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TITLE: Gasification Systems to Produce Low Cost Synthesis Gas

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Introduction

Within DOE, METC is responsible for research on processes for the production of synthesis gas as part of the Surface Coal Gasification Program. All METC programs are organized to develop integrated systems for specific applications. The Surface Gasification Program, includes the development of systems for the production of power, which involves the development of IGCC systems for the production of a hot fuel gas and steam; the development of systems for the production of industrial fuel gas, which involves the development of instrumentation, materials, and components for gasification systems; the development of systems for the production of co-products, which involves the development of mild gasification processes to produce high value solid, liquid and gaseous products; and the development of systems for the production of synthesis gas. For the production of synthesis gas the objective is to develop improved routes to lower cost synthesis gas, including improved process concepts, gasification reactors, gas cleanup and gas separation processes, and shift catalysts.

Each program includes the development of improved process concepts, modelling and economic analysis studies, performed by both outside contractors and by METC's Systems and Technology Support Division. Also within the METC organization, the Office of Applied Science and Technology is doing research in house to expedite the commercialization of these technologies. Other closely related activities at METC include programs to develop hot-gas cleanup technologies to fit specific applications, such as the production of synthesis gas, including methods to remove particulates, sulfur, alkali, and trace contaminates from gasified coal, generally at temperatures from 1,200° to 2,000°F. Two of these technologies which are particularly applicable to the production of synthesis gas are the development of the zinc ferrite external desulfurization process and the cross-flow filter for particulate removal.

Matching Synthesis Gas Production and Use

Processes for the production of synthesis gas from coal, shown in Figure 1, include coal handling and preparation, gasification, cleanup, and shift

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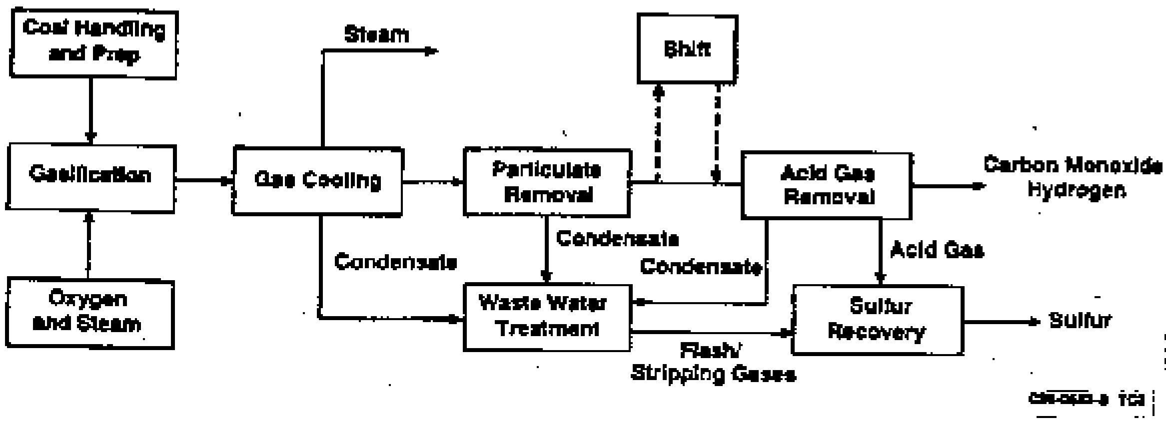
Figure 1
Typical Process for the Production of Synthesis Gas



and/or gas separation to adjust the hydrogen/carbon monoxide ratio. Almost all of the organic matter in coal can be converted to crude syngas. The byproducts include sulfur, ammonia, carbon dioxide, heat and steam. Environmental concerns must also be addressed. The conversion of coal to clean synthesis gas generally accounts for 70-80 percent of the capital cost of an indirect liquefaction plant (Haag, Kuo, and Wender June 1987, p.118).

