part of the overall program, three special tests were conducted that were aimed at improving the performance and economics of commercial low-Btu gas plants. In one of these, limestone was injected into the fluidized bed along with coal to test the capture of sulfur compounds generated during coal gasification. The addition of limestone did not have adverse effects in the gasifier, ash discharge, or fines recycle. Data indicated that a large portion of the spent limestone exited the gasifier as $CaSO_4$ rather than CaS. The former is the preferred by-product because of its stability in an atmospheric environment. The degree of sulfur reduction in the product gas could not be precisely determined because of the difficulty in measuring relatively low concentrations of sulfur compounds (the coal contained only 0.6 wt% of sulfur). :

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Fig. 3.3-5. Results of the test conducted with Utah coal in the U-GAS pilot plant; coal conversion = 96.0%; C* represents MAF-coal.

In another special test, we evaluated the high-temperature coal-fines filter. If coal fines could be removed from the low-Btu product gas at high temperatures (1000° to 1500°F), then product gas could be utilized directly, thus simplifying the commercial plant design and improving efficiency and economics. A hot ceramic candle filter was installed in the pilot plant on a slipstream after the primary cyclone. The filter operated during the test in a completely automatic mode throughout the six-day test and removed all of the dust from the hot product gas. There was no blinding of the filter medium or any continuous increase in pressure drop or cycle time of the filter system. The measurement of dust in the filtered gas was conducted using a photometric particle counter. The results of the measure at one of the set points is shown in Fig. 3.3-6.

The combustion characteristics of the low-Btu product gas resulting from operations at three of the set-points were evaluated in a specially-installed burner and furnace. Stable combustion was achieved with gases from all set-points. The SO₂ and NO_x emissions were measured during the combustion tests; in addition, both thermal and fuel NO_x formations were determined.

A complete environmental characterization of the low-Btu product gas was made by using a specially designed sampling loop. These results indicate that the gas does not contain any significant quantity of tar and oils and both the gas-purification and waste-water treatments in a U-GAS plant could be handled by conventional technologies.

3.3-3H. Pilot-Plant Tests with a French Coal

A French Merlebach coal was successfully gasified in the U-GAS pilot plant during tests conducted for CdF. Two tests were conducted: The first test provided useful information on operational characteristics of the coal. The second test yielded a long steady-state operating period in which all of CdF's test objectives were achieved. These objectives were: (i) demonstration of the operability of the U-GAS process with high-ash French coal, (ii) maximization of coal-conversion efficiency, (iii) production of good-quality product gas, and (iv) data for the design of a demonstration plant.

In the second test, the plant was operated continuously for 92 hrs, when 48 tons of coal were gasified during 60 hrs of steady-state operation. Ash-agglomerating and ash-balance operations were maintained during three different operating conditions. These involved (i) testing without recycle of fines from the secondary cyclone, (ii) testing with total recycle of fines, and (iii) testing with a lower steam-to-coal ratio. A coal-conversion efficiency higher than 95% was continuously maintained during the last two tests.

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Fig. 3.3-6. Dust loading in the filter exit gas for one of the set points.

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The gasifier was used to handle coals with ash contents from 20 to 35 wt%. In addition, because the coal was unwashed, it contained a large quantity of shale, which was also handled by the gasifier without any detrimental operational effects. Once steady-state operation was achieved and ash agglomeration established, 96% of the ash discharged was withdrawn through the bottom venturi; the remaining 4% of ash was withdrawn through the overhead along with the fines. No ash buildup occurred in the fluidized bed, despite the uneven ash-feed rate to the gasifier.

The quality of the product gas in the U-GAS process is strongly influenced by the characteristics of the feed coal. Despite the combination of a high ash and a low volatile matter content with the Merlebach coal, the U-GAS pilot plant yielded a good-quality product gas with an HHV of about 215 Btu/SCF (8600 kj/m³). The pilot plant has relatively high heat losses compared to its coal-feed capacity. In addition, excessive cooling of the recycled fines occurs both in the primary water-jacketed cyclone and the first-stage quench. Our estimate is that a commercial gasifier with appropriately designed cyclones and experiencing lower heat loss per unit volume of product gas will produce a gas with a heating value from 250 to 270 Btu/SCF (10,000 to 10,800 kj/m³). During the last set-point in the Merlebach coal test, it was demonstrated that the heating value of the product gas could be significantly improved by appropriate optimization of operating parameters. When generating synthesis gas from coal to produce chemicals, a more critical number than gas-heating value is the combined yield of H_2 and CO; any CH_4 in the product gas is considered to be by-product. In the U-GAS pilot-plant test, the yield of H_2 +CO was up to 20 SCF/1b $(1.25 \text{ m}^3/\text{kg})$ of MAF coal.

During the test (see Fig. 3.3-7), we demonstrated with the U-GAS process the ability for a total recycle of fines that is necessary to achieve high coal-conversion efficiency. The fines from the primary cyclone were recycled during the latter two set points only. Secondary fines recycle was shown to be easily initiated and controlled. The testing also demonstrated that occasional minor interruptions in the recycle of the secondary fines did not reduce gas production or cause operating upsets. In fact, the automatic oxygen/temperature controller employed by the U-GAS process promptly responded to these interruptions and maintained the gasifier under stable operating conditions. Recycle of fines was maintained

for more than 34 hrs and conclusively demonstrated that the fines could be gasified to extinction while the resultant fine ash was agglomerated and discharged along with the bed ash through the venturi, without buildup of fines or ash in the gasifier system. د. در دکتره به در در در در در در در در در

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The pilot-plant test showed that the ash from the Merlebach coal could be readily agglomerated in the U-GAS process. This was demonstrated by classification and withdrawal of only high ash-content material through the venturi.

3.3-4. Other Gasifiers

A comprehensive review of selected gasification systems and associated coals has been prepared for EPRI by Synthetic Fuels Associates.⁶ We refer to this study and references cited therein for descriptions of the Lurgi Dry Ash, BGC/Lurgi, KilnGas, and other gasifiers. Descriptions of a number of currently active gasification technologies will be found in Chapter 4.



Fig. 3.3-7. Results of the test conducted with French coal in the U-GAS pilot plant; coal conversion = 95.3%; C* represents MAF-coal.

References for Section 3.3

- "Texaco Coal Gasification Process," Texaco Development Corporation, Montebello, CA (1986).
- 2. W.G. Schlinger and G.N. Richter, Hydrocarbon Processing 59, 66 (1980).
- 3. W.G. Schlinger, J.H. Kolaian, M.E. Quintana, and T.G. Dorawala, Energy Progress <u>5</u>, 234 (1985).
- W.L. Heitz and M. Nager, "Status of the Shell Coal Gasification Process (SCGP)," Fifth Annual EPRI Contractors' Conference, Palo Alto, CA (October 30-31, 1985).
- Electric Power Research Institute, "Evaluation of US Coal Performance in the Shell Coal Gasification Process (SCGP), Report No. EPRI AP-2844, Palo Alto, CA (1984).
- Electric Power Research Institute, "Coal Gasification Systems: A Guide to Status, Applications, and Economics," Report No. EPRI AP-3109, Palo Alto, CA (1983).

3.4 Research Recommendations for Improving Gasifiers

Primary motivations for supporting research are the needs for cost reduction and operating-life extensions of gasifiers.

There are two important identified research areas, the pursuit of which may lead to improved performance in the SCGP and TCGP. These are reduction or elimination of fouling¹ and elimination of failure caused by high-temperature corrosion fatigue.²

3.4-1. Fouling and Slagging

According to the authors of Ref. 1, research on slagging is expected to lead to improved methods for predicting fouling in practical systems. At

^{*} We are indepted for helpful comments to M. Nager and W. Schlinger in the preparation of this section.

present, the methods used are largely empirical and based on static models, which do not correspond to actually existing conditions in combustors or gasifiers where many different sizes of pulverized coals are utilized. An improved ASME procedure is required to define slagging conditions for coals since the ash-fusion temperature has been shown to be an inadequate measure for slagging. The authors of Ref. 1 suggest the use of bench-scale experiments, with special emphasis on innovative approaches.

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Research should include the following types of studies. (i) Predictions of the slag viscosity, especially under gasifier conditions. Slag viscosity is of critical importance in assuring that the slag is removed continuously from the gasification chamber. This problem is complicated by the fact that slags appear in homogeneous and multi-phase systems. (ii) Phase diagrams incorporating new and existing empirical data, especially for binary, ternary and higher-order mixtures. To use the results properly, the equilibrium behavior of ash must be determined. This approach will also lead to improved understanding of wall-and tube-deposit formations. (iii) Many modern dynamic experiments are performed with large variations in conditions. Data from different experiments may be difficult to compare. Applications to practical systems present even greater challenges. Since experiments may be performed that represent reasonable simulations of actual combustion conditions, standardization of experimental test procedures would be desirable. (iv) The use of improved diagnostic techniques is recommended to verify or improve fundamental understanding of gasification rates and mechanisms and the best available modeling procedures. (v) Static experiments on bulk samples are attractive because of their relatively low costs and simplicity. If possible, static experiments should be devised that provide useful information on fouling and slagging.

3.4-2. Corrosion and Fatigue

Three research areas are suggested in Ref. 2: (i) Measurements of high-temperature, corrosion-fatigue data for alloys of commercial interest under accurately controlled and well-defined conditions. (ii) Information on the kinetics and mechanisms of corrosion-fatigue damage formation. (iii) An augmented model incorporating the results obtained under (i) and (ii) into design calculations. There has been special emphasis on the reducing

conditions found in coal gasifiers, but other environments could be usefully employed to obtain data over wider ranges of conditions. Interesting temperature ranges lie² between 350 and 700°C, while pressures fall in the 20-60 atm range.

New studies should be performed on the effects of cyclic loadings (50 to 5000 cycles) to identify the influence of cycling on failure rates.

3.4-3. <u>High-Temperature Sulfur Removal</u>

Application of a high-temperature sulfur-removal process will significantly improve the efficiency of an IGCC system and a DoE-supported program in this area is therefore recommended.

3.4-4. Gasifiers for Low-Rank Coals

Gasifiers for IGCC (cf. Sec. 3.3) have been extended to low-rank coals. EPRI has made a preliminary evaluation of this proposal for the Texaco gasifier using CO_2 -lignite slurries as gasifier feed. The Shell, Dow and other gasifiers have also been demonstrated as applicable to low rank coals.

3.4-5. Low-Cost Gas Separation and Air Enrichment

The Shell and Texaco gasifiers, as well as other gasifications systems, will benefit from lower costs if improved gas-separations with air-enrichment systems are developed. This important topic is addressed in Chapter 13.

References for Section 3.4

- "Recommendations for Research Leading to New Bench-Scale Experiments for the Prediction of Slagging and Fouling Behavior," ASME Research Committee on Corrosion and Deposits from Combustion Gases (March 18, 1985).
- W.T. Bakker, "Suggestions for Direction Low Cycle Fatigue Program," Report of the Second Meeting of COGARN, pp. 212-215 (February 25, 1986), unpublished.

CHAPTER 4: COAL GASIFICATION FOR SNG PRODUCTION*

4.1. Introduction

4.1-1. The Great Plains Coal Gasification Plant (GPCGP)

In the early 1970s, when "Project Independence" was being defined by the Federal Government and serious concerns were being raised about the natural gas (NG) reserves and long-term supply of NG, there were more than 100 major projects under consideration that involved the production of substitute natural gas (SNG) from coal. These projects generally involved plants that would produce the equivalent of 250 million standard cubic feet of gas per day (SCF/d) with a heating value of 950-1000 Btu/SCF. Some of these plants were on a schedule that would have placed them on-stream in the mid- to late-1980s. However, the world energy picture changed dramatically and the requirement for producing pipeline-quality gas from coal moved further into the future. Now, SNG from coal is being considered as a potential pipeline-quality gas supply option for the post-2000 time frame.

