FUTURE CATALYST METALS AVAILABILITY AND ASSESSMENT OF WASTE CATALYST RECLAMATION

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INTRODUCTION

A study of catalyst technology for synthetic fuels production has been conducted, in order to develop the basis for projection of potential catalyst metal demands and for examination of options for mitigating adverse impacts upon the supply of strategic or critical metals. The study included direct and indirect coal liquefaction; coal gasification to substituted natural gas (SNG); and shale oil/heavy oil processing.

Options considered for modifying demands for catalyst metals include substitute and improved catalysts. Spent catalyst reclamation processes were also examined.

CRITICAL METALS AND CATALYTIC METALS

United States and world catalyst use is growing in response to increased energy demands and stiff environmental regurations, and is very markedly affected by the trend in petroleum refining towards processing of heavier feedstocks which drastically shortens catalyst life by coke deposition and heavy metal contamination.

Numerous metals are utilized as catalysts; among the 92 natural elements, transition metals are most heavily used. Many of the transition metals are critical or semi-critical metals, based on definition in this study as follows: critical metals-- 50% or greater import reliance; semi-critical-- 25-50% import reliance. U.S. Bureau of Mines statistics[1,2] served as the basis for identifying the critical and semi-critical metals, as shown in Figure 1.

The list of critical metals includes a number of metals, which are now used as catalysts, of these petroleum hydrotreating catalysts are most heavily used. The principal function of hydrotreating catalysts is removal of heteroatoms such as sulfur and nitrogen. Cobalt-molybdenum catalysts are effective and extensively used; other hydrotreating catalysts are nickel-molybdenum, and tungsten-molybdenum.

Catalysts for direct coal liquefaction, shale oil and heavy oil hydroprocessing are adopted from the commercial catalysts used in petroleum refining. Therefore, cobalt, molybdenum, nickel and tungsten will be most heavily used in synthetic fuel production processes.

CATALYTIC METALS DEMANDS BY SYNFUEL PROCESSES

Four general synfuel process types were chosen: direct and indirect coal liquefaction, coal gasification to SNG, shale oil processing, and tar sands or heavy oils processing.

Syncrude oils were assumed to be acceptable quality feedstocks for existing petroleum refining processes. Nitrogen specification (500 ppm or less) for the syncrudes of coal, shale and heavy oils are seldom met by their preliminary processes alone. Additional hydrotreating is accordingly required, but the catalyst metal requirment is small relative to the demands by the main process and was accordingly ignored.

This study of catalytic metal consumption from selected synfuel processes were based on a 50,000 BPD syncrude plant, or a 300 million SCFPD SNG production plant. To estimate the catalyst metal consumption of each process, three kinds of information have to be given, namely, catalyst metal composition, space velocity of feedstock, and the catalyst lifetime. In spite of substantial literature on synfuel processes, firm information and data on catalysts were quite limited due to the proprietary nature of the technology and the uncertainties of a developing technology including particularly limited duration test. Therefore, some results were best-estimated from available information and from industry contacts. The incremental catalyst metal demands for various 50,000 BPD coal liquefaction plants, typical process types for 300 million SCFPD SNG coal gasification plants, and 50,000 BPD shale oil hydrotreating plants are shown in Table 1, 2, and 3, respectively.

Catalyst consumption by tar-sands or heavy oils depends highly on dissolved heavy metals concentration in the primary hydrotreating unit for heavy resid or bottom cuts, where most catalyst-contaminating metals tend to concentrate. Employment of a coking process, as well as a demetallization unit such as guard bed, Demet III, or Antimony Passivation processes would drastically reduce the catalyst-contaminant metal concentration from 500 ppm to a few ppm level for some heavy oils. Major catalyst deactivation metals are nickel, vanadium, iron and arsenic for some tar sands bitumen. Shioiri[3] developed a correlation for hydrotreating catalyst consumption based on the vanadium and nickel present in the feedstock, shown in Figure 2. It can be seen that catalyst replacement increases rapidly with vanadium content and to a lesser degree with nickel content.

The major catalytic metals which would be used in the manufacture of synthetic fuels have been identified as cobalt, molybdenum, iron, nickel, chromium, and tungsten with minor amounts from the platinum and rare earth groups. It is technically possible to operate a synthetic fuels industry without critical materials through the use of alternative catalysts, such as molybdenum[4] for coal liquefaction, and iron-titanium or cerium-molybdenum[5] for methanation, instead of cobalt-molybdenum, and nickel, respectively. A second thrust in catalyst development of potential impact on metal consumption is directed at longer service life as well as higher reactivity of catalysts[6].

