FUTURE AVAILABILITY OF CATALYST METALS FOR SYNFUEL PROCESSES. FINAL REPORT

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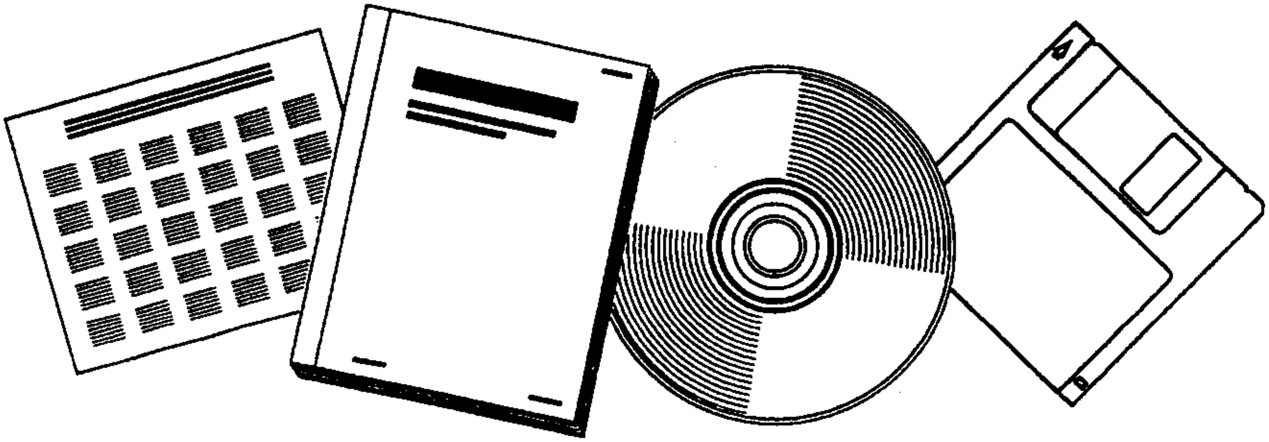

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FUTURE AVAILABILITY OF CATALYST METALS FOR SYNFUEL PROCESSES

by

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FINAL REPORT

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PREFACE

This is the final report covering work performed under Contract No. DE-AC01-81-ER30015 with the U.S. Department of Energy. The program consisted of an evaluation of potential catalyst metal usage in a synthetic fuel industry to form a basis for comparing potential metal consumption with metal supply or availability.

The principal investigator was Dr. Shuji Mori, who was assisted by Dr. A. D. McElroy. Dr. Justin Beeson provided technical and administrative supervision for the program.

Approved:

MIDWEST RESEARCH INSTITUTE

D E Fiscus

for K. P. Ananth, Director
Energy and Materials Science
Department

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TABLE OF CONTENTS

I. SUMMARY

This report describes the investigation of the future availability of catalyst metals for the manufacture of synthetic fuels from coal, oil shale, and tar sands. The commercialization of various processes for producing synthetic fuels in terms of their impact on the consumption of catalyst materials was investigated, using a standard 50,000-BPD plant or a 300 million-SCFD substitute natural gas (SNG) plant as a basis for comparison. These results were then scaled up to national replacement levels of 6 million BPD synthetic crude oil and 10 billion SCFD of SNG. These figures would correspond to a 40% replacement of petroleum and a 20% replacement of natural gas at current consumption rates.

In a thorough review of the literature, the major processes for producing synthetic crude oil from coal by direct and indirect liquefaction were analyzed for catalyst type and usage. Six direct and three indirect processes were included in the study in addition to three processes for manufacturing SNG and three upgrading technologies for upgrading shale oil.

In the study, processes for making synthetic crude oil were considered as producing feedstocks for further processing in an infrastructure of conventional petroleum refining equipment.

The major catalyst metals required for a synthetic fuels industry would include cobalt, molybdenum, nickel, iron, chromium, and tungsten, with minor amounts of the platinum and rare earth group metals. Certain options were found to be at least technically feasible; molybdenum alone can be used to catalyze the direct liquefaction of coal, and an alloy of iron and titanium can be used as a methanation catalyst to replace nickel. Indirect liquefaction processes such as the Sasol technology (Fischer-Tropsch synthesis) or the Mobil MTG (methanol to gas) process need not employ critical metals as catalysts, although some Fischer-Tropsch catalysts are promoted with critical or precious metals.