Synthesis gas has been produced commercially in each of the different generic types of gasifiers shown in Figure 2 (Wilson, Halow, and Ghate 1988). For example, the Lurgi fixed-bed gasifier in the Sasol plants in South Africa, and the Texaco gasifier in the Tennessee Eastman Coal-to-Chemicals plant in Kingsport, Tennessee.

Projected clean gas compositions from each of these gasifiers types is shown in Table 1 (Haag, Kuo, and Wender June 1987, p.183). The varying properties of these gas mixtures, including the temperature, is clear. The variation in these properties requires the use of different gas cleanup techniques and, most importantly, can be used to match the gasifier to the temperature and pressure requirements of the downstream processes. An entrained gasifier produces a relatively hydrocarbon-free gas at a very high exit gas temperature. The reaction takes place at 2,500°F and most of the heat in the gas is removed from the gasifier so that large amounts of heat exchange surface are required to cool the gas and recover the heat. Fluid-bed gasifiers produce gas at intermediate temperatures. After cleaning, the gas contains a few percent of methane. Fixed-bed gasifiers produce gas near the temperature needed for most direct liquefaction processes but the gas typically contains less than 90 percent hydrogen plus carbon monoxide and must be cleaned of significant quantities of methane and condensable hydrocarbons. Each gasifier type can produce synthesis gas at different pressures.

The stoichiometric hydrogen/carbon monoxide ratio required for various products varies depending on the chemical to be produced as shown in Table 2.

