

FUTURE CATALYTIC REQUIREMENTS FOR SYNTHETIC ENERGY FUELS

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ENERGY FUEL NEEDS

Until recently, any discussion of energy fuel requirements would have featured such topics as higher octane for gasoline, lower cost fuels for generation of electricity, and incentives for increasing fuel consumption. Now, dominant issues are protection of the environment, provision of fuels secure within our national borders, and more efficient use of fuels. These new issues have been dictated by the realization that the growth of energy utilization in the United States is so great as to exceed our capability to produce the projected needs of oil and gas, the belief that increasing importation is reaching a level unacceptable from the viewpoints of both national security and balance of trade, and the growing determination to prevent pollution even at relatively high cost.

Oil and gas now supply 75 percent of energy needs in the United States, whereas coal supplies only 20 percent. Our energy resources are about the reverse, coal representing about 75 percent of the currently used fossil fuel resources. Additionally, large supplies of oil shale exist.

The solution to these problems, at least for many decades, is the large-scale manufacture of synthetic fuels that are clean burning, together with more efficient fuels utilization in generating electricity using systems such as advanced power cycles or magnetohydrodynamics.

Recent projections by the Bureau of Mines anticipate a 3.5 percent annual increase in demand for energy. Hence, our energy needs will double in the next 15 years, and are expected to triple by the end of the century. (Figure I and Table I). In 1970, 69 quadrillion Btu's were used in the U.S. In practical terms this is equivalent to consumption for every person, every day, of 50 pounds of fossil fuels, namely, 22 of oil, 14 of coal, and 14 of gas. By the end of the century, coal, oil, and gas needs are each projected to double. Nuclear power generation, while growing rapidly, will then still supply only one-fourth of energy needs.

The future supply of fuels must also take into account various consumer groups or use sectors of energy (2). The four sectors home and commercial, industrial, transportation, and generation of electricity (Table II) now are fairly evenly divided. Each is expected to grow, although fuels for generating electricity, including nuclear, will assume a much larger relative importance, being twice any of the other sectors by the year 2000. Each of the energy uses has special requirements which are reflected in different fuels characteristics. Fortunately, synthetic fuels can provide for each of the energy use sectors as summarized below:

I. Home, commercial, some industrial:

High-Btu gas
(essentially methane, 1000 Btu/Ft³)

II. Generation of electricity, some industrial:

- (a) Low-sulfur, low-ash oil
- (b) Low-Btu gas
(CH₄, H₂, CO mixture, with or without N₂,
150-400 Btu/Ft³)