In the primary upgrading of heavy oils, tar sands, and shale oil, catalyst is lost through the deposition of heavy metals on the catalyst, causing it to become deactivated. There are processes and techniques that can be used to reduce this loss; for example, the heavy metals can be removed with coke in a coking step, or antimony compounds can be added to the feed to passivate the heavy metals, preventing the metallization of the catalyst. Another process, Demet III, can be used to selectively remove deposits of heavy metal from catalysts with good restoration of reactivity and selectivity.

Of the processes studied, the indirect liquefaction and gasification (SNG) processes would have the least impact on critical metal supply because these processes can be operated with catalysts which do not contain critical metals. In current practice, only precious metals are reclaimed from waste catalyst. The development of a catalyst metal reclamation technology would, however, provide a wider choice of catalysts, particularly those containing precious or critical metals as promoters. The effects of a reclamation technology would be expected to be technically favorable and would lead to more efficient processes and equipment, but the development of such a technology would be subject to economic incentives.

II. INTRODUCTION

The current efforts to reduce or eliminate U.S. dependence on imported fuels through the commercialization of processes for manufacturing synthetic or substitute fuels from coal, oil shale, and tar sands have generated the potential for a large increase in the use of catalyst materials. The investigation described in this report explored the effect of such a synthetic fuels industry, as well as the use of alternative catalysts based on noncritical metals.

The study methodology included reviewing the literature on synthetic fuels and tabulating the catalytic aspects of the major synthetic fuel processes which could be commercialized. The reported catalyst usage for each process was then used to prepare estimates of usage for a 50,000-BPD plant or a 300 million-SCFD plant for substitute natural gas (SNG). The procedure for estimating catalyst metal consumption for a 50,000-BPD plant is shown in Appendix B. The potential catalyst usage was then translated to national replacement levels of 6 million BPD for plants producing synthetic crude oil and 10 billion SCFD for plants producing SNG. These catalyst usage levels are shown in Appendix C for fuel replacement by a single process, i.e., 6 million BPD synthetic crude oil produced by the H-coal process or 10 billion SCFD SNG from the Exxon catalytic coal gasification (CCG) process.

Catalyst usage reported here is on a "once through" basis without reclamation or recycle and does not reflect the use of alternative catalysts. The direct coal liquefaction, tar sands, and heavy oil processes have been considered within the context of providing synthetic crude oil feedstock for use in a conventional refinery. Indirect liquefaction plants have been considered within the context of supplying 50,000 BPD of equivalent mixed products.

The catalytic elements in use today are summarized in the periodic table shown in Figure 1 located in Appendix A (all numbered figures will be found in Appendix A). In this study, the term "critical metals" is defined as metals for which import reliance was above 50% in the United States in 1981, and the term "semi-critical metals" represents import reliance between 25 and 50%. The U.S. Bureau of Mines publications[1-6] were consulted for statistical information on metals consumption. Some of these metals, such as cobalt and platinum, are classed as critical elements.[7-17] As will be shown later in this report, the work-horse catalyst metals in a synthetic fuels industry would include cobalt, molybdenum, nickel, tungsten, chromium, and iron. The precious metal catalysts would be used in the infrastructure of petroleum refining, which means that precious metal usage would not be directly coupled to the development of a synthetic fuels industry.

In this report, a brief discussion of the causes of catalyst deactivation is presented followed by detailed exposition of catalyst usage in the various processes for manufacturing synthetic fuels. The processes for the direct liquefaction of coal are considered first, then the indirect liquefaction processes and coal gasification, followed by a discussion of catalyst usage in upgrading shale oil, tar sands, and heavy crude oils. After a brief consideration of the current commercial catalyst market, the use of alternate catalysts is discussed, followed by a section of concluding remarks.

III. POTENTIAL CATALYST DEMAND FOR A SYNFUELS INDUSTRY

In the following section of this report, the major causes of catalyst deactivation are briefly considered, and then the usage of catalytic materials in the major synfuel processes in their present state of development is treated in detail. The direct liquefaction processes are considered first, then the indirect liquefaction processes. After the gasification processes for producing substitute natural gas (SNG), the catalytic aspects of processes for upgrading shale oil, tar sands, and heavy crudes to refinery feedstock are considered.

A. Catalyst Deactivation and Service Life

Oil shale, tar sands, and coal can be converted to hydrocarbon liquids which contain the high levels of heavy metals, nitrogen, and sulfur that are the causes of catalyst deactivation and loss.[18-36] These causes are summarized in Figure 2 for the major processes for manufacturing synthetic fuels.