Figure 2
Generic Coal Gasification Reactors

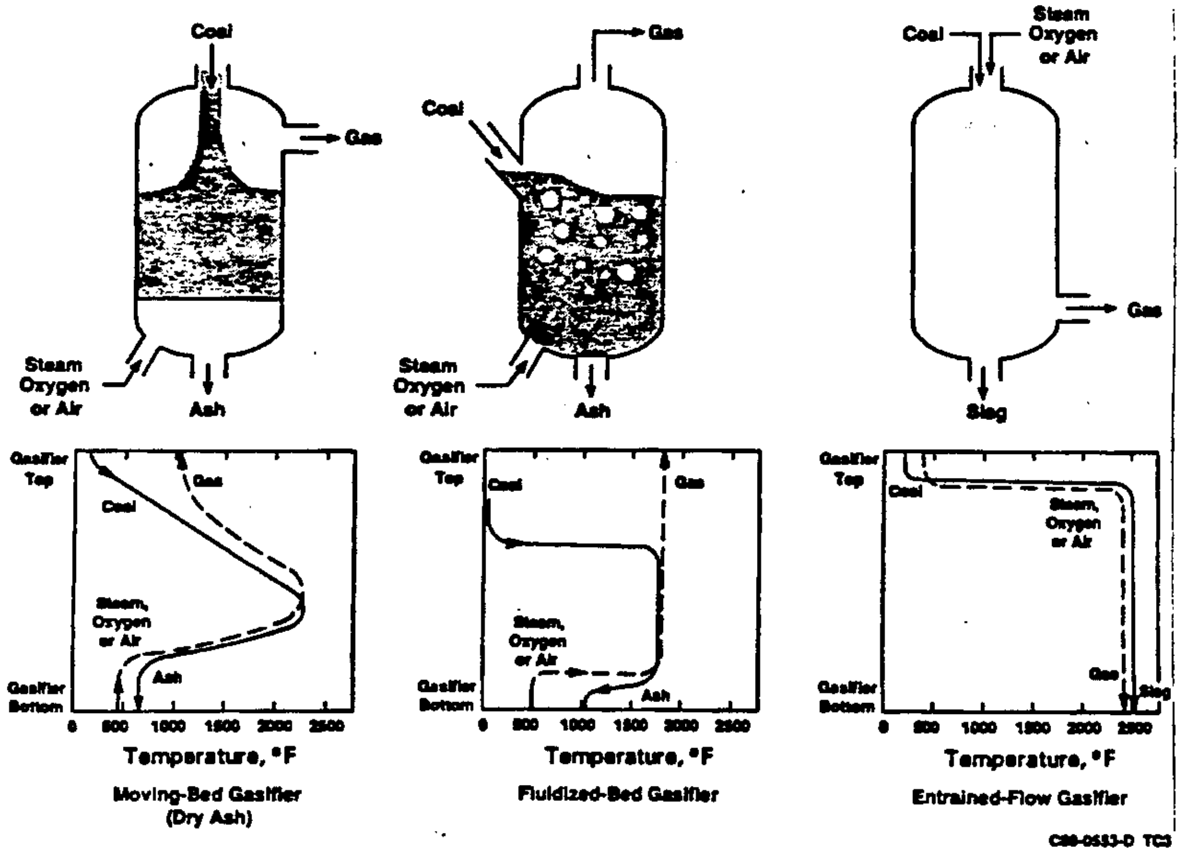
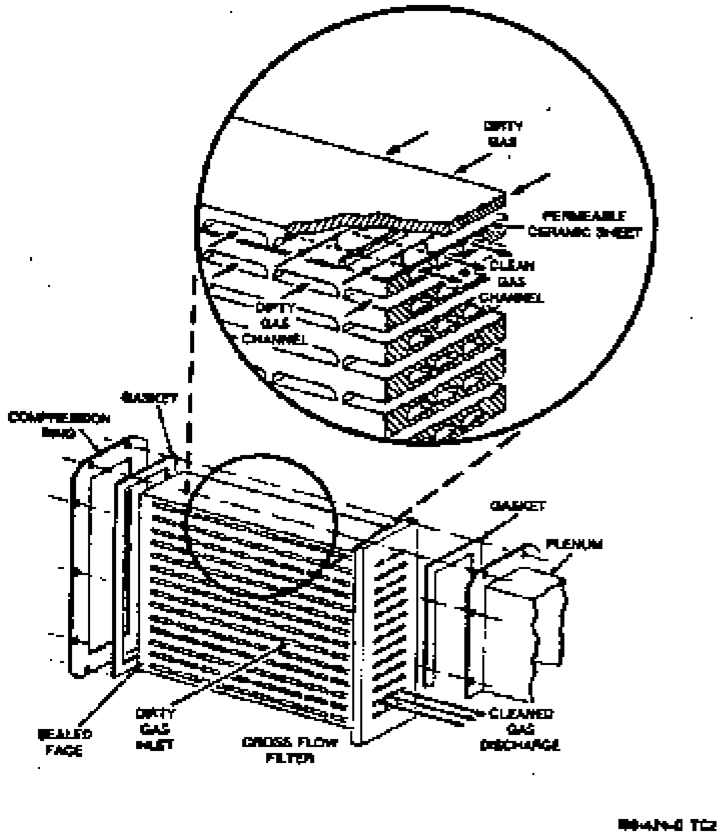


Table 1
Typical Properties of Clean Synthesis Gas

GASIFIER	TEXACO	SHELL-KOPPERS	KOPPERS-TOTZEK	KRW	WINKLER	DRY-ASH LURGI	BGC-LURGI
GASIFIER TYPE	ENTRAINED	ENTRAINED	ENTRAINED	FLUID-BED	FLUID-BED	FIXED-BED	FIXED-BED
COAL	ILLINOIS NO. 6	ILLINOIS NO. 6	TVA	WYOMING	GERMAN BROWN COAL	WYOMING	FRANCES
EXIT PRESSURE, PSIG	600	435	20	415	30	430	365
CLEAN GAS COMPOSITION, MOL %							
H_2	40.0	32.8	38.6	40.1	50.2	55.7	29.4
CO	58.8	66.5	60.1	52.4	46.1	26.9	58.4
CH_4	0.1	--	--	6.8	2.3	16.1	7.0
C_2	--	--	--	--	--	0.9	0.5
N_2	1.1	0.7	1.3	0.7	1.4	0.4	4.7
H_2/CO RATIO	0.679	0.494	0.638	0.763	1.09	2.07	0.504
H_2 + CO, PERCENT OF GAS	98.8	99.3	98.7	92.5	96.3	82.6	87.8