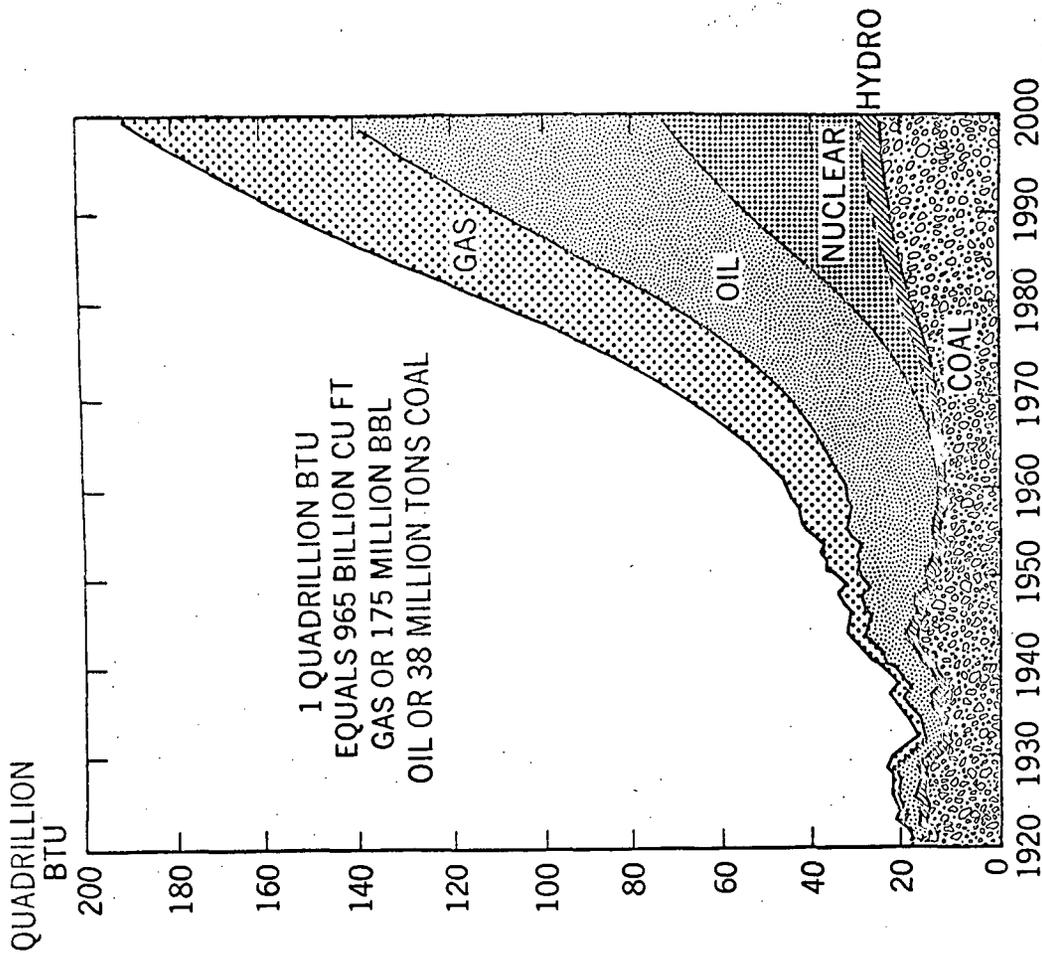


Figure 1 - Energy Usage and Fuels Projections,
 U.S. Bureau of Mines. (1)

U.S. DEMANDS - QUADRILLION Btu

	1970	1975	1985	2000
Petroleum	30	36	47	66
Natural Gas	23	29	39	51
Coal	14	16	22	26
Hydropower	2.6	2.8	3.5	5
Nuclear	<u>0.2</u>	<u>4.8</u>	<u>21</u>	<u>43</u>
TOTAL	68.8	89	133	192

Table I - Reference, U.S. Bureau of Mines.

	<u>QUADRILLION BTU</u>	
	<u>1970</u>	<u>2000</u>
Home & Commercial	14.0	21 - 41
Industrial	20.3	32 - 59
Transportation	16.5	36 - 52
Electricity Generation	<u>16.5</u>	<u>75 - 85</u>
	67.3	165 - 239

Table II. Energy Consumption by Major Consumer Groups.

III. Transportation:

- (a) Gasoline
- (b) Gaseous fuel such as methane and/or hydrogen

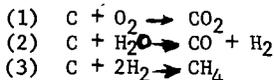
GASIFICATION OF COAL

Pipeline gas now supplies one-third of our national energy needs and in use is by far the fastest growing of all our fossil fuels. The demand/supply situation, shown in Figure 2, reveals that a shortage has already begun and there will be a large deficit

by 1985. Recently, plans have been announced by a number of companies to manufacture synthetic gas from naphtha and coal (4). Insofar as coal is concerned, the older process of gasification used in Europe is the only technology proven commercially. There is a great opportunity to improve technology in modern conversion processes now under development, and specifically through the use of catalysts. In order to provide a basis for the role which improved catalysts could play, the steps of the Bureau of Mines SYNTHANE coal gasification process (5,6,7) are shown in Figure 3. The process steps are pretreatment of the coal with oxygen (to prevent caking and sticking), gasification (reaction with steam and oxygen), purification (removal of CO_2 , H_2S), shift ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$) to bring H_2/CO ratio to 3/1, and finally methanation ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$).

Gasification Catalysis

The most desirable situation would be to have the reaction between coal and steam proceed as follows: $\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + \text{CO}_2$). But this does not happen rapidly enough at lower temperatures, while at higher temperature thermodynamic equilibria are unfavorable for high methane yields. Individual reactions important in gasification are:

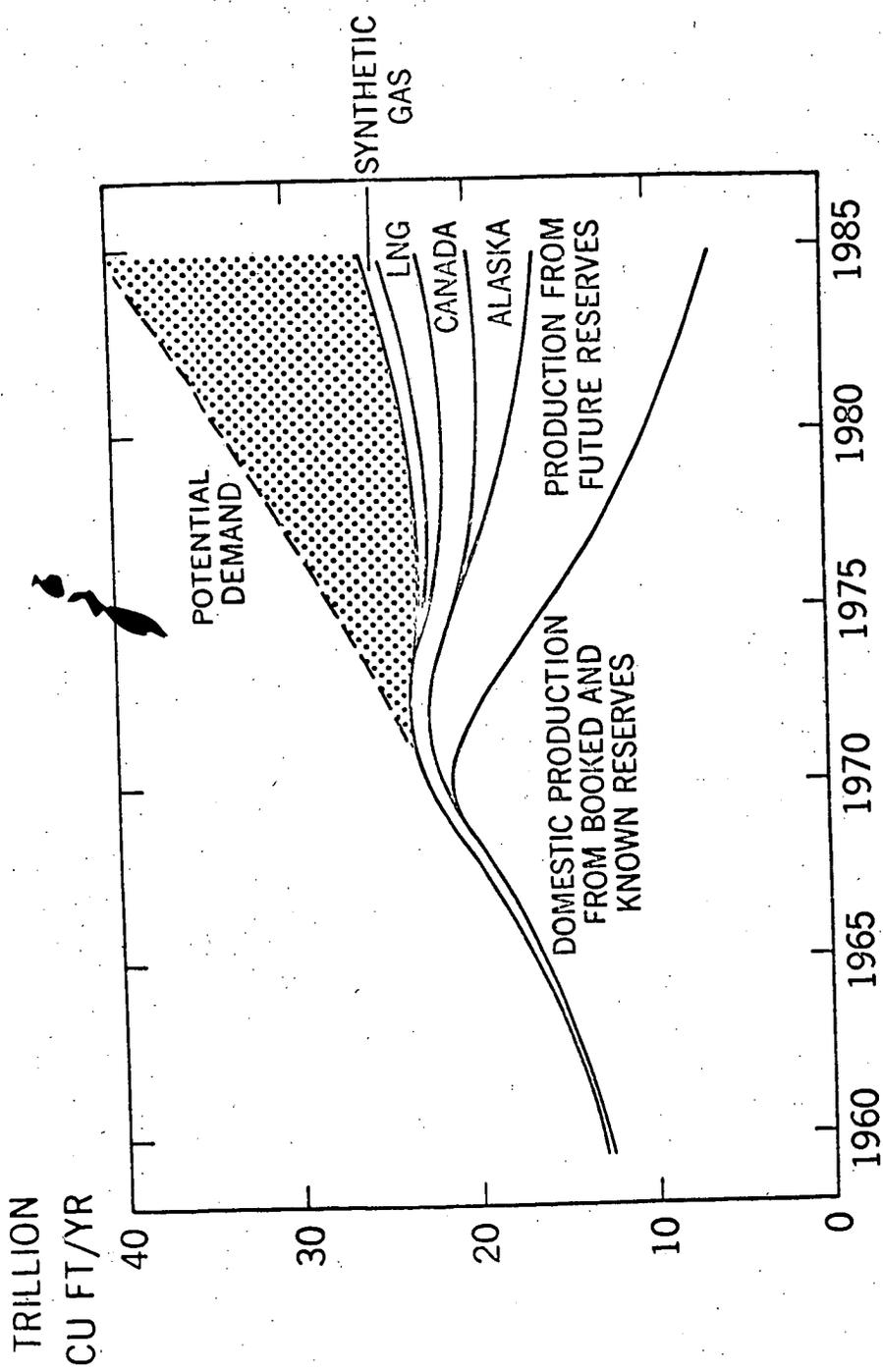


It is endothermic reaction (2) which is too slow. A partial solution to this problem is provided in the SYNTHANE process by having the single fluid bed gasifier operate with two zones. The lower zone is at about 1800°F (982°C), at which temperature reaction (2) occurs relatively rapidly. The upper zone, from which the gas exits, is at about 1400°F (760°C), so that the methane formed by coal devolatilization and reaction (3) is maximized.

There is a need to catalyze reaction (2) to decrease equipment needs and, more importantly, to permit operation at a lower temperature, because of thermodynamic equilibrium considerations, a higher methane content of the gases leaving the gasifier is achieved at lower temperatures.

Catalysis of the steam carbon reaction has been reported recently by the Bureau of Mines (8), and is also discussed later in the section concerned with the related process of naphtha gasification. Earlier investigators have shown that the percentage of methane in water gas made from coke can be increased significantly by adding lime or certain other salts to coke. In experiments carried out at 850°C (1562°F) and 300 psig, Haynes, Nelson, and Field (8) passed steam over a pretreated bituminous coal to which was admixed 5 wt% added material whose catalytic properties were to be determined. The results are given in part in Table III.

Additional experiments were carried out using nickel, either as an added salt or in a novel approach in which an inert probe coated with Raney nickel was inserted into the gasifier.