Shioiri[27] developed a correlation for hydrotreating catalyst consumption based on the vanadium and nickel present in the feedstock, as shown in Figure 3. The figure shows that catalyst replacement increases rapidly with nickel content and to a lesser degree with vanadium content. In operating a water gas shift reactor, small amounts of chlorine have been reported to poison the catalyst. Overall, a synthetic fuel industry is expected to consume more catalyst material than a comparable crude oil industry producing similar products because of the high levels of heavy metals present in the feed streams.

B. Consumption of Designated Catalysts and Metals

Most of the designated catalysts used in the first generation synfuel processes were developed for the petroleum refining industry and are commercially available. To estimate the catalyst metal consumption for a given process, information on the composition of catalyst metal, the space velocity of the feedstock, and the service life of the catalyst is required. In this study, the required information was obtained from literature sources and private communications. In some cases, the needed information was not available because of the proprietary nature of the technology, or a real lack of experimental data; in these instances estimates were based on reasonable practice.

For each process considered in this study, a simplified flow diagram is shown with a brief discussion of the process and catalysts used. Direct coal liquefaction, indirect coal liquefaction,[37-92] coal gasification,[93-159] shale oil processing,[160-186] and heavy oil and tar sands processing[187-200] are considered in turn. In direct liquefaction processes, coal is slurried with a donor solvent/recycle oil; the slurry is processed at high pressure under hydrogen and temperatures of 350° to 450°C. It is generally accepted that hydrogen is transferred to the coal through the recycling solvent vehicle. In some processes, the donor solvent is reactivated by hydrogen in the dissolution reactor; in others, the hydrogen donor solvent is regenerated in a separate step. Direct coal liquefaction catalysts, especially the well-known cobalt-molybdenum catalysts, are combinations of the oxides of cobalt, molybdenum, nickel, and tungsten.

In this study, direct coal liquefaction, shale oil, and tar sand processes are considered as producing synthetic crude oils capable of being processed in conventional petroleum refining processes to obtain finished products. Although a sulfur content of 0.5% or less is adequate for boiler fuel, it is desirable that refinery feedstocks have a nitrogen level of 500 ppm or less. Nitrogen is difficult to remove; as shown in Figure 4, hydrotreating liquified coal with H-coal catalyst will reduce sulfur to very low levels, but with little attendant reduction in nitrogen. Hydrotreating to necessary nitrogen levels converts much of the aromatics content to naphthenes. Upgrading of SRC-I product to refinery feedstock quality, however, requires high severity processing consuming as much as 4,000 SCF/BBL hydrogen and may cause plugging of the catalyst bed.

1. Catalyst demand for H-coal process: The H-coal process (Figure 5) is a direct catalytic hydroliquefaction process developed by Hydrocarbon Research, Inc.[47,59,62,65] The feed coal is slurried with recycle oil; the slurry is then mixed with hydrogen, heated, and fed to an ebulated bed reactor containing a solid phase catalyst. The catalyst phase is maintained in the fluidized state and can be withdrawn or replenished as required during operation of the reactor. Spent catalyst is not recovered at this time; there are no other catalytic reactors in the process train.

The process employs a commercially available hydrotreating catalyst produced by American Cyanamid (HDS-1442 A extrudate) as the designated catalyst. The catalyst use rate, determined by Hydrocarbon Research's experience, is 1.0 lb catalyst per ton of dry coal in both the syncrude and fuel oil modes of operation for either Illinois No. 6 or Wyodak coals as feedstock. This is equivalent to consumption of approximately 0.4 lb of catalyst per barrel of liquid product, as shown in Table 1. This catalyst contains 2.15% cobalt and 8.92% molybdenum by weight, corresponding to 70.5 metric tons of cobalt per year and 292.5 metric tons of molybdenum per year for a 50,000-BPD plant. This consumption rate is compared with consumption rates in the Exxon donor solvent process and the Dow liquefaction process described in Table 2.

The demand for cobalt, molybdenum, and nickel for a petroleum replacement level of 6 million BPD is shown in Figure C-1 of Appendix C for the H-coal, Exxon donor solvent, and Dow processes, using an index of 100 for the consumption of these metals in the United States in 1980.

2. Exxon donor solvent process: A simplified process flow diagram of the Exxon donor solvent (EDS) process[49,67,82] is shown in Figure 6. Feed coal is slurried with recycle oil, and the slurry is preheated and passed through a reactor; the reactor effluent is separated by flash distillation into a light fraction which is then combined with the low vacuum gas oil and hydrogenated in a separate step to obtain the recycle oil needed to operate the process.