Figure 3
Ceramic Cross-Flow Filter

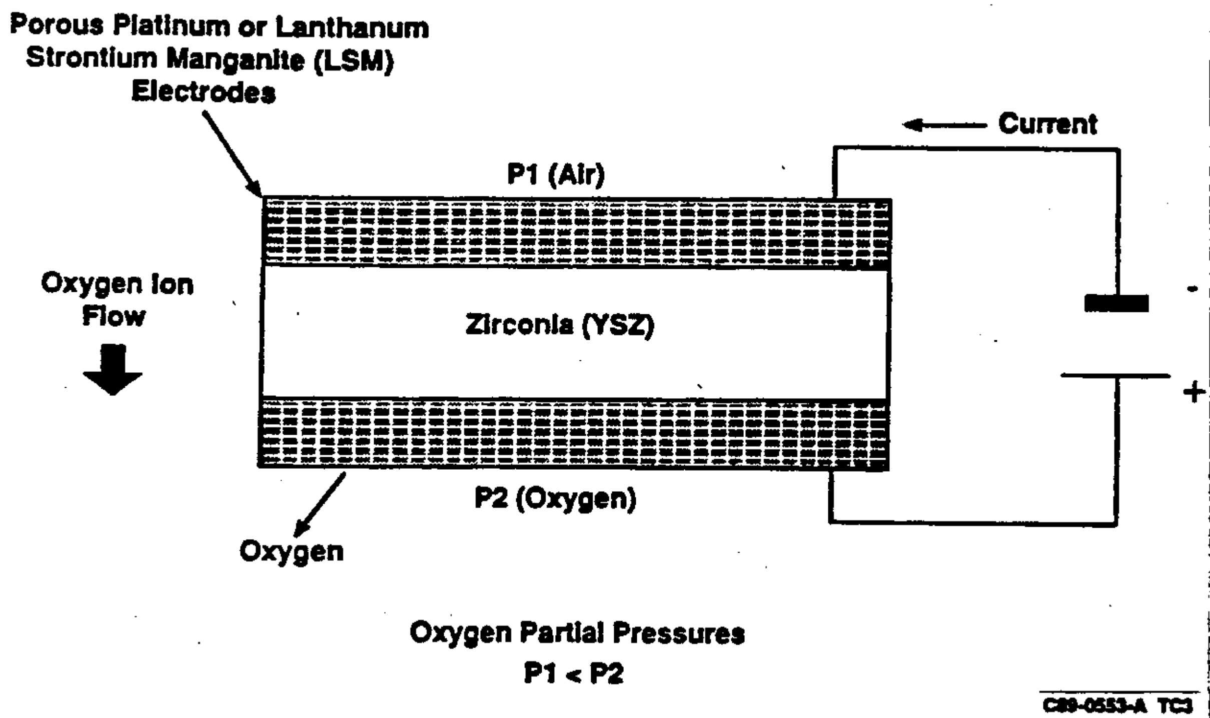


Gas Separation

The Jet Propulsion Laboratory is developing a solid electrolyte method, called the Zirconia Cell Oxygen Production Source, for producing lower cost oxygen for coal conversion plants. The technology is intended for use in applications requiring less than 50 tons/day oxygen, where it is projected to be economically competitive with cryogenic plants. A diagram of the zirconia membrane is shown in Figure 4.