UNITED STATES GAS SUPPLY TRILLION CUBIC FEET/YEAR

Figure 2. Reference. Humble Oil and Refining Company. (3)

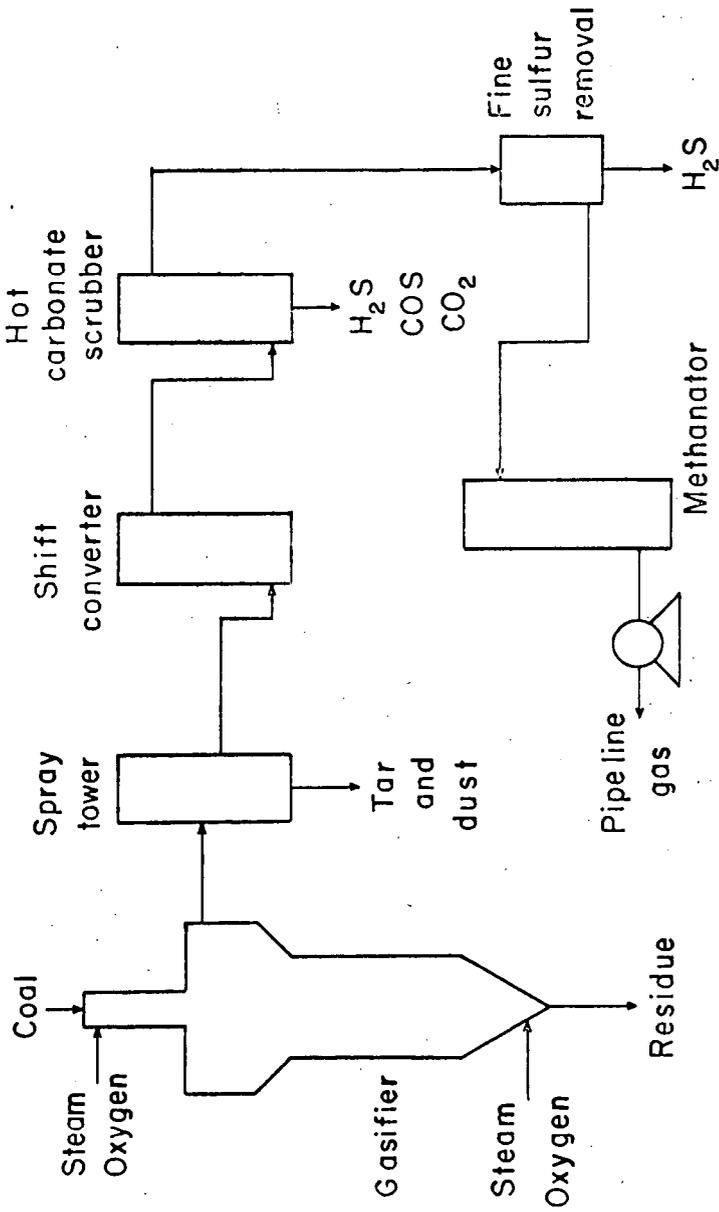


Figure 3 - SYNTHANE Coal Gasification Process

<u>CH₄</u>	<u>H₂</u>	<u>CO</u>	<u>C gasified</u>
Li ₂ CO ₃ - 21	K ₂ CO ₃ - 83	K ₂ CO ₃ - 91	K ₂ CO ₃ - 62
Pb ₃ O ₄ - 20	Li ₂ CO ₃ - 55	Li ₂ CO ₃ - 72	Li ₂ CO ₃ - 40
Fe ₃ O ₄ - 18	Pb ₃ O ₄ - 39	Fe ₃ O ₄ - 60	Pb ₃ O ₄ - 30
MgO - 17	CuO - 37	Cr ₂ O ₃ - 55	Cr ₂ O ₃ - 26
Cr ₂ O ₃ - 16	MgO - 35	Pb ₃ O ₄ - 52	MgO - 26
CuO - 15	Fe ₃ O ₄ - 33	CuO - 49	Fe ₃ O ₄ - 23
Al ₂ O ₃ - 14	Al ₂ O ₃ - 33	Al ₂ O ₃ - 45	CuO - 22
K ₂ CO ₃ - 6	Cr ₂ O ₃ - 25	MgO - 28	Al ₂ O ₃ - 22

Table III. Coal Gasification - Percentage Increase of CH₄, H₂, CO and Carbon Gasified Upon Addition of 5% of Salts Shown.

The overall results of this investigation show that the use of suitable additives improves the steam-coal gasification reaction considerably. In connection with possible benefits to the "SYNTHANE" process, it appears that appropriate additives could significantly increase production of methane and hydrogen in the gasification step, thereby reducing both the size of gasifier required and the processing work required downstream of the gasifier, such as the shift reaction, CO₂ removal, and catalytic methanation.