TABLE 1

CATALYST METAL DEMAND FOR THE H-COAL PROCESS

	Operating Mode and Feed Coal		
	Syncrude Illinois No. 6	Fuel Oil Illinois No. 6	Syncrude Wyodak
Oil Product Yield (BBL oil/ton dry coal)			
Naphtha	0.86	0.98	1.35
Fuel Oil	1.68	0.80	1.22
Residual Fuel Oil	-	0.72	-
Total	2.54	2.50	2.57
Catalyst Consumption[a] (lb catalyst/BBL oil)	0.934	0.400	0.389
Metal Consumption for 50,000 BPD plant			
Cobalt (metric tons cobalt/yr)	69.4	70.5	68.6
Molybdenum (metric tons molybdenum/yr)	287.9	292.5	284.5

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[a] Catalyst as total material.

The recycle solvent hydrogenation is carried out in a fixed bed reactor packed with conventional petroleum hydrogenation catalysts--either cobalt-molybdenum or nickel-molybdenum. The space velocity, a measure of the solvent rate for the hydrogenation system, is on the order of 1 to 2 lb of recycle solvent per pound of catalyst per hour, which would require a large catalyst inventory in the fixed beds. Based on data in the literature and from private communications, catalyst lifetimes are projected to be 1.5 to 2 years. This corresponds to a catalyst consumption of approximately 0.1 lb/BBL of product, or 830 metric tons per year, for a 50,000-BPD plant. With a nickel-molybdenum catalyst the specific demand for nickel will be about 23 metric tons, and for molybdenum about 85 metric tons annually, as shown in Table 2.

3. Dow liquefaction process: In the Dow process[66] a homogeneous molybdenum catalyst is used which was originally intended to be discarded and not recovered for recycle (Figure 7). The catalyst is introduced as ammonium molybdate in a water-oil slurry in the range from 80 to 1,300 ppm molybdenum. Catalyst demand is about 0.2 lb molybdenum/BBL of product at the preferred level of 100 ppm molybdenum, corresponding to 1,700 metric tons molybdenum per year for a 50,000-BPD plant.

TABLE 2

INCREMENTAL CATALYST METAL DEMAND FOR FIVE DIRECT LIQUEFACTION PROCESSES

Process	Metals of Designated Catalyst	Consumption (g-metal/BBL)[a]	Incremental Demand for 50,000-BPD Plant Syncrude Plant (metric ton/yr)	Alternate Catalyst
H-Coal	Cobalt-Molybdenum	3.86 16.0	70.5 292.5	Nickel-Molybdenum Molybdenum
Exxon Donor Solvent	Nickel-Molybdenum	1.25 4.67	22.8 85.3	Cobalt-Molybdenum
Dow[b]	Molybdenum	95.2	1,738.0	NDA[c]
Bergius-Pier	Iron	3,895.0	71,000.0	NDA
Two-Stage	Nickel-Molybdenum	5.81 26.0	106.0 474.0	Cobalt-Molybdenum Nickel-Tungsten

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[a] As metal element.

[b] Dow process catalyst demand based on 100 ppm molybdenum in coal-oil slurry.

[c] NDA = No data available.

The Dow process molybdenum consumption is about 20 times that of the EDS process, as shown in Table 2.

4. Solvent refined coal process: A flow diagram of the solvent refined coal process[48,51,69] is shown in Figure 8. In operation, coal is slurried with a process-derived recycle oil. The slurry is mixed with hydrogen and passed through the dissolver. The process, which is noncatalytic, can be operated to produce fuels which are either liquid or solid at room temperature.

5. Bergius-Pier process: Since 1927, gasoline from coal has been produced in commercial plants in Germany by the following processes: Bergius-Pier, Pott-Broche, and Fischer-Tropsch synthesis. The Bergius-Pier process,[63] shown in Figure 9, is still under development in Germany. This process, also known as the IG process, has been developed by Ruhkohle/Veba and is financed by the German government. Currently, a pilot plant of 200 TPD capacity is under operation at Bottrop, West Germany. The plant produces 61.3 TPD of gas, 24.4 TPD of naphtha, 69.0 to 74.7 TPD of gas oil, and 68.6 to 74.3 TPD of residual oil. The dissolution reaction is carried out in a recycled vehicle oil under high pressure hydrogen. It employs an expendable Fe_2O_3 catalyst in the ratio of 50 tons of coal per ton of Fe_2O_3 which is impregnated on the coal before it is added to the reactor. The catalyst is subsequently discarded with the ash. The incremental catalyst metal demand for a 50,000-BPD plant was shown in Table 2, and the relative usage figure based on current total U.S. consumption of iron is shown on Figure C-2 of Appendix C.