The membrane consists of the zirconia sandwiched between electronically conductive porous electrodes. Oxygen molecules diffuse through the porous electrode to the zirconia interface, where they are decomposed to single oxygen ions. Electrons are supplied from the DC power supply, which drives the oxygen ions into the zirconia membrane where they are transported through oxygen vacancies to the second electrode. At this point they recombine into oxygen molecules and the electrons are given up to complete the circuit. The zirconia electrolyte operates at 1470-1830°F to increase oxygen vacancy mobility. The cells will be stacked and combined into modules with appropriate piping to admit and exhaust gases and oxygen. It may be possible

Figure 4
Zirconia Membrane



to manifold the modules in such a way that they can act as heat exchangers to remove heat from the gasified coal and obtain the high temperature needed for operation. The major effort at this time is on the production of thinner zirconia sheets to improve the oxygen production rate.

Organic membranes are also being studied for use in gas separation. One example is a project by the National Institute for Standards and Technology (NIST) to demonstrate the use of carrier impregnated ion exchange membranes for the selective removal of acid gases. Such membranes have excellent selectivity, are simple, and require low energy. A smaller membrane can be used when the acid gases rather than the bulk gas stream pass through the membrane. However, the membranes are temperature sensitive and expensive. A diagram of the system being studied by NIST is shown in Figure 5.

The membrane is a polysulfonic acid material called Nafion, a DuPont product, with a chemically bonded ethylenediamine carrier. The acid gases interact selectively with the carrier and are conducted through the membrane by passing from one carrier molecule to another. A solvent swelling step has been developed to improve facilitated transport through the membrane at 25-200 degrees C and atmospheric pressure.

Table 2

Hydrogen/Carbon Monoxide Ratio Requirements for Various Synthesis Gas Applications

Chemical	H2/CO Stoichiometric Ratio
Carbonization	Pure CO
Acetic Acid	1.0
Ethylene Glycol	1.5
Ethylene	2.0
Methanol	2.0
Ethanol	2.0
Ammonia	Pure H2

For the most common uses, hydrogen is deficient in most gasification product gas streams. Tradeoffs must be made. Gasification rates and coal throughput are favored by higher gasifier temperatures but the production of hydrogen is favored by lower temperatures, as are the formation of methane and other liquid hydrocarbons, which must be removed from the gas. Therefore, hydrogen concentration is generally increased in a separate water-gas shift reactor in the presence of a catalyst.

Other properties of synthesis gas are also important. Typical synthesis gas properties required for various indirect liquefaction applications are shown in Table 3 (Haag, Kuo, and Wender June 1987). The Sasol Arge process produces mostly diesel oil and heavier material and the Synthol process produces lighter material, boiling predominately in the gasoline range.

Table 3
Synthesis Gas Properties for Indirect Liquefaction

PRODUCT	MeOH LOW PRESSURE	SASOL I ARGE	SASOL I SYNTHOL
CATALYST	$Cu/ZnO/Al_2O_3$	$Fe/Cu/K/SiO_2$	$Fe/K/Mg/Al_2O_3-SiO_2$
PRESSURE, PSIG	730	360-380	335-350
TEMPERATURE, °F	482	698	563
H_2/CO	> 2:1	1.5-2.5:1	2.0-3.0:1
ALLOWABLE SULFUR LEVELS, PPM	0.2	1-2	1-2
OTHER CATALYST POISONS	Ni, Fe		

The required temperature of the gas is low, from 480°-700°F and the pressure is moderate, in the range of 335-730 psig. The requirements for low temperature do not appear to require hot-gas cleanup. However, there are some

IGCC applications where one-pass methanol formation may be incorporated to produce peaking fuels for utility applications while the major product is fuel gas, and heat must be conserved for producing steam.

The level of sulfur removal required is high, with the sulfur concentration which must be achieved in the 1-2 ppm range. Sulfur removal processes and sulfur resistant water-gas shift catalysts are therefore needed. Ash concentrations in the gas must also be virtually nil. Particle removal systems which do not involve the addition of large amounts of water to the gas stream are also needed.