The study of gasification catalysts thus far has shown the following:

1. Alkali metal compounds and many other materials such as oxides of iron, calcium, magnesium, and zinc significantly increase the rate of carbon gasification and the production of desirable gases such as methane, hydrogen, and generally carbon monoxide during steam-coal gasification at 850°C (1562°F) and 300 psig.
2. The greatest yield of methane occurred with the use of a probe insert flame-sprayed with Raney nickel catalyst which has a limited life of activity. Significant methane increase resulted from the addition of 5 percent by weight of Li₂CO₃, Pb₃O₄, Fe₃O₄, MgO, and many other materials.
3. The increased gasification resulted whether the extent of coal gasification was small or great.
4. Catalytic effectiveness decreased above 750°C (1382°F).
5. Residue from total gasification of coal mixed with potassium compounds still contained a significant concentration of potassium (over 10 percent) and was effective as an additive in increasing production of hydrogen and methane.

Shift Catalysis

The shift reaction, $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$, is moderately exothermic, and the equilibrium is affected by temperature to a considerable extent as follows:

ΔH	$K = \frac{(\text{CO}_2)(\text{H}_2)}{(\text{CO})(\text{H}_2\text{O})}$
calories per mole	
227°C (440°F) - 9,520	126
327°C (620°F) - 9,294	27
427°C (790°F) - 9,051	7

Although high operating temperatures are desirable from the standpoint of rate of catalytic reaction, they are undesirable from the viewpoint of equilibrium which becomes unfavorable with increasing temperature.

Prior to 1963 the "standard" shift catalyst was a relatively sulfur-resistant catalyst of 70-85% iron oxide promoted by 5-15% Chromia. It was operated at about 650°F (343°C). Because of equilibrium limitations at this relatively high temperature, it was the practice to use two catalyst beds with interbed cooling and CO₂ removal.

In naphtha gasification, a guard case has been advocated to prevent fouling of the shift catalyst by unsaturated hydrocarbons, especially acetylenes, or by a combination of oxygen and diolefins. Examples of the guard catalyst are Ni-Mo-Al₂O₃ or Ni suboxide on sepiolite (9).

The shift conversion processing steps were greatly simplified when catalyst manufacturers made low-temperature shift catalyst available to the industry in 1963. This is a copper-zinc based catalyst, sometimes containing chromia, which is active at temperatures as low as 375°F (10). It is used in the 375-450°F (200-232°C) range where the equilibrium of the shift reaction is so favorable to carbon dioxide and hydrogen formation that the carbon monoxide content can be reduced to the 0.3-0.5 mole percent range without intermediate removal of CO₂. The catalyst is more sensitive to poisons, particularly sulfur and chloride, than the high-temperature shift catalyst.

Recently, shift catalysts have been described which are very active so that they can operate at low temperatures, are active in their sulfided form, and are resistant to loss of activity and loss hardness, even if contacted inadvertently with liquid water. Auer, Lorenz, and Grundler (11) described a new type of catalyst - a cobalt/molybdenum catalyst supported on spinel - which can be operated successfully below 600°F (316°C). The catalyst is active as a sulfide, so that H₂S partial pressure and the H₂S/H₂O ratio are important. It was reported that start-up procedure is of critical importance, since the catalyst in its oxidized form is active to the exothermic methanation reaction. Unless care is taken in sulfidation, temperatures increase to about 1700°F (927°C), which deactivates the catalyst. Using a start-up procedure that avoided overheating, an active catalyst was put on stream and long plant life was attained.

Shift catalyst work has been directed particularly to the manufacture of hydrogen. However, the improvements made also demonstrate the opportunity for developing improved catalysts for manufacture of synthetic fuels - namely, those active at lower temperatures, able to withstand sulfur, and capable of avoiding coke formation.

Methanation

The methanation reaction, $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$, is highly exothermic. The heat of reaction is minus 50, 353 calories at 127°C (260°F). Catalytic methanation has been known for 70 years and has been utilized extensively in removing small amounts of CO from hydrogen-containing gases. For every 1% CO the temperature rise is over 100°F (380°C). The equilibrium is unfavorable at high temperatures, so a temperature over 825°F (440°C) is avoided, and a maximum of 2% (CO + CO₂) in the feed is usual. The composition of a typical catalyst is 77% Ni oxide and 22% Al₂O₃. It is easily poisoned by sulfur and also rendered inactive by carbon deposition and by sintering. Greyson (12) has reviewed methanation thoroughly from thermodynamic and catalytic viewpoints. The group VIII transition elements mainly iron, nickel, and cobalt, appear to be the most suitable for use as methanation catalysts. A very wide range of catalysts has been reported, especially by members of the British Gas Research Board and the U.S. Bureau of Mines. Likewise a variety of reaction systems has been used to overcome the severe problems of the high heat release.