6. Two-stage coal liquefaction process (C.E. Lummus): The two-stage coal liquefaction process, shown in Figure 10, is being developed by the C.E. Lummus company and the U.S. Department of Energy.[39,43] Coal is slurried with a process-derived recycle solvent, mixed with hydrogen, heated, and passed through a non-catalytic reactor. After separating out the ash and unconverted coal, the liquids are fractionated and the high boiling fraction hydrocracked by the L. C. Fining process. In this process, hydrogen consumption is less than for single stage processes; yields of distillates are also higher than for single stage processes. In experimental results obtained thus far, a nickel-molybdenum catalyst was found to be better than cobalt-molybdenum or nickel-tungsten catalysts. The catalyst demand for a 50,000-BPD plant was shown in Table 2 for a catalyst make-up rate of 1 lb/ton feed coal.

7. Indirect coal liquefaction process: In indirect coal liquefaction the feed coal is first converted to synthesis gas via steam/oxygen gasification. The synthesis gas is then converted to liquid products in catalytic reactors via the Fischer-Tropsch synthesis in a single step,[55,72,76] or to methanol with subsequent conversion to gasoline liquids via the Mobil MTG process.[44,70,75,78,83] Extremely versatile, the Fischer-Tropsch synthesis can be used to make a wide variety of products such as alcohols, aldehydes, and a wide range of paraffinic hydrocarbons. The commercially available catalysts for methanol synthesis are composed of mixtures of copper, zinc, and chromium, and are highly selective.

a. Mobil process: The indirect liquefaction of coal by the Mobil MTG process is shown in Figures 11 and 12. In operation, the coal is first converted to synthesis gas; the synthesis gas is then purified to remove acid gases (H_2S, CO_2), after which it is converted to methanol. The purge gas from the methanol reactor can be converted to methane or recycled to process. The methanol is passed through two catalytic reactors where the conversion to gasoline fraction is carried out; in the first reactor the methanol is converted to dimethyl ether, and in the second, the dimethyl ether is converted to a mixture of olefins, aromatics, and branched paraffins, all in the gasoline boiling range. The catalyst in the second reactor (ZSM-5 zeolite) is proprietary. The catalyst metal consumption for the mobil MTG process is summarized in Table 3.

b. Sasol process: In the Sasol process, shown in Figure 13, feed coal is converted to synthesis gas using Lurgi gasifiers; after purification, the clean synthesis gas is passed through the synthol reactor, shown in Figure 14, which contains a fluidized bed of Fischer-Tropsch catalyst. By changing operating conditions, the spectrum of products can be changed from low molecular weight hydrocarbons to diesel fuels and waxes. The original process, which was invented in Germany in the 1920's, employed cobalt as a catalyst. In subsequent developments, promoted iron catalysts were and still are used. Sapienza* has studied new composite catalysts containing cobalt, platinum, molybdenum, and other metals. Sasol II has been reported to employ a polyphosphoric acid based catalyst, but no information has been obtained about usage. The catalyst consumption of the Sasol process is also shown in Table 3.

The catalyst metal demand for the Mobil MTG and Sasol processes for the production of 6 million BPD crude oil equivalent is shown in Figure C-2 of Appendix C.

8. Coal gasification processes: The production processes for SNG[85-151] can be classified by the various ways the processing of the crude gases downstream from the gasifier is handled. These differences reflect whether the shift and/or methanation catalysts are sulfur resistant,[110] and also whether the water-gas shift and methanation steps are combined.[91,110,122,151,111,135]

Methanation processes employ nickel-based catalysts. The use of these catalysts is constrained by the following operational parameters which limit catalyst lifetime: (1) sulfur levels above 0.5 ppm in the feed gas; (2) carbon deposition on the catalyst at high CO/H_2 ratios and high temperatures by the Boudouard reaction ($2CO = C + CO_2$); (3) sintering and recrystallization at high temperature.[101]

The methanation reaction is strongly exothermic, which makes temperature control difficult. The Haldor Topsoe Company has developed a ceramic-based nickel catalyst[130] which exhibits both high reactivity over a wide temperature range (270° to 700°C)[112] and a service life of 2 years or more for sulfur levels of 0.1 ppm or less in the feed gas.