Research and Development Needs for the Production of Synthesis Gas

An extensive discussion of the research and development needs for the development of gasification systems for the production of low cost synthesis gas has been published recently (Haag, Kuo, and Wender June 1987). The overall process economics must always be considered. Among the recommendations and comments are the following:

- Integrate the gasifier with downstream indirect liquefaction processing.
- Integrate the production of synthesis gas with the production of energies in various forms, including uses for hydrogen, steam, heat and possibly carbon dioxide.
- Enhance co-production applications by the use of hot-gas cleanup techniques to preserve heat in the gas stream.
- Use oxygen in the gasifiers because of the need for high hydrogen plus carbon monoxide partial pressures in the indirect liquefaction processes. (It is also cheaper to compress oxygen than the resulting synthesis gas.) But define the optimum oxygen purity requirement. The oxygen need not be pure in all applications and the production of pure oxygen is a high-cost component of gasification processes.
- Study the use of low volatile content coals in gasifiers with short residence times to minimize hydrocarbon formation.

METC Programs on Systems for the Production of Synthesis Gas

METC currently has projects in progress on improved gasifier operation, catalytic gasification, hot-gas particulate removal, sulfur resistant water-gas-shift catalysts, gas separation, the zinc ferrite hot-gas desulfurization process, acid gas removal, and system optimization studies. There are many projects currently in progress on operation of gasifiers, primarily coupled with hot-gas cleanup. These and the zinc ferrite hot-gas desulfurization process development, which is also being developed in many separate projects, will not be discussed in this paper. Details of these projects are available (Kothari and Longanbach May 1988).

A discussion of several current METC-sponsored projects with application to the development of systems for the production of synthesis gas follows.

Catalytic Gasification

Lawrence Berkeley Laboratory is continuing a program called Fundamental Studies of Catalytic Gasification. The objective of this work is to investigate the role of catalysts in low temperature steam gasification of coal chars. They have shown that catalysts composed of mixtures of calcium and potassium oxides are almost as active as nickel/potassium mixtures and are not deactivated by the presence of metals and sulfur on the char surface. The catalysts react by dissociating water on the char surface and produce hydrogen and carbon monoxide at temperatures greater than 1300°F and hydrogen and carbon dioxide at 1080-1300°F. They have found no evidence for water-gas shift on the catalyst surface by following the presence of carbon monoxide using Auger spectroscopy and temperature-programmed desorption of carbon monoxide. All types of char have been shown to have the same energy of activation, indicating a common reaction mechanism. Low rank coals gasify faster due to greater catalyst coverage which is proportional to the larger surface area in coals as coal rank is decreased.