As a result of changes in the energy market, only the GPCGP was constructed. This plant is located in Beulah, North Dakota, and was developed through the combined efforts of a consortium of natural gas companies and the Federal Government. Start-up operations began in 1984, with a nominal output of 125 million SCF/d (at a 90% stream factor) of pipeline-quality gas. This plant uses North Dakota lignite as the feedstock and its operation is based on dry-bottom Lurgi gasification technology together with commercially available methanation, gas conditioning and clean-up technology.

*This chapter has been written by Kermit E. Woodcock and Vernon L. Hill of GRI.

To date, the GPCGP is clearly a technical success.¹ It was constructed within cost, completed on schedule and has involved only minimal problems during its initial period of operation. The plant was designed to produce 137.5 x 10^6 SCF/d, but has operated consistently at levels exceeding the original design capacity. In March 1986, the plant production was as follows: highest daily rate = 154.7 x 10^6 SCF (112.5% of design), highest weekly rate = 1.0463 10^9 SCF (109% of design), highest monthly rate = 4.536 x 10^9 SCF (106.4% of design).

In the current economic climate resulting from low world oil prices, the GPCGP is not economically competitive with other gas-supply options. However, the experience gained through the construction and operation of this plant is providing the gasification community with a bench mark of the real costs of SNG based on commercially available technology. In addition, it is helping to identify where process improvements can be effected through engineering changes or process selection and where supporting research and development efforts could have an impact.

4.1-2. <u>General Thermodynamic Considerations</u>

The atomic ratio of H to C in coals is less than one. As a result, in order to convert coal to pipeline-quality gas efficiently at an H/C ratio of 4, it is necessary to provide a source of H_2 . This is usually accomplished by the addition of steam. The overall reaction scheme for producing pipeline-quality gas from coal, with water as source of the necessary hydrogen, represented by

$$coal + H_2 0 \longrightarrow CH_4 + CO_2.$$
 (4.1-1)

In most gasification processes, however, this overall reaction is not realized in a single step but is accomplished through a series of steps to provide reaction environments for which conversions proceed at acceptable rates. These steps are the unit operations of coal-gasification plants. As reaction temperatures are raised to higher values (where gasification reactions proceed at adequate rates), the stability of CH_4 (methane) is reduced and, at the higher temperatures such as those associated with entrained-flow

gasifiers (i.e., $1250-1370^{\circ}$ C), there is no methane production in the gasifier. Typical off-gas compositions from fixed-bed, fluidized-bed and entrained-flow gasifiers are presented in Table 4.1-1, which show the ranges of methane production that can be expected. These data also provide an indication of the additional conversion to methane that must be accomplished in order to approach the overall reaction scheme represented by Eq. (4.1-1).

As the reaction temperature is raised, the reactions that dominate the gasification process include

coal
$$\longrightarrow$$
 CH_A + char + tars, oils, (4.1-2)

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char +
$$H_2^0 \longrightarrow C0 + H_2^{-},$$
 (4.1-3)

char +
$$0_2 \longrightarrow CO + H_2$$
, (4.1-4)

$$co + H_2 o \iff co_2 + H_2, \qquad (4.1-5)$$

$$CH_4 + H_20 \iff CO + 3H_2, \qquad (4.1-6)$$

$$2CH_4 + O_2 \iff CO + 4H_2,$$
 (4.1-7)

$$2C0 \Leftrightarrow CO_2 + C.$$
 (4.1-8)

In addition to the principal reactions, which control the concentration of the major products of gasification, there occur also a series of reactions involving trace constituents in the coals, such as the nitrogen, sulfur and mineral matter, which result in the formation of additional gaseous species $(H_2S, NH_3, COS, mercaptans, sulfides, etc.)$. The nature of these additional gaseous species depends on the gasifier conditions and coal type and must also be dealt with as part of a coal-to-SNG process.

When the gasification process is controlled by the types of reactions represented by Eqs. (4.1-2) through (4.1-8) and when SNG is the desired end product, additional processing steps are required to convert the CO and H₂ produced in the gasifier to methane. The principal reactions to accomplish this conversion are (a) the water gas shift reaction (WGSR) of

Eq. (4.1-5), which provides the desired initial H_2/CO ratio and (b) a methanation reaction which may proceed according to the following steps:

· · · · · · · · · · · · · · · · · · ·	Moving-bed Gasifiers		Fluidized-bed Gasifier	Entrained-flow Gasifiers		
Parameter	Lurgi dry-ash (commercial)	BGC slagging Lurgi (pilot plant ^a)	Winkler (commercial)	HYGAŚ (pilot plant ^a)	Koppers- Totzek (commercial)	Texaco (pilot plant ^a)
Gas exit T, °C	580	440	700	340	1290	1290
p, psi	430	290	14.7	1000	14.7	580
Gas analysis, vo1%						
coz	29.7	2.5	20.0	24.7	7.1	10.6
CO	18.9	60.6	34.0	24.0	58.7	51.6
H ₂	39.1	27.8	41.0	30.5	32.8	35.1
CH	11.3	7.6	3.0	19.4	-	0,1
Othersb	1.0	1.5	2.0	1.4	1.4	2.6
H ₂ /CO volume ratio	2.1	0.46	1,21	1.27	Ø.56	0.68
Product utilization Equivalent SNG, ^C nM ³ /1000 kg of coal	1884	1939	1596	1850	1845	1988
Equivalent CH ₄ , ^d nM ³ /1000 kg of coal	529	517	413	542	462	470

Table 4.1-1. Commercial and developmental gasification processes, oxygenblown reactant consumption and gas production.

^aPilot plants are of various sizes: BGC/Lurgi, 1200 kg/h; HYGAS, 2500 kg/h; Texaco, 6500 kg/h.

^bThis value includes nitrogen and various impurities (H₂S, COS, NH₃, etc.).

^cThe SNG is assumed to be equal to the sum of the concentrations of H_2 , CO, and $3 \times CH_4$.

^dThe methane potential is assumed to be equal to the methane (CH₄) concentration plus (1/4) of the (H₂+CO) concentration.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O,$$
 (4.1-9)

$$2C0 + 2H_2 \longrightarrow CH_4 + CO_2,$$
 (4.1-10)

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O_4$$
, (4.1-11)

These reactions depend on the overall initial gas composition and the methanation catalyst used.

Workers at Exxon, through the use of alkali metal or alkaline earth salts as gasification catalysts and an innovative concept, were able to provide a reaction environment in the gasifier such that all of the methane was formed in the gasifier itself and additional methanation steps were not required (compare Sec. 7.2). However, the methane was still only one constituent of a multi-component gas mixture, and separation and gas clean-up steps were required to develop a final product stream of pipeline-quality gas.

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4.1-3. General Flow Sheets

Because of the heterogeneity of coal, the presence of heteroatoms and interactions of chemical kinetics and thermodynamics, the production of pipeline-quality gas from coal requires integration of many process steps, regardless of the type of gasifier employed. Typical block diagrams showing the number and sequence of major process steps needed for processes in which







Fig. 4.1-2. Coal-to-SNG in the Exxon gasification process.

methanation is required downstream of the gasifier and where all methane formation is achieved in the gasifier, as in the KRW and Exxon catalytic processes, are shown in Figs. 4.1-1 and 4.1-2; the Exxon process is described in detail in Sec. 7.2.

These diagrams emphasize the importance of effective process integration and indicate that there are many opportunities where process improvements, achieved through continued research and development, can have a positive impact on process configurations, capital costs, operating costs and, ultimately, the end-product cost of pipeline-quality gas. While all process elements contribute to the final end-product cost of SNG from coal, the gasifier, methanation process and clean-up systems represent major determinants in other process requirements and overall process integration.

4.2. Advanced Gasification Technology for SNG

The development of gasification technology to convert coal to SNG has been the subject for extensive research, developments and demonstration programs for at least three decades. In the US in the mid-1970s, over 20 conversion progresses were in various stages of development, and other approaches were being evaluated in Europe. These efforts encompassed exploratory projects, bench-scale studies, evaluations at the engineering-test unit (ETU) and process-development unit (PDU) scales, pilot-plant studies, and detailed design studies for demonstration plants and possible commerical operations. Process concepts that have been or are being evaluated include the following: Lurgi dry-botton (Lurgi GmbH), Bi-Gas (Bituminous Coal Research, Inc.) CO₂-Acceptor (Conoco Coal Development Co.) Synthane (U.S. Bureau of Mines), HYGAS (Institute of Gas Technology), COGAS (FMC Corporation), High Mass Flux (Bell Aerospace), Flash Hydropyrolysis (Rockwell International), Exxon Catalytic (Exxon Research and Engineering), Winkler (Rheinsiche Braunkohlenwerke AGR), U-GAS (Institute of Gas Technology), KRW Ash-Agglomerating (Westinghouse/KRW Energy), Hydrane (U.S. Bureau of Mines), Slagging-Fixed-Bed (British Gas Corporation/Lurgi GmbH), Fluid-bed Hydrogasification (Rheinische Braunkohlenwerke AGR), Ruhr-100 (Ruhrgas/Lurgi GmbH).

Each of these processes was conceived in an effort to improve the commercially available technology with respect to process efficiency, feedstock utilization and flexibility or to reduce the potential for unfavorable environmental interactions with the recognition that improved technology would translate into lower end-product gas costs. As the R&D program progressed and data became available for use in comparative economic evaluations, work was discontinued on most of these approaches when it was shown that sufficient economic incentives could not be identified to justify continued R&D expenditures. Today, as a result of the available data bases and the supporting economic studies, development work is still proceeding on the ash-agglomerating, fluid-bed technology (U-GAS, KRW Ash Agglomerating-process), the British Gas/Lurgi slagging gasifier, and the Rheinbraun direct, fluid-bed hydrogasification process for SNG production because of the unique characteristics of the available cost resource base and the advanced stage of the R&D program.

Other than the fluid-bed hydrogasification technology, continued gasifer development work is being justified primarily because of process flexibility and the potential for applications in areas other than SNG production (e.g., IGCC for electric power generation).

A brief summary of the technologies still under development, which can be applied to coal-to-SNG processes, is given in the following subsections, except for the U-GAS process which is described in detail in Section 3.3-3.

4.2-1. BGC/Lurgi Slagging Gasifier

The BGC/Lurgi slagging gasifier is a fixed-bed gasifier (Fig. 4.2-1) and consists of a vertical cylindrical reactor into which coal is injected through a lockhopper and a rotating coal distributor. The coal moves slowly down the reactor in contact with gases passing countercurrently through the bed. A mixture of steam and oxygen is injected at the bottom of the bed through nozzles (tuyeres). The base of the coal bed is called the raceway and is the location where high temperatures cause the ash to melt, yielding a fluid slag which drains from the hearth through a centrally-placed slag tap. The slag is quenched in a chamber filled with water to form a glass frit and is subsequently removed via a slag lockhopper.