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* Private communication.

TABLE 3

INCREMENTAL CATALYST METAL DEMAND FOR MOBIL AND SASOL INDIRECT COAL LIQUEFACTION PROCESSES

Process	Reactor	Designated Catalyst Metal	Consumption (g metal/BBL)	Incremental Demand for 50,000-BPD (FOE[a]) Plant (metric tons/yr)
Methanol-to-Gasoline (Mobil)	Shift	Cobalt	1.22	22.0
		Molybdenum	4.87	87.6
	Methanol Synthesis	Copper	0.68	12.4
		Zinc	1.31	23.9
		Chromium	0.24	4.4
	DME	Zeolite	1.5	27.4
	M-Gasoline	ZSM-5 Zeolite	9.8	179.0
Fischer-Tropsch (Sasol I)	Shift	Cobalt	1.22	22.0
		Molybdenum	4.87	87.6
	Fischer-Tropsch	Iron	418.0	7,628.5

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[a] Fuel oil equivalent including hydrocarbon oil and gas products.

Carbon deposition on the catalyst can be reduced by the addition of steam to the methanation feed, but condensed water has been found to deactivate the catalyst. Some efforts to improve catalyst reactivity by adding platinum group metals have been made. In one study, the addition of less than 1% by weight iridium to a nickel catalyst increased reactivity significantly,[111] and this catalyst was found to perform well with 3 ppm H_2S in the feed gases. There have been other efforts to develop sulfur-tolerant methanation catalysts.[6]

Catalysts for the steam shift reaction have been developed along two routes: (1) nickel catalysts promoted with molybdenum, copper, or ruthenium to improve reactivity, for use with sulfur-free feed gases,[135] and sulfur-resistant catalysts using cobalt-molybdenum and nickel-molybdenum.

Sulfur-resistant catalysts have been adapted from hydrotreating catalysts,[5,10] and the performance of such catalysts can be improved by presulfiding. These catalysts are, however, deactivated by ammonia, benzene, and phenol. These catalysts can be partially reactivated, but losses in reactivity are irreversible after a few cycles. Three processes for SNG production (Figure 17) are compared for catalyst metal consumption in Table 4.

a. Separate shift reaction: The Conoco group has designed a commercial plant for manufacture of 241.7 million SCFD SNG (Figure 15).[95,96,97] This process would employ the British Gas/Lurgi slagging gasifier followed by the steam shift reactor, a Rectisol unit for sulfur removal, and then a methanator to produce SNG. The product SNG would be dried and compressed prior to delivery to the distribution system. The shift reactor and the methanator would use commercially available catalysts which require replacement once every 3 years and annually, respectively.

The catalyst compositions were not available, but for this study, the sulfur-tolerant shift catalyst was assumed to contain 3% Co and 12% Mo, and the methanation catalyst 15% Ni. The incremental metal demand is summarized in Table 4, and the consumption of required chemicals is shown in Table 5.

b. Combined shift and methanation process (IGT and others): Considerable process simplification can be obtained by combining the steam shift and methanation reactions into a single reactor. In particular, steam consumption in the shift reactions can be greatly reduced. Attempts to combine the shift and methanation reactions have been reported,[3] as have been the testing of catalysts[111,91,135] for this application. Streeter, who worked with sulfur-free synthesis gas showed that copper-molybdenum-nickel and ruthenium-molybdenum catalysts performed well, with no noticeable deactivation after 30 days' continuous use. In view of its many attractive features, future development of this process is expected. This study used a life of 2 years to estimate usage of ruthenium and nickel metals.

TABLE 4

INCREMENTAL CATALYST METAL DEMAND FOR THREE COAL GASIFICATION PROCESSES

Process	Reactor	Catalyst Metal	Consumption (g metal/6 MSCF[a])	Incremental Metal Demand for 300-MMSCF/D Plant (metric tons/yr)
Separate Shift Reaction	Shift	Cobalt (3%)	1.32	24.1
		Molybdenum (12%)	5.29	96.1
	Methanation	Nickel[b] (15%)	4.90	89.5
Combined Shift/Methanation	Shift/Methanation	Nickel[b] (15%)	1.60	29.2
		Ruthenium (0.5%)	0.05	0.97
Catalytic Gasification (Exxon CCG)	Gasifier	Potassium	8,600[c]	156,900

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[a] 6 MSCF equivalent to 1 BBL oil product heating value.
[b] Assumed.
[c] KOH consumption depends on ash content of coal.