Ceramic Cross-Flow Filter

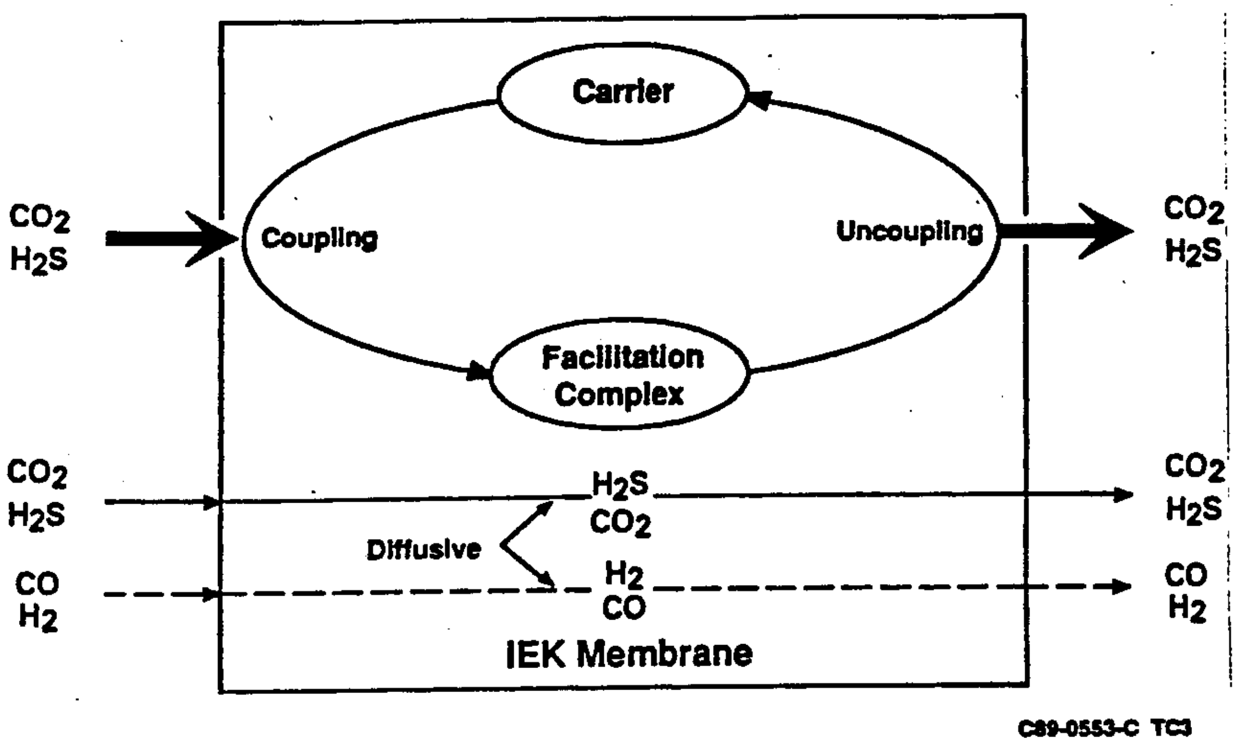
The Westinghouse R&D Center is developing the ceramic cross-flow filter. The objective of one of the current programs is to verify the suitability of ceramic cross-flow filter technology for use in a coal gasification environment. A diagram of the current configuration of the ceramic cross-flow filter is shown in Figure 3.

The filter is a 4 inch x 12 inch x 12 inch module which consists of alternating channels and porous ceramic plates. The dirty gas passes into the filter through one set of channels, passes through the porous ceramic plate, and exits through a second set of channels. These filters have been successfully tested in a pressurized-fluidized bed combustor (PFBC) environment and, at METC, on a gasifier. The filter will be now be tested on a Texaco gasifier and, using a simulated gasifier product stream with 2000-3000 ppm ash on a test loop at 1,500°F and 160 psig and 100 acfm gas flow.

Low Temperature Water-Gas Shift Catalysts

SRI International has recently completed a program to investigate the development of a novel homogeneous, low-temperature, water-gas shift catalyst. The goal of the work was to find a single homogeneous, carbonyl-complex catalyst which could convert greater than 95 percent of the carbon monoxide to hydrogen at 390°F in an aprotic solvent/amine base system. After screening a series of catalysts they identified ruthenium and molybdenum-iron catalysts as candidates for further testing and showed that 1,000 ppm of hydrogen sulfide had little effect on the performance of these catalysts. However, the turnover frequency for these catalysts is not high enough to support further development.

Figure 5
Facilitated Transport Membrane Mechanism



Economic Analysis of Coal-to-Chemicals Processes

An economic analysis of coal-to-chemicals processes, recently completed at METC, concluded that fluid-bed gasification with zinc ferrite desulfurization and cross-flow filter hot-gas cleanup seems to be the most economical process combination. Fluid-bed gasification produces gas at a pressure and temperature reasonably close to that required by indirect liquefaction processes. Zinc ferrite sulfur removal and cross-flow filter particulate removal processes preserve heat in the gas stream. The heat and power evolved during gasification must be integrated into the indirect liquefaction process.

Summary

METC has identified key technical issues in the low cost production of synthesis gas and hydrogen and initiated research and development activities to address some of the issues. System studies are continuing to analyze and develop optimum process configurations for the integration of gasification and indirect liquefaction processes.

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