WASTE CATALYST METAL RECLAMATION

Several categories of technologies are available for the reclamation of waste catalysts. Among those, methods by wet-chemistry are typical and the schematic diagrams are shown for recovering cobalt, molybdenum and platinum in Figure 3. In recovering cobalt and molybdenum, the cobalt is converted to cobalt sulfate while the molybdenum is recovered as molybdate compounds. For platinum on alumina, it can be recovered either by dissolving platinum or alumina to separate components.

With the exception of precious metals, reclamation of metals from catalysts is not generally practiced. Current reclamation is carried out by companies specializing in the technology, so that some reclamated metals are not recycled into catalysts, but reenter the metals market in a nonspecific way. With increased consumption, demand for reclamation technology would be expected to increase, but would materialize only with adequate economic incentives.

CONCLUSION AND RECOMMENDATIONS

The main conclusions and recommendations can be summarized as follows:

1. The catalytic metals which would be used in the manufacture of synthetic fuels have been identified as cobalt, molybdenum, iron, nickel, chromium, and tungsten with minor amounts from the platinum and rare-earth groups.

2. Metals consumption in the designated catalysts for commercialized direct coal liquefaction and heavy oil synfuel

processes would exert substantial impacts on the metal markets for cobalt, nickel, and molybdenum.

3. Molybdenum, iron and other non-critical metals are potential replacements for the more critical metals, particularly cobalt and nickel.

4. However, the greatest impact on metals consumption in the catalyst industry will come via catalyst reclamation. The reclamation technology is available, though not generally tailored and developed for spent catalyst processing.

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TABLE 1

COMPARISON OF INCREMENTAL CATALYST METAL DIMAND FOR VARIOUS 50,000 BPD COAL LIQUEFACTION PLANTS

Process	Reactor	Designated Catalyst	Metal Consumption (gr-metal/BBL)*	Incremental Demand For a 50,000 BPD Syncrude Plant (metric ton/yr)
H-Coal		Cobalt	3.86	70.5
		Molybdenum	16.0	292.5
EDS		Nickel	1.25	22.8
		Molybdenum	4.67	85.3
DOW**		Molybdenum	95.2	1,738.
SRC		-	-	-
Two-Stage		Nickel		
		Molybdenum	5.81	106.
			26.0	474.
Bergius-Pier		Iron	3,890.	71,000.
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-Zeolite	9.8	179.0
Fischer-Tropsch (Sasol-I)***	Shift	Cobalt	1.22	22.0
		Molybdenum	4.87	87.6
	F-T	Iron	418.	7,628.

* As metal element.
** Dow process catalyst demand based on 100 ppm molybdenum in coal-slurry.
*** FOE: fuel oil equivalent including hydrocarbon oil and gas products.

TABLE 2

COMPARISON OF INCREMENTAL CATALYST METAL DEMAND FOR VARIOUS 300 MMSCFD COAL GASIFICATION PLANTS

Process	Reactor	Catalyst Metal*	Metal Consumption (gr-metal/6MSCF)**	Incremental Demand for a 300 MMSCFD SNG Plant (metric ton/yr)
Generic Type Gasification	Shift	Cobalt(3%)	1.32	24.1
		Molybdenum(12%)	5.29	96.1
	Methanation	Nickel(15%)	4.90	89.5
Combined Shift/ Methanation	Shift/ Methanation	Nickel(15%)	1.60	29.2
		Ruthenium(.5%)	0.05	0.97
Catalytic Gasification (Exxon CCG)	Gasifier	Potassium	8,600.***	156,900.

* Metal content assumed as ().
** 6MSCF equivalent to 1 BBL oil product heating value.
*** KOH consumption depends on ash content of coal.

TABLE 3

COMPARISON OF INCREMENTAL CATALYST DEMAND FOR 50,000 BPD SHALE OIL HYDROTREATING PLANTS

Process	Designated Catalyst	Metal Consumption (gr-metal/BBL)*	Incremental Demand For a 50,000 BPD Syncrude Plants (metric ton/yr)
Preliminary 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