The U.S. Bureau of Mines made a fairly complete study of a reduced and nitrided steel-shot catalyst. The effects of temperature on the activity and specificity of this catalyst in a fluidized-catalyst-bed reactor are shown in Figure 4. The formation of hydrocarbons higher than methane is indicated, and is a reminder of the other type of reaction - namely, the Fischer-Tropsch reaction - in which the synthesis of hydrocarbons in the gasoline range is the objective. Greyson also discussed catalyst life in terms of sulfur poisoning, thermal stability, and carbon deposition.

Recently, Forney and associates (13, 14) have described a very interesting catalyst termed the tube-wall reactor. This catalyst is prepared by flame-spraying a nickel-aluminum alloy on tubes of 2-inch diameter so as to form a bonded layer. The coating is then partially leached with caustic to form a Raney-type catalyst adherent to the tube wall. By having a heat transfer material such as Dowtherm on one side of the tube, which makes for a more practical engineering system, and the SYNTHANE pilot plant is being designed with this form of a tube-wall reactor.

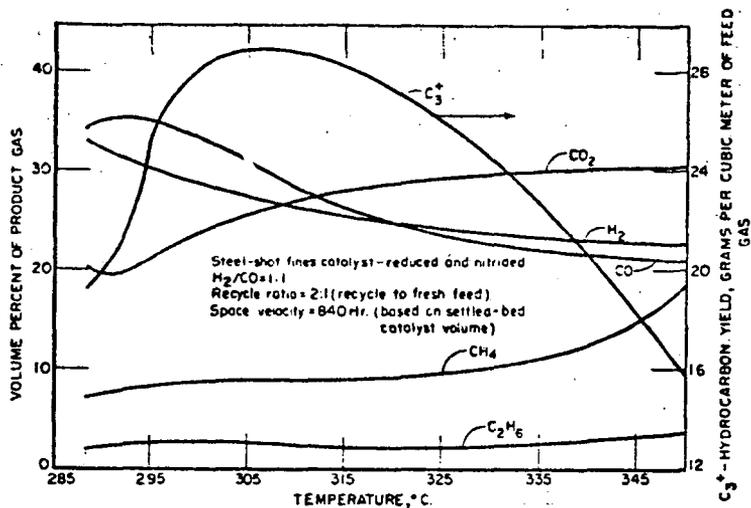


Figure 4.

Effect of temperature on products; 100 psig.

Further improvements in methanation catalysts are one of the most fertile fields for research. Catalysts are needed that are much less sensitive to sulfur (present requirement is about 0.1 ppm H₂S) and that are able to withstand higher temperature increases without sintering and loss of activity. Also needed are catalytic reactor systems capable of removing heat without costly equipment or high recycle gas rates.

Catalysis for Synthetic Fuels Manufactured by Naphtha Reforming

Reforming naphtha consists of its reaction with steam to produce a gaseous mixture containing CO₂, CO, H₂, and CH₄. These gases may be employed for hydrogen manufacture or for their fuel gas utility. The development of nickel-containing catalysts permitted the introduction of a continuous process in England with great success (15).

For manufacture of hydrogen, a low area catalyst operating at high temperature is most suitable. For maximum production of methane however, a high area catalyst active at lower temperature is preferable. Elevated pressure and temperature are employed. Recently (1971), with the critical shortage of gas in the U.S., six plants have been announced for naphtha gasification in the U.S. using the British CRG Process.

The relationship between catalytic formulation and catalytic performance is crucial (16). The main causes of catalyst failure are sintering, with resultant loss of active area, and fouling by the deposition of coke. First of all, it is necessary to keep the (CO)/(CO₂) ratio low enough to prevent the reaction $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ from occurring. More important it is necessary to catalyze the oxidation of carbon with steam ($\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$). It has been found possible to operate at a lower steam ratio (defined as moles of steam per carbon atom in the feed) with a supported nickel catalyst, using a basic support.

The influence of supports on carbon-forming tendencies has been tested (17), and the results are expressed as minimum steam ratio to prevent coking. For china clay support it is about 10, for alumina about 4.3, and for magnesia 3.7, under one set of conditions. From these results it was deduced that the greater the acidity of the support, the greater the ease of carbon formation. This consistent with the fact that silica-alumina is a good cracking catalyst.

Urania and alumina have been used as supports for nickel-containing steam-reforming catalysts (17). It has been reported that urania is more active in promoting steam cracking than gamma-alumina, because it is an oxygen-deficient compound.