The predominant reaction in the raceway is combustion of devolatilized coal, yielding a product stream of hot gases that contain steam and carbon oxides. As this gas moves up through the fixed bed, carbon is rapidly gasified by steam and carbon dioxide. Since these reactions are highly endothermic, the temperature drops rapidly, effectively limiting the very high temperature slag liberation zone to a small area. The small slag liberation zone is beneficial in reducing the heat transfer to the coal resulting in progressively lower temperatures, eventually reducing reaction rates to the point where gasification reactions effectively stop. Above this zone, rapid heating of the fresh coal results only in drying and devolatilization reactions. These reactions yield tars and oils, significant amounts of methane, sulfur compounds, steam, and other minor products, which are carried out of the gasifier by the product gas. The BGC/Lurgi slagging gasifier offers potential advantages over the dry-bottom

Lurgi technology since it can accommodate caking coals more effectively, utilizes coal fines, and has lower oxygen and steam requirements.

4.2-2. KRW (Kellogg-Rust-Westinghouse) Ash-Agglomerating, Fluidized Bed Gasifier

The KRW (Kellogg-Rust-Westinghouse) process is a fluid-gasifier (Fig. 4.2-2) in which coal and recycled fines are reacted with steam and oxygen to form a synthesis gas consisting mainly of CO, CO_2 , H_2 , CH_4 , and steam. The process development unit (PDU) gasifier is a vertical, refractory-lined vessel operable up to 230 psig and 1000°C and consisting of four sections: the freeboard, gasifier bed, combustion zone, and char-ash separator.

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Fig. 4.2-1. The BGC/Lurgi slagging gasifier.

Raw coal, ground to 3/16"xO" (and dried to 5% surface moisture when necessary), is fed pneumatically to the gasifier through a lockhopper system, along with the char fines from cyclones downstream of the gasifier. Feeding is accomplished by means of star wheel feeders and recycle gas. The coal and char are fed to the gasifier along its center line and combusted in a stream of oxidant (oxygen or air) fed through a coaxial feed tube. When oxygen is employed, steam is used together with the oxidant as the gasifying medium.

There are several other key flows into the gasifier, as shown in Fig. 4.2-2. A flow of steam is provided by annular flow around the nozzle tip to prevent carbon deposition at the base of the jet. Additional recycle gas or steam is injected radially at a location near the middle section of the injection nozzle. This flow mildly fluidizes and cools the ash for withdrawal; the sharp temperature gradient at the char/ash interface is utilized to control withdrawal rate. Recycle gas is also injected through a sparger ring at the base of the ash bed to aid in ash withdrawal.

The coal, char and steam reactions in the gasifier form hydrogen, carbon oxides and residual steam as the product gas. The carbon in the char is consumed by combustion and gasification as the bed of char circulates through the jet. The temperature near the bottom of the bed is maintained high enough to ensure that the ash-rich particles resulting from reactions soften, agglomerate and defluidize. The agglomerates migrate to the annulus around the feed tube and are continuously removed by a rotary feeder to lockhoppers. The major portion of the gasifier operates in an essentially isothermal condition up to 1,000°C. The lower portion of the annulus operates at about 260°C. Carbon conversion is typically 90-95% on an overall basis, while the ash is concentrated to 85% in the agglomerates.

The raw product gas containing no tars or oils passes from the gasifier to two refractory-lined cyclones in series, where the char particles are removed. The fines collected in the cyclones are cooled, inserted into a recycle gas stream and reinjected into the gasifier, either with the coal feed or separately into the lower section of the bed. The product gas is then quenched, cooled and scrubbed of any remaining fines (usually 1%) before further processing and recycling. Experiments at the PDU scale have demonstrated that high conversion efficiencies can be achieved

with a wide variety of feedstocks, including both caking and non-caking coals, and that coal fines can be effectively consumed in the gasifier.

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Fig. 4.2-2. Functional schematic of the Westinghouse gasifier.

4.2-3. Rheinbraun AG, Hydrogasification

Rheinbraun AG has been proceeding² with the development and evaluation of a process to produce SNG through the direct reaction of hydrogen and coal via the overall reaction

 $coal + H_2 \longrightarrow CH_4 + char.$ (4.2-1)

The overall process under consideration will utilize two fluid-bed reactors. In the upper bed, hydrogen is used as the fluidizing agent for the primary coal feedstock. The resulting product gas is a mixture of CH_4 , H_2 , CO, and CO_2 , along with H_2S and NH_3 , that must subsequently undergo clean-up, separation and upgrading steps to achieve the final SNG product stream. The residual hydrogen fraction of the stream is separated cryogenically and recycled to the reactor.

A schematic diagram of the pilot plant used to develop data for the hydrogasification reactor is shown in Fig. 4.2-3. Table 4.2-1 presents operating data from the hydrogasification pilot plant for the relatively reactive Rhenish brown coal and also for West German anthracite.



Fig. 4.2-3. Pilot plant for hydrogasification of coal (Rheinbraun AG); gasification pressure: up to 1750 psi; coal throughput: up to 9.6 dried tons/hr; gasification temperature: up to 950°C; gas production: up to 7800 m³ (i.N.)CH₄/hr.

	1976-1982		
Parameter	Rhenish Brown Coal	Anthracite	
Coal throughput, maf	1782 tons	13.6 tons	
Special coal throughput, maf	max.700 lb/hr	\max . 350 lb/hr	
Methane content of crude gas	up to 48 vol%	up to 25 vo1%	
Degree of C-gasification	up to 82%	up to 47%	
Operating temperature	800-1000°C	940-960°C	
Operating pressure	800-1375 psi	1150-1250 psi	
Solids residence time	9-80 min	28-38 min	
Plant in operation with coal throughput	26987 hr 12253 hr		

Table 4.2-1. Operating data of the semi-technical pilot plant for hydrogasification of coal at Rheinbraun AG.

The hydrogen required for hydrogasification is produced in the lower fluid-bed. Residual char from the hydrogasification stage is reacted with steam and oxygen to generate SNG that can be shifted to provide the necessary concentrations of hydrogen. The basis for the char gasifier is the high-temperature Winkler process, a pressurized, fluid-bed gasifier that is also being developed by Rheinbraun. The high-temperature Winkler is an extension of earlier, atmospheric pressure, fluid-bed gasifier technology and is designed to provide for higher temperature and higher pressure operation. The higher temperature lowers the make of liquid byproduct and increase carbon utilization. Higher pressures increase the gasifier throughput.

The high-temperature Winkler technology has been demonstrated in a nominal 45 TPD pilot plant at pressures to approximately 130 psi and temperatures to approximately 1100°C. All types of coal have been processed and it has been demonstrated that the addition of limestone to the fluid-bed can significantly reduce the H_2S content of the raw gas.

4.2-4. <u>Catalytic Coal Gasification</u>

Exxon Research and Development has conducted an engineering development program through the PDU stage (1-ton/day) to evaluate the potential for using coal gasification catalysts and a unique process flow sheet to produce SNG from coal in a fluid-bed reactor, without the use of an oxygen plant or a separate methanation step. The catalyst, together with the process concept, led to the direct formation of methane in the gasifier according to the overall reaction

$$coal + H_2 0 \longrightarrow CH_4 + CO_2.$$
 (4.2-2)

This technology, which is specifically focused on the production of SNG from coal is discussed in Sec. 7.2.

4.3. <u>Catalytic Methanation</u>

Catalytic methanation has been studied extensively since 1902, when Sabatier and Senderens published their classical paper on Ni catalysts.³ Many catalysts were subsequently tried. By 1925, many effective metal catalysts had been identified.⁴ An excellent description of commercial processes is given in Ref. 5. Although this subject is considered in Chapter 7, we shall discuss it here from a somewhat different perspective because of its potential importance for SNG production.

4.3-1. <u>Chemistry and Thermodynamics</u>

Catalytic methanation involves the exothermic formation of CH_4 , usually starting with a mixture of H_2 and CO, although methanation can also be achieved with mixtures of H_2 and CO_2 . Methane is formed in many coal gasifiers, with the lower temperature gasifiers producing relatively more CH_4 . Thus, some amount of CH_4 may be present in the feed gas to the catalytic reactor. Steam is usually present or is added to the feed to avoid carbon deposition. The heat release depends on the amount of CO present in the feed gas: for each 1% of CO, an adiabatic reaction will experience a 60°C temperature rise.
The pertinent reactions are 4,5

$$^{3H}_{2} + ^{CO} \rightleftharpoons ^{CH}_{4} + ^{H}_{2}^{O}, \qquad (4.3-1)$$

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$$^{2H}_{2} + 2CO \rightleftharpoons CH_{4} + CO_{2}, \qquad (4.3-2)$$

$$^{4H}_2 + ^{CO}_2 \rightleftharpoons ^{CH}_4 + ^{2H}_2^0, \qquad (4.3-3)$$

 $2C0 \quad \rightleftharpoons \quad C + CO_2, \qquad (4.3-4)$

 $c_0 + H_2 0 \rightleftharpoons c_2 + H_2.$ (4.3-5)

If methanation begins with a mixture of H_2 and CO and nickel-based catalysts are used, the desired H_2/CO ratio of the feed gas is 3:1 [reaction (4.3-1)]. When catalysts such as GRI's sulfur-tolerant, direct methanation catalyst are used, the desired initial H_2/CO ratio is 1 and Eq. (4.3-2) forms the basis for the methanation reaction.

Other methane-producing processes include the hydrocracking of higher hydrocarbons, typified by

 $C_2H_6 + H_2 \longrightarrow 2CH_4.$ (4.3-6)

Values of Δ H°_R and Δ G°_R for reactions (4.3-1) through (4.3-5) are given in Table 4.3-1 for temperatures between 27 and 727°C. These data show that all reactions are exothermic, with all but the shift reaction (4.3-5) being strongly exothermic. Furthermore, the free-energy values in Table 4.3-1 show that lower temperatures favor methane production; thus, there must be effective heat-removal methods. At temperatures below ~ 425°C, the methane yield is not notably affected by pressure.

Carbon deposition, which leads to catalyst fouling, can be encountered under certain operation conditions. These conditions are highly dependent on initial gas composition, catalyst properties, temperature, and pressure. Experience with sulfur-tolerant, direct methanation catalysts has shown that H_2/CO ratios as low as 0.1 can be processed without carbon deposition. With catalysts that accomplish methanation through the overall

reaction represented by Eq. (4.3-1) and for which feed gas H_2/CO ratios of 3 are desired, carbon deposition occurs more readily and much larger regions of temperature and H_2/CO ratios must be avoided, as is shown in Fig. 4.3-1.

4.3-2. Catalysts

In order of activity, the most important metal catalysts are Ru > Ni > Co > Fe > Mo.⁴ Nickel is the most commonly used catalyst in commercial processes because of its relatively low cost. Despite the excellent catalytic performance of Ru, its high cost has precluded its widespread use. The activity of Ni is generally second to that of Ru, but it is far cheaper and has therefore become the most-used catalyst in commercial methanation processes.^{4,5} Nearly all commercially available methanation catalysts are rapidly poisoned by S-containing compounds and it is necessary to reduce the concentration of sulfur species in the inlet gas to less than 0.5 ppm in order to maintain adequate catalyst activity for long periods of time. The sulfur-tolerant methanation catalysts currently under development do not have a similar requirement for low concentrations of sulfur species in the feed streams and thus afford the opportunity to make major changes in the process elements and their integration in downstream processing trains.

The catalyst base used and the composition of the Ni-based alloy are important. Investigators developing Ni-based catalysts have tried to find materials that yield optimum performance in terms of high CO-conversion, low C deposition, high methane selectively, and yield. Other desirable properties are long, stable catalyst life, ability to accept feeds with low H_2/CO ratios, and high space velocities over a range of temperatures and/or pressures. A summary of the many different Ni-based catalysts is given in Table 5 of Ref. 4.