TABLE 5

CONSUMPTION OF CHEMICALS IN THE CONOCO GAS GASIFICATION PROCESS

Chemical	Incremental Demand for 300-MMSCFD Plant (metric tons/yr)
Caustic	493.0
Alum	317.0
Lime	4,434.0
Na_3PO_4	113.0
Soda Ash	15,485.0
Cr Inhibitor	211.0
Zn Inhibitor	63.0
H_3PO_4	35.0

c. Exxon catalytic coal gasification process: Exxon Research and Engineering Company developed the catalytic coal gasification (CCG) process for production of SNG using potassium salts as catalysts (Figure 16). The principal benefits derived from using potassium catalysts are as follows: (1) the rate of gasification is increased; (2) swelling and agglomeration are prevented when handling caking coals; and (3) methanation production is promoted.

According to available information, the catalyst make-up requirement is dependent on the ash content of feed coal,[93,116] as shown in Table 6. The comparison of incremental catalyst metal (potassium) consumption that was in Table 4 is based on Illinois No. 6 coal (9% ash) as the feedstock. The incremental catalyst metal demands for the three processes for coal gasification to produce 10 billion SCFD of SNG are shown in Figure C-3 in Appendix C.

TABLE 6

CHANGE OF CATALYST MAKE-UP REQUIREMENTS WITH ASH CONTENT OF THE FEED COAL FOR 300-MILLION SCFD EXXON CATALYTIC COAL GASIFICATION PROCESS PLANT

Ash Content of Feed Coal (%)	Make-Up Catalyst (Tons KOH equivalent/day)
9.0	680
6.0	320
1.5	120

9. Shale oil upgrading process: Shale oil retorting processes do not employ catalysts, but the syncrude oil product requires upgrading to meet the feedstock quality requirements for further refining. Two categories of upgrading processes for crude shale oil are possible: thermal processing and catalytic processing. Thermal processes include delayed coking, fluid coking, vis-breaking, and thermal cracking, which are well established processes in petroleum refining technology.[86,87] The advantages of thermal processes are their economical operation and ability to eliminate residual material and solid shale material from the liquids. The disadvantages arise from operational difficulties such as corrosion, plugging, and fouling. Catalytic processes can produce products of high and uniform quality, but the capital and operating costs tend to be high. Suspended mineral matter, especially arsenic, in the syncrude oil can cause severe poisoning of the upgrading catalysts.

A group at TRW (Thompson Ramo Woolridge) made an economic study of three integrated schemes for upgrading paraho shale oil.[177] These upgrading processes would also be applicable to retorted western crude shale oil. These process schemes include refining units to produce finished products.

Since this study is intended to provide estimates of catalyst consumption for feedstock for existing refinery plants, consideration of the secondary stages of hydrotreating and hydrocracking catalysts was omitted. The catalyst metal consumptions for shale oil upgrading were estimated by assuming a catalyst cost of $2.00/lb of catalyst for a designated catalyst containing 3% Ni and 12% Mo and an alternate catalyst containing 3% Co and 12% Mo. Higher nitrogen and crudes containing heavy metals respond more readily to a nickel-molybdenum hydrotreating catalyst than to a cobalt-molybdenum catalyst. The three processes are shown in Figure 17. Processes A and C in the figure employ direct first stage hydrotreating, while process B employs a delayed coker with subsequent hydrotreating to produce synthetic crude oil. The incremental catalyst metal consumption for shale oil syncrude upgrading processes of 50,000-BPD capacity with two types of hydrotreating schemes (A and C) using designated nickel-molybdenum catalyst is shown in Table 7; for an alternate cobalt-molybdenum catalyst, in Table 8. High nitrogen content is probably the greatest concern in hydrotreating crude shale oil, and the technology for processing high nitrogen crudes is not well developed.[155] In the current technology, relatively high hydrogen consumption and extensive hydrocracking attend the reduction of the nitrogen level to refinery feedstock requirements.[6]

10. Heavy oil and tar sands processes:[178-196] The amount of heavy oil in the world is thought to equal the amount of lighter crude oil.[193] The purpose of upgrading heavy crude oil is to make a heavy oil into suitable feedstock for existing refineries, and also make it suitable for transport by pipeline. Various processing schemes for upgrading heavy crudes have been considered.[27,178,183,185,190,191] Some typical boiling point curves for heavy oils are shown in Figure 18, which compares shale oil and tar sands with a normal crude oil and H-Coal oil.