In order to operate at an even lower steam ratio, a further catalytic species must be incorporated which catalyzes the steam oxidation of carbon. (16, 18). This becomes more important as the molecular size of the hydrocarbon charge increases, since larger molecules crack and form polymers more rapidly. The steam-carbon reaction rate must exceed the rate of hydrocarbon cracking and carbon deposition. The group I alkalis fulfill this function without excessively poisoning the reforming activity of the nickel.

Probably the success of alkalinized nickel-reforming catalysts is due primarily to their ability to increase the rate of removal of carbon residues from the nickel surface by steam gasification ($\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$).

The available evidence suggests that the mobility of alkalis on the catalyst surface accounts for their effectiveness in catalyzing the steam-carbon reaction. The mobility of the alkalis has several other effects, including some loss in activity of the nickel, neutralization of acid catalyst sites, and physical loss of alkali. Incorporation of a non-volatile alkali-containing constituent has been reported which, during the operation of the reformer, very slowly decomposes, liberating alkali (15).

Although the excellent catalytic work on steam-reforming catalysis is of great interest for reforming naphtha, the ideas and findings should also be applicable in future development of catalysts for solid and residual fuels gasification. Here, also, the incorporation of alkali substances can become of greatest importance.

Coal Liquefaction Catalysis

Coal liquefaction has assumed a new importance in its potential for manufacture of a clean-burning fuel for powerplants. There is a great need for a low-sulfur, low-ash synthetic fuel to satisfy environmental requirements. The rapidly escalating prices of such a fuel now make coal liquefaction attractive for this purpose.

As is well known, coal liquefaction has already been demonstrated in the remarkable German achievement of providing synthetic fuels from coal during World War II. Iron or tin catalysts were used successfully to hydrogenate coal to liquid form. Since that time, great improvements have been made by the petroleum industry in providing catalysts such as platinum alumina and cobalt-molybdena-alumina capable of upgrading crude oils. These catalysts will contribute greatly in converting low-quality tar from coal into high-quality petroleum products including gasoline.

A number of new catalytic systems have been reviewed recently (19). These include transition metal complexes, alkali metals, volatile catalysts, hydrogen-donor liquids, reductive alkylation, hydrogen generated by reaction of CO and water, and basic catalysts.

Particular mention should be made of the invention of the ebullated catalyst bed reactor utilized by the H-Coal process. (20) The catalyst brings about coal liquefaction and hydrodesulfurization. A unique feature of this reactor system is the ability to operate a catalyst system continuously with a feed consisting of solids, liquid, and gas. The upward flow of the feed maintains the catalyst in a state of random motion that results in a system of minimum pressure drop, isothermal conditions, and continuous passage of unconverted coal and ash from the reactor. Catalyst can be added to and removed from the reactor during operation.

Another process of considerable promise is known as the PAMCO or solvent refined coal process (21). A mixture of coal and oil is contacted with hydrogen at 1000 psi or more, bringing about coal liquefaction. A tar is produced which can be filtered when hot so as to make a low-ash fuel product. Some desulfurization occurs also, so that by starting with a fairly low sulfur coal such as lignite, a low-sulfur synthetic fuel is obtained. While no catalyst is added, it seems likely that certain elements in the ash are effective in hastening the action of hydrogen.

Recent work at the Bureau of Mines has shown that under similar conditions CO containing gases plus water bring about coal liquefaction even more readily than hydrogen alone (22).

In another approach by the Bureau of Mines (23), it was reported that under conditions of highly turbulent flow of hydrogen, a high-sulfur bituminous coal suspended in coal tar can be hydrodesulfurized by continuous processing through a fixed bed of pelletized cobalt-molybdena-alumina catalyst. High yields of low-sulfur oil were obtained. For example (table IV), using the feed containing 30% coal of 3.4% sulfur suspended in a tar of 0.6% sulfur and process conditions of 200^o psig and 450°C (842°F), the whole liquefied product was 93% of the feed and had 0.4% sulfur. The benzene-soluble fraction of this product gave an 87% yield of fuel oil having only 0.14% sulfur.