Cobalt has also been found to be quite active as a methanation catalyst.^{6,7} However, compared to Ni, Co suffers more severe carbon deposition, 6 requires higher temperatures for similar CO conversions, 7 and is less methane-selective. 6,7

Iron-catalyzed methanation has been described in two papers.^{8,9} The long-term effectiveness of this catalyst was limited by C deposition. Because Fe has very poor methane selectivity, even at high H_2/CO ratios,⁸ it is considered to be more suitable for Fischer-Tropsch syntheses than for

Temperature,	Reaction							
°C	(4.3-1)	(4.3-2)	(4. 3-3)	(4.3-4)	(4, 3-5)			
Heat of Reaction, ΔH_R^o , kcal/mole								
27	-49. 298	-59.136	-39.460	-41, 227	-9.838			
1 27	-50.360	-60.070	-40.650	-41.434	-9.710			
227	-51, 297	-60.815	-41.779	-41.499	-9.518			
327	-52.084	-61.376	-42.792	-41,460	-9.292			
427	-52.730	-61.780	-43.680	-41,350	-9.050			
527	-53.248	-62.047	-44.449	-41.190	-8.799			
627	-53.654	-62.203	-45.105	-40.996	-8.549			
7 27	-53,957	-62.261	-45.653	-40.729	-8.304			
	Free Energy of Reaction, ΔG_R^o , kcal/mole							
27	-33.904	-40.731	- 27.077	-28,621	-6.827			
127	-28.610	-34.451	-22.769	-24.385	-5.841			
227	-23.062	- 27.956	-18,168	-20.111	-4.894			
327	-17.338	-21.329	-13.347	-15.836	-3.991			
427	-11.493	-14.620	-8,366	-11,574	-3.127			
527	-5.567	-7.865	-3,269	-7,332	-2.298			
627	+0.594	-1.079	+1.921	-3.108	-1.500			
7 27	+6.444	+5.715	+7.173	+1.090	-0.729			

Table 4.3-1. Heats of reaction and free energies of reaction for reactions (4.3-1) through (4.3-5); reproduced from Ref. 4.

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Fig. 4.3-1. The effects of synthesis gas ratio and pressure on carbon deposition. Carbon deposition may occur for conditions below the curves.



methanation catalysis. Typical yields consisted of 20% methane and 80% Fischer-Tropsch products when 1:1 synthesis gas was used. 8

Molybdenum and W have only moderate activity and require high temperatures for methanation.^{10,11} The motivation for examining these catalysts is their high resistance to sulfur poisoning.^{10,12}

Noble metals have also been studied for applications in catalytic methanation.¹⁰ Their activities are generally quite low, but Pd, Rh, Os, and Re have the advantage of being highly methane-selective.

4.3-3. <u>Commercial Processes</u>

Methanation systems are used commercially to remove small amounts of CO and CO₂ because these oxides are catalyst-poisons for many chemical manufacturing systems. An example of a commercial system for which this removal is necessary is found in ammonia \hat{p} lants where the methanation systems serve as gas purifiers. As a result, input CO and CO₂ concentrations to the ammonia synthesis reactors are usually less than 1%.⁵

When scaling up this technology to the methanation systems required in a coal-gasification plant producing SNG, consideration must be given to a number of potential problem areas. The SNG systems will be much larger and will be required to handle input gases with much higher CO concentrations. Because of the high heat release associated with high CO input-gas concentrations, adequate heat removal must be incorporated into the reactor design. Sulfur poisoning, catalyst deactivation by high temperature sintering of Ni catalysts or by C deposition must also be addressed.

Nickel-based catalysts are currently used in the fixed-bed methanators at the GPCGP. The feed gases are preprocessed by acid-gas removal-systems to reduce the sulfur content to acceptable levels (less than 1 ppm) before they enter the methanation units.

The status of recent advanced methanation technology development activities is summarized in the following sections.

4.3-4. Direct Methanation

Since 1978, GRI has funded the development of the direct methanation process because of the potential for improving the coal-to-SNG economics.¹³ Process development has included catalyst development, catalyst evaluation, evaluation of materials of construction, and preliminary assessment of process economics. Direct methanation is a process based on a catalyst that methanates equi-molar concentrations of H_2 and CO, producing CO₂ rather than steam as a product via the reaction

$$2H_2 + 2CO \rightleftharpoons CH_4 + CO_2.$$
 (4.3-7)

Accordingly, the process has no requirement for steam, either to shift the gas to an H_2/CO ratio of 3 or to prevent caking, as is required for Ni-based catalysts. Sulfur removal is not required prior to methanation since the catalyst is not poisoned by any sulfur compounds present in coal-derived gas. As a result, the process can be used to treat the raw, quenched gas from a coal gasifier with little or no pretreatment. This procedure allows use of the acid-gas removal-system to treat a reduced volume of the acid-gas stream to remove H_2S and CO_2 . Polishing methanation may be required to bring the gas to US pipeline standards.

To date, more than 800 catalyst formulations have been tested, resulting in several compositions that have promise for application in the direct methanation process. Carbon formations have not been observed, even with H_2/CO ratios as low as 0.1 in a dry gas stream.

GRI catalysts promote the methanation reaction at temperatures from 260 to 650°C, pressures from atmospheric to 1000 psig, feed gas $H_2/C0$ molar ratios from 3 to less than 0.4, steam concentrations from 0 to 15 mol%, and in the presence of up to 1 mol% of sulfur. Carbon formation was not detected under any of these conditions. HC additions of up to 2 mol% C_6H_6 , 0.05 mol% C_6H_5OH , and 0.3 mol% HN₃ also did not poison or foul the catalyst. Limited reforming tests have indicated that the catalysts can yield a single-pass conversion of almost 25% of 22 ppm H_2 S-containing NG at 870°C.

Catalyst samples have been exposed to a Lurgi-type raw gas for 2300 hr (Fig. 4.3-2) under controlled conditions with maintenance of activity, as well as for 10,000 hr under a variety of test conditions. Based on these tests, a minimum of a 1-yr catalyst life has been projected for commercial application.

Table 4.3-2 lists the ranges of operating conditions over which the catalyst has been tested. The pressure range is typical of anticipated operating conditions downstream of a coal-gasification plant. The catalyst can be operated up to 660°C, which is indicated by the upper limit of the temperature range studied. The experiments were conducted using gases which reflect (a) anticipated raw gas compositions and H_2/CO ratios for a variety of coal-gasification processes and (b) gas compositions anticipated at the outlet of a number of direct-methanation reactors operating in series. The catalyst has been tested for heavy HC and sulfur concentrations in the range of 50 to 1350 ppm. The catalyst has also been operated over a wide range of space velocities and feed-gas water concentrations to obtain a range of CO conversions and CH_4 selectivities.

The results of laboratory experiments to determine the conversion characteristics of a GRI direct-methanation catalyst, under conditions simulating the first stage of a methanation process, are presented in Fig. 4.3-3. These data show the effect of temperature and space velocity on CO conversion and provide a basis for developing process-flow sheets that can be integrated into conceptual designs of coal-to-SNG plants.

Workers at Haldor Topsoe, Inc., have been evaluating S-tolerant catalysts for converting CO/H $_2$ mixtures to methane.¹⁴ They have demonstrated that the catalyst can also be an effective shift catalyst and,



Fig. 4.3-2. Life-test data of the GRI-C-500 and GRI-C-600 catalysts using a dry-bottom Lurgi-type raw gas (450 psig, 6000 SCF/hr-ft³, 930 to 980°F, 10 g of -12 to +20 mesh catalyst).

Table 4.3-2. GRI tests on direct methanation-catalysts.

Types of feed gases simulated (gasification process/coal type): BGC/IL No. 6, KRW/Pittsburgh No. 8, KRW/Wyodak, Lurgi/ North Dakota Lignite, Lurgi/Rosebud, Shell/Wyodak, UCG/Rosebud.					
Feed-gas compositions					
Species	Vol%				
CO	4-42				
coz	0-42				
H ₂	8-44				
CH4	6-30				
C ₂ H ₆	0-0.7				
$C_2 H_4$	0-0.7				
	0-0.2				

0-90 ppm 0.05-3

0 - 0.14

0.3-1.5

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0-38

0-2.5

0-1

100 ppm - 3

0.6 to 3

Reactor conditions: p = 50-1000 psig, outlet T = 400-680°C.

Space velocity = 500-25000 SCF/ft³-hr.

C4H10

H₂S COS

N₂

Н20

C₆H₆

NH3 Total S

C6H5OH

H₂/CO ratio

Results: 18-86% CO conversion (defined as percentage of CO in the feed converted), 21 to 100% CH_4 selectivity (defined as the amount of CH_4 produced as a percentage of the amount of CO converted).

under some conditions, leads to the formation of other low molecular weight, saturated, HCs in addition to methane. The general physical characteristics of the catalysts are shown in Table 4.3-3 and the range of test conditions investigated using simulated raw gas is shown in Table 4.3-4.

In addition to laboratory experiments, a methanation PDU was constructed and operated on a slip-stream from an entrained-flow coal gasification PDU being evaluated by Mountain Fuel Resources. The entrained-flow gasification experiments involved five different coal feedstocks and provided different raw gas feed streams to the methanator. The results of these experiments are shown in Fig. 4.3-4 as relative catalyst activity vs time. The activity was calculated as the space velocity for 90% conversion based on the rate-limiting component (i.e., the minor component which is H_2 for $CO/H_2 > 1$ and CO for $CO/H_2 < 1$). Data are also included from the laboratory experiments carried out with the catalyst prior to performing the integrated PDU tests.

A total of 1080 hr of testing was completed with catalyst activity levels remaining high throughout the test. The type of coal appeared to have no effect the activity of the catalyst and the effects of variations in H_2S concentration were also small. There appeared to be no effect of H_2S on activity below a 0.07 vol% concentration. The catalyst activity remained constant during a 100-hr test with the H_2S partial pressure as low as 1 ppm.

4.3-5. <u>Comflux Process (Fluid-Bed Methanation)</u>

The Comflux process is an Ni-catalysed, pressurized, fluid-bed process to convert CO-rich gasification gases into SNG in a single step.¹⁵ This process performs both shift and methanation reactions simultaneously in a single reactor with complete CO conversion. The water formed in the methanation reaction is available for water-gas shift reaction. Thus, a gas with $H_2/CO < 3$ can be methanated without adding steam.

A simplified process flow diagram for the Comflux process is shown in Fig. 4.3-5. The desulfurized feed gas is preheated by heat exchange with the product gas to the reaction-initiation temperature and then fed into the reactor. The gas fluidizes the catalyst, and both methanation and water-gas shift reactions take place simultaneously in the fluidized bed. The axial temperature gradient in the fluidized bed is extremely small, and the reactor is operated under high loads almost isothermally. Heated catalyst particles are cooled sufficiently fast by mixing with colder particles and by contact with integrated heat exchangers so that the high heat of the methanation reaction does not cause superheating of the bed. The product gas with less than 0.1 vol% of CO is cooled and process water condensed. If the feed gas has $H_2/CO < 3.0$, the CO₂ formed with the reaction must be removed to meet pipeline-quality gas specifications. The resulting product gas is SNG with a heating value of 926-1016 BTU/SCF and chemical properties identical to NG.