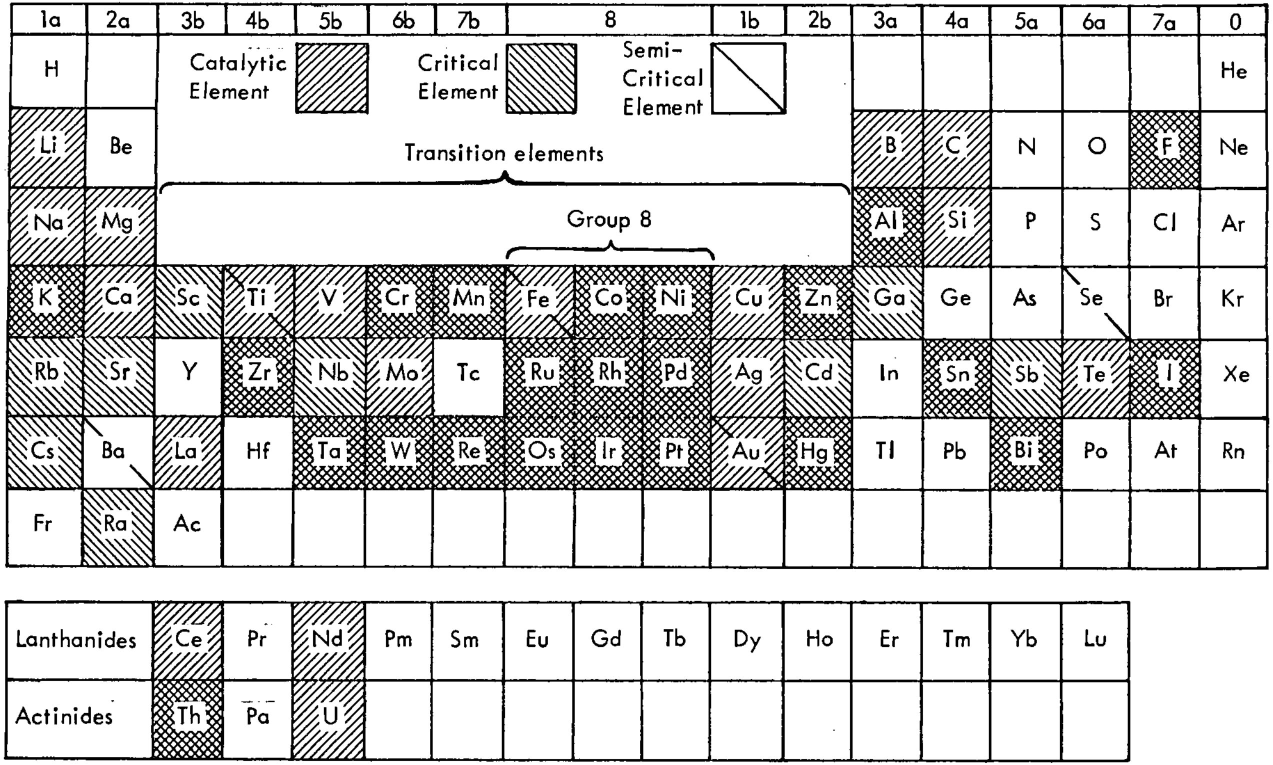

Figure 1. Periodic Table for Critical and Catalytic Elements

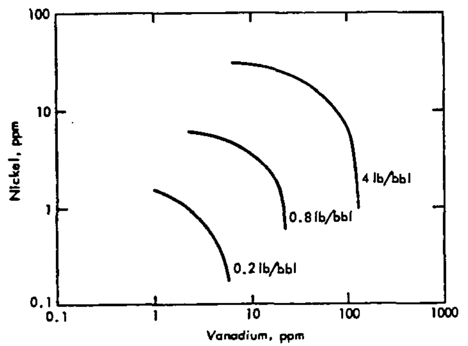

Figure 2. Catalyst Replacement Rate for Heavy Oils Hydrotreating by Metal Consumption in Feedstock (Metal Concentration Level on Catalyst 2%).

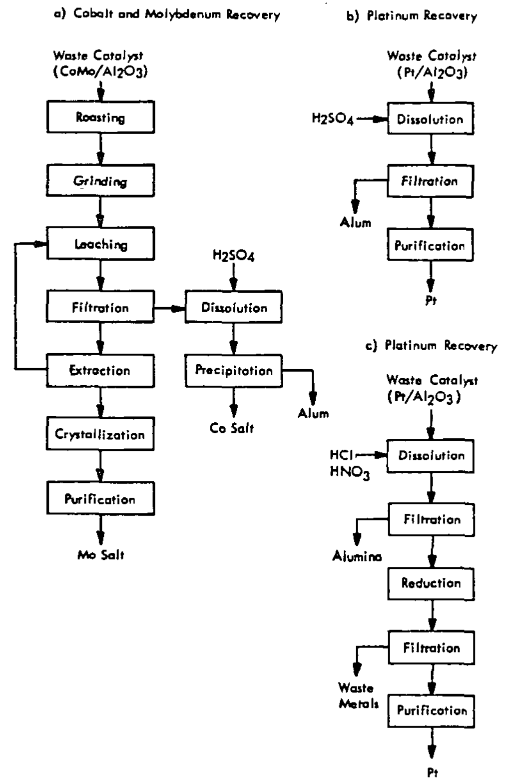

Figure 3. Typical Waste Catalyst Metals Recovery Schemes by Wet-chemistry.