A number of processes for upgrading heavy feedstocks are available on an off-the-shelf basis:

TABLE 7

INCREMENTAL CATALYST METAL DEMAND FOR SHALE OIL HYDROTREATING PROCESSES PRODUCING SYNCRUDES

Process	Designated Catalyst	Consumption (g metal/BBL)	Incremental Metal Demand for a 50,000-BPD Syncrude Plant (metric tons/yr)
First Stage Hydrotreating	Nickel	0.35	6.4
	Molybdenum	1.39	25.4
Delayed Coking-Hydrotreating	Nickel	0.16	2.9
	Molybdenum	0.64	11.6

TABLE 8

INCREMENTAL CATALYST METAL DEMAND FOR TWO TYPES OF SHALE OIL HYDROTREATING PROCESSES PRODUCING SYNCRUDE OIL

Process	Catalyst	Consumption (g metal/BBL)	Incremental Metal Demand for 50,000-BPD Plants (metric tons/yr)
First Stage Hydrotreating	Cobalt	0.35	6.4
	Molybdenum	1.39	25.4
Delayed Coking Hydrotreating	Cobalt	0.16	2.9
	Molybdenum	0.64	11.6

Process	Licensor
Flexicoking	Exxon
L. C. Fining	C. E. Lummus
HOD	M. W. Kellogg
H-Oil	Hydrocarbon Research Institute
Resid HDS	Gulf Research
Unicracking/HDS	Union Oil
RCD Unibon	UOP
Aurabon	UOP
Eureka	Kureha Chemical

All of these processes can be used to upgrade tar sands, and they all employ the general features shown in Figure 19. In operation, the heavy feed is first topped and then the bottoms are sent to the primary upgrading step, which is either a coking or a hydrotreating step. Coking is a convenient method for demetallizing the feed, but it may generate unwanted light gases (C_1-C_4); catalyst deactivation by contamination with heavy metals, however, is avoided.

At least one economic study has shown that catalytic primary upgrading is more profitable than coking for feedstocks having an API gravity greater than 25.[190] Most tar sands are heavier than this, so that primary upgrading by coking is expected to be popular. When catalytic primary upgrading is used, guard beds are frequently used to remove heavy metals from the feed and lengthen the service life of the hydrotreatment catalysts.

Catalyst consumption in heavy oil upgrading varies with the metal, sulfur, and nitrogen content of the feedstock; little information on catalyst consumption in the processes named above has appears in the literature. Most Canadian tar sands contain up to 500 ppm heavy metals; if these metals are removed in a coking step, the consumption of downstream hydrotreating catalyst would be slight compared to consumption in a catalytic primary upgrading step. A coking plant can reduce the heavy metal content of a heavy crude to approximate 0.5 ppm.[192] In Figure 3, shown earlier, the variation of catalyst consumption with vanadium and nickel content is shown. From the figure, the catalyst consumption for upgrading the raw feed can be estimated from the nickel and vanadium content of the feed. In a similar fashion, the catalyst consumption for upgrading the products of the coking operation can be estimated; thus, for a heavy metal level of 460 ppm, about 20 lb/BBL catalyst would be required if metal deposition on the catalyst is limited to 2% by weight. Up to 20% by weight heavy metals can be deposited on the catalyst without serious loss in reactivity, so that by allowing the metal to build to 20% by weight, catalyst consumption would be 2 lb/BBL.

These two cases (catalytic primary upgrading and coking) are compared in Table 9 for a cobalt-molybdenum catalyst. In the case of catalytic primary upgrading, the consumption of cobalt and molybdenum would be 19.5 and 50.9 g/BBL, respectively. When the feed is demetallized by coking, the consumption is reduced to 0.7 and 3.0 g/BBL cobalt and molybdenum, more than an order of magnitude change. The metal demand for 50,000-BPD plants using these two processing schemes is also shown on the table.

TABLE 9

INCREMENTAL CATALYST METAL DEMAND FOR TWO TYPES OF HEAVY OILS UPGRADING PROCESSES PRODUCING SYNCRUDE OIL

Process	Catalyst	Consumption (g metal/BBL)	Incremental Metal Demand for 50,000-BPD Plants (metric tons/yr)
Catalytic Primary Upgrading	Cobalt	19.5	355.8
	Molybdenum	80.9	1476.0
Coking Primary Upgrading	Cobalt	0.7	12.8
	Molybdenum	3.0	54.8