The Comflux process was evaluated initially in a 1.3 ft. diameter ETU and later at the pilot plant scale with a 3.3 ft. diameter reactor and SNG production up to 112,000 SCF/hr. Performance data from these development programs are summarized in Table 4.3-5.

4.3-6. <u>HICOM</u>

HICOM methanation is a fixed-bed process and is being developed by the British Gas Corporation to accommodate the relatively low H_2/CO -ratio product-gases produced by gasifiers such as the BGC/Lurgi slagging gasifier, KRW (Fluidized bed), U-GAS (Fluidized bed), Shell (entrained-flow), and Texaco (entrained-flow).¹⁶ Typical off-gas compositions for these gasifiers and the dry-bottom Lurgi gasifier are shown in Table 4.3-6. The gases will also contain compounds of sulfur (H_2 S, COS, etc.) at levels dependent on the sulfur contents of the coals.

The HICOM process employs a series of methanation stages, each of which involves a fixed bed of catalyst; each is connected as shown in the simplified process flow diagram of Fig. 4.3-6. The principal method used to control the temperature rise in each stage is recycle of cooled, equilibrated product gas to dilute the feed gas. The amount of recycle gas is minimized by passing it through at least two stages, with fresh gas added to each stage (split-stream operation). Product gas from upstream stages (split-stream operation) also helps control the temperature rise in each subsequent reactor and high-grade heat is recovered immediately downstream of each reactor. The effect of using split-stream operation in order to

Name	SMC 324
Size, $L \times D$	4.5 mm×4.5 mm (0.18"×0.18")
Density ,	1.75 gm/cm ³ (109 lb/CF)
Bulk density	1.275 kg/f (80 lb/CF)
Surface area	100 m ² /gr
Crushing strength	$600 \text{ kg/cm}^2 (8700 \text{ lb/in}^2)$

Table 4.3-3.	Physical	characteristics	of the	catal	yst te	sted	by	Haldor	Topsol,	Inc
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Parameters	Range of Test Conditions	Typical Test Data	
Pressure, psia	90 - 300	300	
Volumetric flowrate, SCF/hr	1 - 8	3	
Inlet conditions (adjusted with H ₂)			
CO/H ₂ volume ratio	0.7 - 1.5	1.0	
H ₂	30 - 45	35	
со	30 - 45	40	
co ₂	10 - 40	15	
H ₂ S	1 ppm - 3.5	0.1	
CH4	0 - 13	1	
N ₂	2 - 11	5	
Outlet conditions			
H ₂	0 - 15	8	
CO	2 - 15	8	
co ₂	40 - 55	50	
H ₂ S	2 ppm - 4.5	0.1	
CH4	16 - 39	25	
C ₂ H ₆	1 - 4	2.5	
C ₃ H ₈	0,2 - 0.7	0.5	
N2	Balance	Balance	
Fractional conversions			
CO	70 - 100	90	
H ₂	70 - 100	90	

Table 4.3-4. Summary of direct methanation test conditions and results; concentrations are given in mol%.

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Fig. 4.3-4. Relative catalyst activity vs time in the methanation PDU at Mountain Fuel Resources.



Fig. 4.3-5. Simplified process-flow diagram for the Comflux process.

- A. Operating Conditions: output capacity = $3500 12300 \text{ ft}^3/\text{hr}$, p = 290 870 psi, T = 400 - 500°C, H₂/CO volume ratio = 1.8 - 3, recycle volumefeed ratio = 0 - 0.5, gas velocity = 0.16 - 0.82 ft/sec.
- B. SNG production in vol%: methane = 86 96, $H_2 = 2 8$, CO = 2 6; gross heating value = 926 1016 BTU/SCF.
- C. Operational Data for the Pilot Plant: reactor diameter = 3.28 ft (internal), reactor height = 36.0 ft, p = 190 870 psi, fluidized bed temperature = 450 550°C, feed gas = 112,000 400,000 SCF/hr, H₂/CO volume ratio = 2.0 3.0, recycle-gas volume ratio = 0 0.3, gas velocity = 0.16 1.0 ft/sec, SNG production = 45,000 112,000 SCF/hr, steam production = 1.0 5.2 t/hr, steam temperature = 370 480°C, fluidized-bed height = 6.4 12.9 ft, catalyst charge = 0.8 1.6, catalyst-particle size distribution = 10 400 µm.

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Species	Lurgi Dry-Ash	BGC/Lurgi Slagging	Shell	Texaco	KRW (Westinghouse)
H ₂	40	29	29	35	27
CO	17	60	65	43	55
co ²	32	3	2	20	6
CH ₄	10	6	0.1	0.3	9
N ₂	1	1	4	2	3
Steam/dry gas ratio	1.4	0,13	0.03	0.23	1.0

Table 4.3-6. Typical gasifier-product gases (in mol%) for a number of gasifiers and corresponding steam to dry-gas ratios.

reduce the amount of recycle gas needed for control of the temperature rise in the reactor beds is shown in Fig. 4.3-7.

The HICOM process employs nickel-based catalysts and uses excess steam in the feed gas to prevent carbon deposition. The process was

initially evaluated in small-scale laboratory experiments and subsequently tested at the semi-commercial scale on a slip stream from the BGC/Lurgi slagging gasifier at Westfield, Scotland. In the integrated tests at Westfield, purified gases from the gasifier were successfully processed at a nominal rate of approximately 4.5×10^6 SCF/day.

4.3-7. Liquid Phase Methanation



(a) Typical gas compositions from a HICOM pilot test

Component	Feed to the HICOM Reactor, mol%	Product from the HICOM Reactor, mol%
co	12.6	1.1
coz	43.0	53.1
H ₂	11.7	5.5
CH4	31.7	39.3
N2	1.0	1,1

(b) Range of operating conditions

Inlet T	230 - 320°C	
р	25 - 70 bar	
Maximum T	460 - 640°C	
Total test time	15,000 hr	

Fig. 4.3-6. The HICOM process diagram; gas compositions (a) and range of operating conditions (b).



Fig. 4.3-7. Effect of the temperature rise on the required recycle ratio (= recycle flow/product flow).

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Workers at Chem System, Inc., have developed a liquid-phase methanation system in which a granular Ni-catalyst is immersed in a mineral-oil coolant bath, which serves to control the reactor temperature. ^{17,18} Fluidization of the catalyst occurs by circulating the oil and fresh SG upward through the reactor. In a large-scale process, heat is recovered from the oil and from the hot product gases. Feed streams with $H_2/CO < 3$ are accommodated by adding steam to the feed, thus forcing the shift reaction. Multiple reactors are required to obtain a CO-concentration below 0.1%. Operating temperatures are between 300 and 380°C and pressures between 300 and 1000 psi. Very good CO conversions have been demonstrated, but carbon deposition and catalyst disintegration have been problems for some operating regimes.

4.4. Acid Gas Removal

4.4-1. Commercial Processes

An essential element of a coal-to-SNG process is the removal of gases such as CO_2 , H_2S , COS, mercaptans, and organic sulfides from the product stream in order to satisfy process constraints (such as catalyst poisoning), environmental constraints or product requirements (such as heating value and trace-constituent levels). Because requirements have existed for the removal of these types of gases from a wide variety of

process streams that are encountered in the chemical industry, in petroleum refining and NG production, a large number of unit processes have been developed and can be used in the downstream processing trains of coal-gasification plants.

Table 4.4-1 contains a list of technologies that have been examined and/or developed for specific applications. Currently, there are more than 90 Rectisol units in operation or under construction in various parts of the world. The Rectisol technology, which uses methanol as the physical solvent, is in use at the SASOL plants and is also employed in the downstream processing train the GPCGP. The Benfield Process, which uses a hot K_2CO_3 solution for the chemical absorption of CO_2 , H_2S and COS, is in use or being considered in over 520 applications throughout the world.

The Selexol process, a physical absorption process which uses the dimethyl ether of polyethylene glycol as the solvent, has been installed at approximately 30 commercial and/or pilot-plant facilities. This technology is currently being used at the Cool Water IGCC project.

4.4-2. Advanced Technologies

Because of the extensive catalog of commercially available technologies for acid-gas removal and the large data base that exists on the properties of potential sorbents for the gases of interest, there is only a limited effort devoted to the development of new processes that could improve the economics of producing SNG from coal.

GRI, together with DoE and Consolidated Natural Gas (CNG), has been evaluating an advanced acid-gas removal process specifically for coal conversion. This process relies on the unique gas-solid-liquid equilibrium phase relationships that exist for CO_2-H_2S mixtures. Hydrogen sulfide and carbonyl sulfide are soluble in liquid CO_2 . However, when the temperature of a CO_2/H_2S solution is reduced to the point where crystallization occurs, the solid phase that results is almost 100% CO_2 and contains essentially no sulfides. This phase behavior provides an effective means for removing acid gases such as CO_2 , H_2S and COS from a coal-gasification process stream and subsequently increasing the concentration of H_2S in a stream where it can be effectively converted to elemental sulfur.

Table 4.4-1. Summary of commercial and developmental acid-gas removal processes; abbreviations: for the process type, AD=adsorption, AB=absorption, CD=cryogenic distillation; for the solvent, C=chemical solvent, P = physical solvent; for the clean-up mode, S=selective, NS=non-selective.

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Name of Process	Туре	Solvent	Mode	Major Contaminants Removed
Activated carbon	AD	С	NS	H ₂ S,oil
ADIP	AB	, C	NS	H ₂ S, CO ₂
Alkazid	AB	С	S, NS	H ₂ S, CO ₂
Amisol	AB	C/P	S, NS	H ₂ S, CO ₂
Benfield	AB	С	NS	H ₂ S, CO ₂
Catacarb	AB	С	NS	H ₂ S, CO ₂
Chemsweet	AD	С	S	H ₂ S
CNG	AB	P	s	H ₂ S, CO ₂
Estasolvan	AB	Р	S, NS	H ₂ S, CO ₂ , oil
Flexsorb SE	AB	С	S	H ₂ S, CO ₂
Fluor Econamine	AB	с	NS	H ₂ S, CO ₂
Fluor Solvent	AB	Р	NS	H ₂ S, CO ₂ , oil
Ġiammarco-Vetrocoke	AB	с	S	H ₂ S, CO ₂
MEA	AB	С	NS	H ₂ S, CO ₂
MDEA	AB	с	S, NS	H ₂ S, CO ₂
Molecular sieves	AD	P	s	H ₂ S
Purisol	AB	P	S, NS	H ₂ S, CO ₂
Rectisol	AB	Р	S, NS	H ₂ S, CO ₂
Ryan Holmes	CD	CD	s	H ₂ s, co ₂ , c ₂ ⁺
Seaboard	AB	С	S	H ₂ S
Selexol	AB	P	S, NS	H ₂ S, CO ₂ , oil
Sepasolv MPE	AB	P	S, NS	H ₂ S, CO ₂ , oil
SNPA - DEA	AB	С	NS	H ₂ S, CO ₂
Stretford	AB	C	S	H ₂ S
Sulfiban	AB	С	NS	H ₂ S, CO ₂
Sulfinol	AB	C/P	NS	H ₂ S, CO ₂
Tripotassium phosphate	AB	с	S	H ₂ S
Vacuum carbonate	AB	с	S	H ₂ S
Zinc oxide	AD	с	s	H ₂ S

A conceptual flow diagram for the CNG acid-gas removal process is shown in Fig. 4.4-1. The raw feed gas is cooled and residual water vapor is removed in a dehydration system to prevent subsequent icing. The water-free crude gas is further cooled to its CO_2 dew point (-56°C) by countercurrent heat exchange with return clean gas and CO_2 . Depending on the CO_2 dew point, a fraction of the CO_2 in the crude gas stream is condensed together with the sulfur compounds. The gas at -55°C is then scrubbed by liquid CO_2 to remove H_2S , COS and other trace impurities. This absorption is essentially isothermal since the heat of absorption is dissipated as heat of vaporization of a small portion of the liquid CO_2 .