	OPERATING	PRESSURE
	psi	
	4000	2000
Sulfur in Feed - wt. pct.	1.41	1.41
Sulfur in Whole Product - wt. pct.	0.30	0.42
Yield of Whole Product - wt. pct. feed	94.0	92.9
Oil (Hexane + Benzene Sol) - wt. pct. product	91.2	87.1
Sulfur in Oil - wt. pct.	0.09	0.14
Residue (Ash + Organic) - wt. pct. product	8.8	12.9
Sulfur in Residue - wt. pct.	2.91	1.88
Product, wt. pct.		
Hexane Sol	82.1	69.2
Benzene Sol, Hexane insol.	9.1	17.9
Benzene Insol. Residue	8.8	12.9

Table IV. Hydrodesulfurization of Indiana No. 5 Steam Coal Suspended in Tar (30:70 Coal: Tar) at 450°C Over Co-Mo-Al₂O₃ Catalyst.

Special catalyst and process techniques are needed because of the unusual chemical nature of coal, which contains fairly large molecules containing clusters of aromatic nuclei, and relatively high quantities of heteroatoms, and because of the presence of ash.

Such catalysts should have a pore size distribution so that large coal molecules enter freely, but ash, consisting of fine clay particles, is excluded. Catalysts are needed that are capable of breaking up the nuclear clusters, and that have a high ratio of hydrogenation/cracking functions so as to minimize hydrogen consumption. Maintenance of activity is most important. Possibly entirely novel chemistry is needed; for example, alkylation, which is now known to cause solubilization, presumably by bringing irregularities to the coal structure.

In summary, catalytic coal liquefaction, although having an outstanding history, presents a tremendous field for future catalytic developments using modern technology (24).

REFERENCES

1. Morton, Rogers C. B. Statement before Committee on Interior and Insular Affairs, U.S. Senate, (SR 45), June 15, 1971.
2. Mills, G. A., Perry, H., and Johnson, H. R. Environmental Science and Technology, 5, No. 1, 30 (1971).
3. Wright, M. A. Statement before the Governors Conference, 1971.
4. Mills, G. A. Environmental Science and Technology, 5, No. 12, 1178, 1971.
5. Forney, A. J., Gasior, S. J., Haynes, W. P., and Katell, S. U.S. Bureau of Mines, Technical Progress Report 24, 1970.
6. Forney, A. J., Katell, S., and Crentz, W. L. Proceedings American Power Conference, 32, 428, 1970.
7. Mills, G. A. Proceedings 3rd Synthetic Pipeline Gas Symposium, p. 57, 1970.
8. Haynes, W. P., Neilson, H., and Field, J. H. Presented Petroleum Division American Chemical Society, Los Angeles, 1971.
9. Newlin, W. B. S., and Rich, J. Shift Conversion at Near Atmospheric Pressure. Res. Communication GC 120 British Gas Council, 1965.
10. Moe, J. M. Preprints, Div. Pet. Chem., Am. Chem. Soc., Sept. 1963.
11. Auer, W., Lorenz, E., and Grundler, K. H. Pres. 68th Nat. Meet. A.I.Ch.E., Houston, 1971.
12. Greyson, M. Ch. 6, vol. 4, Catalysis Ed., Emmett, P. H., Reinhold, New York, 1956.
13. Field, J. H., and Forney, A. J. Proceedings Synthetic Pipeline Gas Symposium, p. 83 1966.
14. Forney, A. J., and Haynes, W. P. The Synthane Coal-to-Gas Process: A Progress Report. Preprints Division Fuel Chem., Am. Chem. Soc., Sept. 1971.
15. Davies, H. S., Lacey, J. A., and Thompson, B. H. Processes for the Manufacture of Natural-Gas Substitutes Res. Communication G.C. 155, British Gas Council, 1968.
16. Andrew, S. P. S. I & E Chem., Product R&D, 8, No. 3, 321, 1969.
17. Bhatta, K. S. M., and Dixon, G. M. I & E Chem., Product R&D, 8, No. 3, 324, 1969.
18. Fox, J. M. and Yarze, J. C. Preprints, Div. Pet. Chem., Am. Chem. Soc., Sept. 1963.
19. Mills, G. A. Ind. Eng. Chem., 61, No. 76, 1969.
20. Johnson, C. A., Hellwig, K. C., Johanson, E. S., Stotler, N. H., Chervenak, M. C., and Layng, E.T. 8th World Petroleum Congress, Moscow, 1971.
21. Brant, V. L., and Schmid, B. K. Chem. Eng. Progress, 65, No. 12, 55, 1969.
22. Appell, H., and Wender, I. Preprints, Div. Fuel Chem., Am. Chem. Soc., Sept. 1968.

23. Akhtar, S., Friedman, S., and Yavorsky, P. M. U.S. Bureau of Mines, Tech. Prog. Rept. 35, 1971.
24. Hill, G. R. Coal's New Roles, Div. Fuel Chem., Am. Chem. Soc., Washington, D. C., 1971.

Reference to trade names is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.