The liquid $\rm CO_2$, together with all of the sulfur compounds, other trace contaminants and some co-absorbed light HCs is combined with the contaminated liquid $\rm CO_2$ that was condensed in precooling the raw gas. The light HCs are stripped from this combined liquid $\rm CO_2$ stream and recycled and mixed with the feed gas. Any higher HCs ($\rm C_4-C_6$) in the feed gas will remain with the condensed $\rm CO_2$.

The contaminated liquid CO_2 stream leaving the light ends stripping tower is processed in a direct-contact, triple-point crystallizer with vapor compression. Solid CO_2 is formed by adiabatic flashing of the liquid CO_2 stream near the top of the crystallizer. An H₂S-rich gas stream is produced and is continuously withdrawn from the top. All C_2 -C₆ HCs entering the crystallizer are removed with the H₂S-rich stream. The solid CO_2 crystals fall to the bottom of the crystallizer, where they are melted by direct contact with condensing CO_2 vapor. Pure CO_2 liquid thus produced is split into two streams: one is recycled to the H₂S absorber and the other is sent back through the process for refrigeration and power recovery and is subsequently delivered as a product stream or vented to the atmosphere.

Carbon dioxide remaining in the gas after removal of sulfur compounds is absorbed at temperatures below the $\rm CO_2$ triple point with a slurry absorbent. The slurry absorbent is a saturated solution of an organic solvent and $\rm CO_2$ containing suspended particles of solid $\rm CO_2$. As $\rm CO_2$ is absorbed (condensed), the latent heat released melts the solid $\rm CO_2$ contained in the slurry absorbent. The direct refrigeration provided by the melting of solid $\rm CO_2$ enables a small absorbent flow to accommodate the considerable heat of condensation and absorption of the $\rm CO_2$ vapor. The





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cold, purified gas stream then leaves the acid-gas removal process after heat exchange with the raw gas stream.

The CO_2 -rich solvent leaving the CO_2 absorber near the triple-point temperature contains no solid CO_2 . This stream is flashed in a drum to vaporize methane or other light components. The CO_2 -rich absorbent is next cooled by external refrigeration and then flashed to lower the pressure in a number of stages in order to generate a cold slurry of liquid solvent and solid CO_2 . Nitrogen stripping of the solvent may sometimes be required to produce a very lean solvent. The regenerated slurry absorbent is recirculated to the CO_2 absorber while the CO_2 -flashed gas is vented to the atmosphere after recovery of refrigeration and power.

4.5. SNG Economics

The economics associated with producing natural gas from coal are a function of coal type and cost, the technologies used in the overall conversion processes, as well as site-specific considerations. Figure 4.5-1 shows a comparison of calculated end-product gas costs (in 1982 dollars) for an ash-agglomerating, fluidized bed gasification technology and also for dry-bottom Lurgi technology with both US Western and Eastern coals as the feedstock. These results are presented as a levelized constant dollar (LCD) cost, where the levelized price represents the average gas selling price required over the life of the plant in dollars for a given year to realize a rate of return on equity of 14.5%. The LCD price also requires that all costs, except that of coal, escalate at the average rate of inflation.

Figure 4.5-1 shows the relative distribution of the major cost elements (i.e., feedstock, operation and maintenance, and capital investment) for each of the four cases considered. A Western coal was used as the feedstock. The contributions of the major elements to the overall end-product gas costs are: feedstock, 25 to 29%; operation and maintenance, 45 to 49%; capital, 25 to 26%). With an Eastern coal, the relative contributions are as follows: feedstock, 42 to 50%; operation and maintenance, 31 to 39%; capital, 19 to 20%.



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Fig. 4.5-1. Comparison of LCD costs of SNG for selected gasifiers. All estimates are based on a 30-yr plant life, 85% debt financing, beginning operation in 1990. Delivered coal prices are assumed to escalate at 2% per year in real terms. Additional primary capital costs were estimated for unknown factors related to potential site requirements (SSF) and state of technology development (PDA).

Figure 4.5-2 shows a comparison of both the levelized constant dollar end-product gas costs and the annual cost of service for coal-to-SNG conversion for a process based on dry-bottom Lurgi gasification and commercially available downstream processes, when using a system based on advanced gasification (ash-agglomerating, fluidized bed) and downstream processing (direct methanation and an advanced acid-gas clean-up system) technologies. Both plants were sized to produce 250 X 10^6 SCF/day of pipeline-quality gas using lignite as the feedstock.

The availability of advanced technologies would reduce the average gas cost from approximately $6.20/10^6$ BTU to approximately $4.80/10^6$ BTU on a cost-of-service basis. The advanced technology would also lead to a first year gas cost that is approximately $2.00/10^6$ BTU less than that estimated for the process based on dry-bottom Lurgi technology. This reduction in

average and first year gas costs will permit coal-to-SNG processes to become economically competitive with other energy- and gas-supply options in an earlier time frame than would otherwise be the case.

4.6. Research and Development Needs

The research and development needs associated with the long-range objective of producing SNG from coal cover a spectrum of activities, ranging from engineering studies to basic research. These needs include: (i) operational/economic data on large, integrated coal gasification plants, (ii) expanded engineering data bases, and (iii) the development of more fundamentally-oriented information on the rate-controlling steps of the various process elements. While these needs are focused on coal gasification as related to the production of high-BTU SNG, many of the needs are generic in nature and will be useful in a variety of coal-gasification applications. Specific research needs are listed here for three categories of R & D.

4.6-1. <u>Engineering Development and Testing</u>

(i) Large-scale operational and performance data are needed on IGCC plants such as Cool Water and also for the GPCGP converting coal-to-SNG.

(ii) Expanded engineering data bases should be developed for oxygen-blown, ash-agglomerating, fluidized bed gasifiers to optimize designs for specific applications (pressure, fines collection and recycle, coal types, in-bed desulfurization).

(iii) Scale-up data for emerging technologies are required for such processes as the direct methanation concept and the CNG advanced acid-gas removal concept.

(iv) Integrated performance evaluations of advanced gasification technologies are needed for technologies such as the BGC/Lurgi slagging gasifier and the ash-agglomerating, fluidized bed process with advanced downstream processing, as well as for concepts such as the direct-methanation process and the CNG acid-gas removal system.



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Fig. 4.5-2. Estimated cost of SNG for dry-bottom Lurgi technology and advanced gasification and downstream-processing technologies (250 mm SCF/ day, lignite); constant 1985 dollars are used.

(v) Development and validation are required of scale-up models, with particular emphasis on coal gasifiers.

(vi) Exploratory studies should be carried out to develop initial data bases for new, advanced process concepts for gasification and downstream processing.

(vii) Improved, high-temperature heat recovery systems are needed.

(viii) Expanded environmental data bases should be established for advanced technologies in the areas of production, fate, control, and disposal or treatment of trace constituents.

4.6-2. <u>Technology Base Data for Design</u>

(i) The development of metal alloys for high-temperature, heat recovery applications should be supported.

(ii) The development of improved ceramics for high-temperature applications (i.e., particulate filters, valves) should be encouraged.

(iii) Expanded data bases are needed on the erosion-corrosion behavior and resistance of metals and ceramics in coal-gasification environments.

(iv) Long-term corrosion data (for more than 10,000 hr) should be obtained in coal-gasification environments, with proper consideration of alkali metals, sulfidation, and chlorides.

(v) Vapor-liquid equilibrium data are needed at elevated pressures and temperatures for selected multicomponent systems involving synthesis gas, steam, heavy oils (tars), light aromatics, phenolics, fatty acids, CH_4 , H_2S , CS_2 , COS, mercaptans, NH_3 , HCL, HCN, AsH_3 , SeH_2 , Hg.

(vi) Transport data (thermal conductivity, viscosity, diffusivity) should be measured for tars and slurries (oil/solids, tar/solids, water/solids).

(vii) Thermodynamic data are required, including improved estimates for free energy of formation, heats of formation, entropies, specific heats.

(viii) Sour-water stripper vapor-liquid equilibria should be measured for $H_2O/NH_3/CO_2/H_2S$ systems at 0 to 100 psig and 20 to 200°F.

(ix) Improved correlations are needed for predictions of mass-transfer coefficients and other engineering design parameters whenever mulitcomponent systems are involved.

4.6-3. Basic Research Needs for Advanced Systems

(i) Improved understanding is needed of the chemical processes associated with and controlling the fragmentation/gasification of coal.

(ii) Improved models are required for predictions of vapor-liquid equilibria in multi-component systems.

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CHAPTER 5:

GASIFICATION FOR THE SYNTHESES OF FUELS AND CHEMICALS*

5.1. Catalytic Conversion of Synthesis Gas to Fuels and Chemicals

5.1-1. Introduction

The competition among the various organic-based fuels (chiefly, natural gas, petroleum, and coal, with shale oil and biomass representing more recent entries) has been waged over the years with strange and intriguing use patterns. All but biomass are fossil fuels, omitting the possibility of the existence of abiotic methane in the earth's interior. All of these fuels may be converted to synthesis gas (SG, syngas), and this resource availability is a potent reason for the use of SG in the production of fuels or chemicals. SG can be and, in several important applications is, a viable source of clean fuels and large-scale chemical manufacture. Molecular hydrogen has a myriad of uses and it is very extensively made from SG.

Natural gas (NG) is now the largest source of SG. By far the chief constituent of NG is methane (CH_4) , an unreactive molecule that is a clean fuel but requires conversion to SG to yield reactive species. Petroleum fractions are the next largest source of SG, and significant quantities are being made from coal.

It is ironic that coal was the first fossil fuel to be converted to SG for commercial use. The manufacture of methanol (MeOH) from coal-derived SG was started in Germany in 1923.¹ In the same year and also in in German, the Fischer-Tropsch (FT) process² was first put into commercial operation. The FT process for the manufacture of fuels and

^{*} This chapter has been written by W.O. Haag and J.C. Kuo (both of Mobil Research and Development Corporation) and I. Wender (University of Pittsburgh).

chemicals is now being carried out on a large scale in South Africa and is still based on coal-derived SG.

The route to MeOH, which is now made commercially in large plants throughout the world, is through SG in all cases, with NG as the chief source of the SG. Since NG has been in short supply in Europe, petroleum fractions have been used as a source of SG. The near-panic programs pursued following the 1973-1974 oil embargo involved coal as the source of fuels and chemicals, including increased gasification of coal to SG. Coal utilization in the US and worldwide increased and this increase has been sustained, but coal research and development have decreased with the decline in oil and gas prices. The instability of oil and gas markets is actually one the the best reasons for sustaining R&D and technology for the use of SG (often referred to as C-1 chemistry). There are a few salient points, most well-known, that apply to the the supply of fuels and chemicals in general and to SG in particular: (i) The most precarious situation involves the availability of petroleum since the largest oil resource exist in politically unstable areas far from the US. In terms of availability, NG and coal constitute large resources and are ubiquitous. (ii) Petroleum, NG and coal will continue to compete for world markets for several decades. Flexibility will be a key so that a particular application will not depend on the availability of one kind of fuel. As for coal, use should not be tied to a particular mine or rank. Since all of these resources are convertible to SG, applications based on SG use will grow. (iii) It is not possible to separate the fuels and chemicals businesses as many traditionalists are prone to do. Fuels use will govern chemicals use, as they have in the petroleum industry. Fuels are sold by the barrel or by the ton; chemicals are of higher value and are sold by the pound. (iv) With regard to coal use, gasification processes are more forgiving than direct liquefaction. Variability in coal source, rank, mineral matter, etc. is more easily accommodated by gasification processes. Indirect liquefaction (via SG) products are relatively easily converted to clean gaseous and liquid fuels and chemicals. (v) In indirect liquefaction, all of the coal is converted to crude SG. The conversion of coal to clean SG generally account to 70 - 80% of the capital cost of the plant. In direct coal liquefaction, the necessary H_2 is obtained by gasification of coal or of some heavy coal-liquefaction product. In this case, gasification costs amount to about 40% of the capital cost of the liquefaction plant.

(vi) SG will continue to be the source of MeOH, although there is significant ongoing research on the direct oxidation of ${\rm CH}_{\rm A}$ to MeOH and products derived from MeOH, such as formaldehyde. (vii) SG will continue to be the world's principal source of H_2 . Hydrogen has a great many uses, including primary application for the manufacture of ammonia (HN_3) . (viii) Environmental factors are the eventual determinants in fossil-fuel use. Even a large amount of an available resource, if environmentally harmful, will lose out sooner or later. For coal gasification, environmental constraints are found in gas clean-up and in the nature of gasification residues. The latter should be characterized, be non-leachable and, if possible, be useful in some way (for roads, driveways, construction, etc.). (ix) It is almost inevitable that future power plants will allow the use of any clean fluid fuel: NG, oil, SG, MeOH, or even an FT-derived liquid. Coal will first be converted to SG, as at Cool Water, and will then be used in a type of integrated gasification combined-cycle (IGCC) mode (see Sec. 3.1 for details). This procedure will result in the proliferation (often nearby) of plants that convert the SG to high-quality transportation fuels or to chemicals or use the gas as a clean industrial fuel. (x) The modern petrochemical industry is based on NG and the by-products of petroleum refining. The so-called petrochemical feedstocks are comprised of ethylene, propylene, the butenes, benzene, toluene, and the zylenes. All of these and liquid fuels can be made from SG and it is therefore possible to envision a petroleum-less refinery. (xi) As tetraethyllead disappears from automobile gasoline tanks, the demand will grow for oxygenated chemicals with high octane ratings. An economical synthesis of such fuel-blending agents or additives is needed. An economical synthesis of ethanol from SG would help solve this problem. (xii) Sulfur and nitrogen compounds are removed from crude SG and can be sold as solid sulfur or an NH_3 , respectively. Gasification processes produce CO_2 in considerable amounts. This gas is in short supply and has growing uses. It is considerably easier to isolate CO, from gasification processes than from flue-gas streams. Efforts should be made to remove CO₂ in a fairly pure state from gasification processes to satisfy the growing demand for this chemical. Original plans for the Northern Great Plains coal-to- CH_4 plant included a pipeline to transport CO_2 to oil fields for enhanced oil recovery; this would have produced revenues of \$17 million per year. Other uses for CO_2 are in syntheses of urea,

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supercritical extraction, refrigeration, carbonation of beverages, synthesis of polymers, etc.

It is of considerable interest, before discussing SG as a source of fuels and chemicals, to gain some idea of the amount of SG used in the world today. About 7.5 trillion standard cubic feet (SCF) of SG are consumed each year for the following uses (in SCG): synthesis of NH_3 , ~5 trillion; MeOH manufacture, ~1 trillion; FT products, ~800 billion; miscellaneous uses (H_2 used in processes other than NH_3 synthesis, i.e., in petroleum refining, hydrogenations, for the production of various chemicals, carbonylation reactions, etc.), ~500 billion; the hydroformylation (OXO) reaction (conversion of olefins to aldehydes and alcohols), ~150 billion. Present, emerging and possible future uses of SG will now be discussed.

SG or medium-BTU gas is itself an excellent fuel. It may be transported economically by pipeline over 100 miles for industrial use or it may be used directly as a fuel for the generation of electricity in IGCCs.

Other ways for utilizing SG may be summarized as follows: (i) direct conversion of SG to fuels and chemicals (Table 2.5-1), (ii) indirect conversion to fuels and chemicals via MeOH or MeOH plus SG, CO or H_2 (Table 2.5-2), and (iii) products obtainable from synthesis gas plus a chemical not derived from SG (Table 2.5-3).

Commercial or near-commercial processes for the production of fuels form SG are outlined in Fig. 5.1-1. Commercial, near-commercial and potential chemicals from SG are given in Fig. 5.1-2. The first integrated US process to produce chemicals for coal-derived SG is shown in Fig. 5.1-3.

5.1-2. Synthesis of Methanol and Higher Oxygenated Compounds

Over ten million tons per year of MeOH are currently produced. There are several reasons why MeOH is an important key to an SG-based fuels and chemicals industry. First, MeOH is synthesized with over 99.9% selectivity, in sharp contrast to the melange of products, for CH_4 to waxes, obtained in the FT reaction. Second, the weight retention of SG $(2H_2/1CO)$ as a feedstock for MeOH approaches 100%. Third, MeOH furnishes selective pathways to a number of important chemicals, including formaldehyde and the widely used two-carbon oxygenated chemicals. This route to fuels and to the two-carbon chemicals from MeOH is presently more attractive than their

direct synthesis from SG. In addition, although many more uses of this versatile compound, chiefly as a fuel, will be discussed,



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Fig. 5.1-1. Commercial, near-commercial, and potential processes for the production of fluid fuels from synthesis gas.

there is the exciting discovery that MeOH can be converted to high-octane gasoline by Mobil's MeOH-to-gasoline (MTG) process using a shape-selective zeolite catalyst (HZSM-5). A plant producing about 14,000 BPD of high-octane gasoline form MeOH went on-stream in New Zealand in late 1985.

There are presently two primary processes for the manufacture of MeOH from SG, namely, high-pressure and low-pressure processes. The high-pressure process is

$$ZnO/Cr_2O_3$$

CO + 2H₂ \longrightarrow CH₃OH , $\Delta H_{298K} = -21.68 \text{ kcal/mol}$; (5.1-1)
25-35 MPa,
623K



Fig. 5.1-2. Commercial, near-commercial, and potential chemicals from synthesis gas.



Fig.5.1-3. First integrated process in the US to produce chemicals from coal-derived syngas (Tennessee Eastman).

the low-pressure process is based on the reaction

$$Cu/ZnO/A1_2O_3$$

 $CO + 2H_2 \longrightarrow CH_3OH$ (5.1-2)
5MPa, 523K

MeOH can be and has been synthesized by the hydrogenation of CO_2 with the same catalysts:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$
, $\Delta H_{298K} = -11.83 \text{ kcal/mol}$. (5.1-3)

All of these reactions are exothermic and involve a contraction in volume. Highest yields and conversions to MeOH are obtained at elevated pressures and low temperatures.

5.1-2A: <u>History of Methanol Production</u>

The commercial source of MeOH, prior to introduction of synthetic processes, was the destructive distillation of wood. In 1905, Sabatier and Senderens³ suggested that MeOH could be synthesized from CO and H₂. In the following years, particularly after the successful high-pressure synthesis of NH₃, there were a number of patent applications by BASF in Germany and Patart in France covering the hydrogenation of CO to oxygenated compounds at elevated temperatures and pressures, with catalysts made up of Cr, Co, and Mn in the metallic form, as oxides, or as other compounds. In 1923, BASF built the first commercial MeOH synthesis plant and, a few years later, started exporting synthetic MeOH to the US at a much lower cost and greater purity than that of wood-derived MeOH. The process used a zinc oxide/chromium oxide catalyst operating at 673K and 20MPa.

At this stage, realizing the MeOH could be manufactured more economically by the catalytic process, Commercial Solvents Corp. and DuPont started experimenting with MeOH synthesis and, in 1927, the commercial production by the high-pressure process was inaugurated in the US. In the Commercial Solvents process, CO_2 produced at the company's butanol fermentation plant was hydrogenated to MeOH at 30.6 MPa with metal oxide catalysts.

In 1927, DuPont operated a plant at Belle, WV, that used coal as the source of the gaseous feedstock. Ammonia and MeOH were manufactured in tandem in the same plant. The raw gas, a mixture of CO, CO_2 , H_2 and N_2 , was produced from coal or coke by the water-gas reaction, purified and passed over a MeOH-synthesis catalyst and subsequently over a methanation catalyst to remove CO. The remaining gases, N_2 and H_2 , were used in the synthesis of NH₃. The DuPont process used SG and catalysts made of zinc-chromium or chromium-copper. Co-production of MeOH and NH₃ continued at the plant until the late 1940s. At that time a plentiful supply of NG became available and coal was abandoned as a feedstock. However, in the long run, coal promises to be the preferred feedstock for the production of MeOH; this belief persists in spite of current low oil prices.

At present, a commercial plant using coal is in operation in South Africa. Here, the SG is produced by the Koppers-Totzek entrained-flow, atmospheric-pressure gasification of coal and the synthesis involves use of the ICI MeOH process. BASF may be credited with the discovery of zinc-chromium catalysts in Germany in 1913. This was a high-temperature catalyst operating at 623-673K because of its low catalytic activity. These catalysts must operate at high pressures (25-35 MPa) because of low SG conversion resulting from less favorable thermodynamic equilibrium limitations at high temperatures. The catalysts are less active than the copper-zinc-based catalysts but are more tolerant towards poisoning by compounds containing sulfur.

ICI introduced the more active copper-zinc based catalysts in 1966. These low-temperature catalysts operate at 523-573K and 5-25 MPa. The use of these catalysts was made possible because more efficient SG purification processes had become available. The copper-zinc catalysts are much more susceptible to poisoning by sulfur compounds and are easily and permanently deactivated at high temperatures. Hence, proper control of reactor temperature is necessary. But, even with the most carefully prepared catalysts, small amounts of CH_4 , dimethyl ether and traces of higher alcohols appear among the products.

5.1-2B. Chemistry of Methanol Synthesis

An early excellent review of the synthesis of MeOH has been

published by Natta.⁴ In this section, we briefly outline the thermodynamics, kinetics and catalysis of the high-temperature synthesis of MeOH and the use of the copper catalysts now employed in most new MeOH plants (the low-pressure process).

The catalysts used in the synthesis of MeOH from SG, which usually contains some CO_2 , are highly active and, most importantly, very selective. Among the many products obtainable from the catalytic reactions of SG, CH_4 is thermodynamically the most favored. Longer chain HCs are the next most favored. Even longer chain alcohols are thermodynamically more favored than MeOH. MeOH synthesis reactors must operate with narrow temperature ranges that are set by too low activity at lower temperatures and a thermodynamic limitation at higher temperatures. The effects of temperature and pressure have been studied in detail and reviewed by Strelzoff.⁵

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It is particularly important to avoid contamination of the MeOH-synthesis catalyst by metals that are FT catalysts. Care is required in catalyst preparation so as to obtain pure MeOH. Nickel and especially iron, both of which form volatile metal carbonyls $[Ni(CO)_4 \text{ and Fe}(CO)_5 \text{ respectively}]$, must not be allowed to come in contact with the SG under reaction conditions. The carbonyls form at lower temperatures and decompose to the metal and CO at higher temperatures, possibly in upstream heat exchangers, etc. The presence of FT metals in the catalyst or on the reactor walls will result in the formation of CH₄, as well as of higher HCs and higher molecular weight oxygenated products. MeOH-synthesis reactor shells are typically lined with copper, although internals may be constructed of 18-8 stainless steel.

The formation of higher alcohols (ethanol, propanol, etc.) can be suppressed by careful exclusion of alkalis from the catalyst. Dimethyl ether is formed by a the dehydration of MeOH or by the hydrogenation of CO and may form in the presence of Al_2O_3 . However, if a CuZnO low-pressure catalyst is employed with about 7.5% Al_2O_3 as stabilizer and promoter, ether formation is negligible. The copper-zinc catalysts vary in zinc-copper composition and contain different amounts of other metals such as Cr, Al, MN, V, Ag, etc.

The Boudouard reaction, $2CO \rightleftharpoons C + CO_2$, which results in carbon laydown, is not significant if the temperature is carefully controlled, despite a highly favorable thermodynamic tendency.

In the high-pressure process, the reaction rate decreases with conversion because the synthesis of MeOH is strongly inhibited, both by approach to equilibrium and by the adsorption of MeOH on the catalyst. the gas leaving the last reaction vessel will typically contain only about 3% of MEOH. The unreacted gases are recycled. In the low-pressure MeOH synthesis, the gas leaving the reactor contains 4 to 6.5 vol% of MeOH.

In practice, SG made from any source contains some CO_2 . SG made by CH_4 reforming has a stoichiometric ratio of H_2 to CO that approaches 3. It contains some CO_2 , which may also be hydrogenated to MeOH. Co_2 may be added to the SG in order to convert some of the excess H_2 to CO via the reverse water-gas shift (WGS), which is favored at higher temperature $[CO_2$ and $H_2 \rightarrow CO + H_2O]$. The presence of 6% by volume of CO_2 in the SG increases MeOH yields by about 23% in the Lurgi MeOH synthesis.⁶ In various operations, CO_2 levels vary from 2 to 6% and are usually specified by the various producers.

As stated, MeOH is made in numerous plants with over 99% selectivity when a mixture of CO, CO_2 , and H_2 is passed over a Cu-ZnO-Al₂O₃ catalyst at elevated pressures and temperatures between 493 and 573K. Surprisingly for such a widely practice process, however, there are few known facts, other than that the reaction is exothermic. ⁷⁻⁹

A major question bedeviling the mechanistic interpretation of MeOH synthesis is whether the alcohol is synthesized from CO or from $\rm CO_2$. Rozovskii et al., ¹⁰ using ¹⁴CO₂, showed that the MeOH synthesis proceeds through CO₂ rather than through CO as follows:

2H2

$$CO + H_2O \rightarrow CO_2 + H_2 \rightarrow CH_3OH + H_2O$$
. (5.1-4)

Chinchen et al.⁷ at ICI have confirmed these findings. MeOH appears to be formed from CO_2 and H_2 , possibly through a surface formate intermediate.

In any event, the hydrogenation of CO to MeOH can be guided by catalysts that, unlike FT catalysts, do not dissociate the CO molecule. It is known that Pd, Pt, Ir, and Cu catalysts chemisorb CO associatively and all are candidates for use in the synthesis of MeOH from SG. Copper-zinc catalysts are presently the catalysts of choice but there is active research on the synthesis of MeOH using Pd (and Pt) catalysts.¹¹
It appears likely that the active components in the copper-based catalysts are $Cu^{\circ}-Cu^{+}$ species in a solid solution of ZnO.¹² The catalyst loses its activity if the SG is completely devoid of CO_2 . The CO_2 and perhaps H_2O or O_2 may preserve copper in the Cu^{+} state. In their absence, Cu^{+} is gradually reduced to metallic copper. The copper-based catalysts, since they are more sensitive to poisoning and sinter more easily, have shorter life spans than the zinc oxide/chromium oxide base catalysts.

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5.1-2C. <u>Kinetics</u>

The kinetics of the MeOH syntheses are complex and are affected by a number of variables, such as the nature of the catalyst, the physical changes of the catalyst as the reaction progresses, the composition of the gas (which is also constantly changing in the reactor), temperature, and pressure. Modern MeOH syntheses use copper-zinc low-pressure catalysts and, since the synthesis reaction proceeds to thermodynamic equilibrium very rapidly, the kinetic behavior of the catalyst is not so important. It should be noted that all commercial catalysts and hence their kinetic behavior are proprietary.

5.1-2D. Feedstocks

The primary raw material as the source of SG for producing MeOH at present is NG, which in 1980, accounted for 70% of worldwide production. Residual fuel oil, naphtha and coal are the other feedstocks. In 1980, they accounted for about 15, 5 and under 2% of worldwide production, respectively. Steam reforming of NG gives SG with a one mole excess of H_2 above the stoichiometric requirement for MeOH synthesis. The excess H_2 can be purged and used as a fuel to generate steam. As mentioned earlier, by adding CO₂ to SG, the excess H_2 can be converted to MeOH. Steam reforming of naphtha gives the required ratio of H_2/CO . Partial oxidation of residual oil produces SG with an H_2/CO ratio of 1:1; this ratio must be shifted to achieve the required gas ratio. Nevertheless, this raw material is attractive, since the bottom of the crude oil barrel is profitably utilized. In the long run, more SG for MeOH manufacture will be made from coal.

5.1-2E. Process Technology and Reactors

The production of MeOH is an established commercial technology. Nevertheless, constant improvements are being made in process technology and reactor design for better recovery, in lower compression costs, and in processing of the raw MeOH. Marschner¹³ and Satterfield¹⁴ have summarized these subjects.

5.1-2F. Liquid-Phase Methanol Synthesis

An MeOH synthesis utilizing a liquid-phase slurry reactor is under development. This concept is being tested in a process-development unit at LaPorte, Texas, by Air Products and Chemicals, Inc., with the technical assistance of Chem. Systems. The project is jointly funded by the US DoE, Air Products, Fluor Corp., and EPRI. The construction of a pilot plant based on this technology using SG derived from coal is under consideration. The SG will probably be made in a Texaco gasifier so that the H₂:CO ratio will be low.

The liquid-phase reactor for MeOH synthesis, in design as well as in operating procedures, is basically similar to that originally proposed by Kolbel for FT synthesis. In laboratory-scale experiments, commercial and experimental MeOH-synythesis catalysts have been tested at 3.5-7.0 MPa in the temperature range 488-523K. Because equilibrium conversion is favored by low temperature and the temperature is well-controlled in the slurry reactor, high single-pass conversion is possible. About 20% conversion of CO to MeOH with a feed gas of balanced composition can be expected.¹⁵

The SG used at LaPorte is a synthetic mixture of H_2 , CO, CO₂, and CH₄, representing gas from conventional or high-temperature coal-gasifiers. In the tests conducted so far, the tail gases are not recycled; instead, they are used to generate power in gas turbines. But it is possible to enrich the exit gases from the reactor with H_2 (by adding steam to the feed gas) so that part of the tail gas can be recycled.

5.1-2G. Other Routes for Methanol Synthesis

The production of MeOH from SG using low-pressure Cu-ZnO-based catalysts will remain dominant in the MeOH industry whether NG or coal is

the feedstock. However, there are other reactions that produce MeOH. One route is through the synthesis of methyl formate and its subsequent hydrogenation to MeOH. The equations for this two-step synthesis are:

$$HCOOCH_3, (5.1-5)$$

$$HCOOCH_3 + 2H_2 \xrightarrow{Cu \text{ catalysts}} 2CH_3OH , \qquad (5.1-6)$$

$$CO + 2H_2 \longrightarrow CH_3OH$$
 (5.1-7)

Methyl formate (HCOOCH₃) is prepared by reacting MeOH and CO in the presence of a homogeneous sodium methoxide catalyst at 353K and 3.0MPa; this step is followed by the catalytic hydrogenation of methyl formate to MeOH at 453K and 3.0MPa. Work by Trimm et al.¹⁶ has shown that the temperature and pressure required for hydrogenation of the formate to MeOH can be lowered significantly. The net result is the synthesis of two moles of MeOH per mole of starting MeOH.

A modified version of this process is described in a German patent,¹⁷ in which the catalyst, operating temperature and pressure for the hydrogenation reaction are copper chromite, 373-443K and 2-6 MPa, respectively. A pilot plant was built in Germany in 1945.¹⁸ The method may be attractive, since lower temperatures and pressures are used than even in the present low-pressure commercial processes. This route to MeOH from SG has high yields in both steps, thus avoiding the equilibrium constraints in the presently practiced MeOH synthesis.

Another route to MeOH involves the partial oxidation of CH_4 and C_2-C_5 HCs. These compounds may be catalytically air-oxidated at 3.0MPa and around 723K to liquid and gaseous oxygenated products. Suitable catalysts for the process are iron, nickel and copper as metals, as oxides, or as mixtures of metals and oxides. Selectivity to MeOH is very poor; acetone and C_1 and C_2 aldehydes are produced in significant amounts. There is increasing research in this area.

Methanol has been synthesized using copper-thorium catalysts. ICI has developed a synthesis of MeOH using an alloy which contains copper with a metal other than radioactive thorium. This alloy catalyst operates at low temperatures (~ 100° C) and therefore gives high conversions to MeOH. Unfortunately, the system is sensitive to CO₂ and the cost of completely

removing CO_2 from the feed gas stream makes this process presently unattractive.

Workers at Brookhaven National Laboratory have discovered a low-temperature, low-pressure system, based on the use of a homogeneous transition metal complex, that yields a selectivity of over 99% of MeOH per pass. Further developments of this and similar systems will be of great interest.

5.1-2H. Methanol from Coal

Coal-based MeOH plants will be more costly and complex than NG plants because of the additional facilities needed to handle coal and solid residues and the required cleanup of resultant gases. The cost and complexity will also be influenced by the type of coal selected and the gasifier used. Some of the features of coal-to-MeOH technology, in which SG is derived from a second-generation slagging gasifier while the MeOH synthesis, at east for the near future, is accomplished by one of the low-pressure processes, are: (i) the gas is mainly H_2 and CO, with smaller amounts of CO₂, and is virtually free of CH₄; (ii) it is at a much higher temperature than the MeOH-synthesis temperature; (iii) the SG is compressed to 3 to 8MPa, thereby eliminating the cost of compression to the MeOH-synthesis pressure; and (iv) it has a low value for the H_2/CO ratio.

The low level of $\rm CO_2$ and $\rm CH_4$ minimizes the buildup of inerts in the MeOH-synthesis loop, thus reducing the amount of purge gas. Excess heat can be recovered in high-pressure steam generators and the steam produced may be used to run compressors and to generate electricity. But the SG is deficient in H₂ and additional units may have to be added to the plant. The H₂/CO ratio must be adjusted to 2:1 or slightly higher by the WGS reaction. Since the shift reaction is exothermic, the heat may be recovered to generate additional high-pressure steam. It is probably not economical to have more than 15% of CO₂ in the feed gas.

The gasifier is a vitally important part of a coal-to-MeOH plant. It influences the synthesis pressure and thus the selection of the commercial synthesis process. It also determines the extent to which the SG must be shifted and the specific plant design to optimize waste heat recovery at different stages. In spite of this complexity, a large coal-to-MeOH industry may well be a reality one day. Several conceptual