DEACTIVATION OF CO-MO CATALYST DURING H-COAL® OPERATIONS

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The H-Coal® Process has been under development for over ten years and has been supported by government and industry. Work has been carried out on bench-scale units handling about 25 pounds of coal per day and in a Process Development Unit (PDU) handling 3 tons per day. Some fourteen coals, including bituminous, subbituminous, lignite and brown coal have been tested without difficulty.

In the H-Coal Process, coal is dried, pulverized, and slurried with coal-derived oil for charging to the coal hydrogenation unit. The heart of the process is the unique reactor design shown in Figure 1. The coal-oil slurry is charged continuously with hydrogen to a reactor containing a bed of ebullated catalyst wherein the coal is catalytically hydrogenated and converted to liquid and gaseous products. In the ebullated bed the upward passage of the solid, liquid, and gaseous materials maintains the catalyst in a fluidized state. The relative size of the catalyst and coal is such that only the unconverted coal, ash, liquid and gaseous products leave the reactor while the catalyst remains therein. Catalyst can be added and withdrawn continuously so a constant activity can be maintained. The reactor provides a simple means of controlling reactor temperature and an effective contact between the reacting species and the catalyst, permitting a satisfactory degree of reaction at reasonable operating pressure. The liquid product from the reactor is a synthetic crude oil which can be converted to gasoline and furnace oil by conventional refining processes. Alternately, under milder operating conditions, a clean fuel gas and low sulfur fuel oils may be produced. The relative amounts of these products depend on the desired sulfur level in the heavy fuel oil.

In September 1974, Hydrocarbon Research, Inc. received an 8.1 million dollar first phase contract to design a nominal 600 ton per day pilot plant to demonstrate the H-Coal Process. The contract is jointly funded two thirds by Government and one third by industry. At the present time two oil companies and Electric Power Research Institute are the industry representatives.

The proposed pilot plant will be located at Catlettsburg, Kentucky, adjacent to the Ashland Oil Refinery. It is designed for two modes of operation, (1) to process 633 tons of coal per day to produce 1,920 barrels of fuel oil with less than 0.7 W % sulfur from coal

containing more than 3 W % sulfur (fuel oil mode), or (2) to process 210 tons of coal per day to produce 740 barrels per day of synthetic crude (syncrude mode). The design basis for the fuel oil mode of operation is based on bench-scale experimentation. The current laboratory program has been directed towards confirming in the PDU the design basis for the pilot plant.

H-COAL CATALYST

The H-Coal Process uses a commercial Co-Mo catalyst developed originally for desulfurizing the petroleum residua. The Co-Mo catalyst selectively hydrocracks the carbon-sulfur bonds to release the sulfur as hydrogen sulfide and to terminate the carbon bond by hydrogenolysis without cracking of the carbon-carbon bond. Bituminous coal and subbituminous coal are characterized by the fact that they are mainly composed of condensed aromatic rings and oxygen-containing functional groups: -COOH, $-OCH_3$ -OH, and "$>$C=O". These first three functional groups are all terminal groups, but the so-called "carbonyl group" ("$>$C=O") exists as an oxygen bridge linking the condensed aromatic rings together. Efficient coal liquefaction with minimum hydrogen consumption can be achieved if the "$>$C=O" linkage is selectively hydrocracked. Since the organic functional groups containing oxygen or sulfur behave similarly, the use of Co-Mo catalyst for coal liquefaction and desulfurization has given reasonably good performance.

HRI has accumulated nearly 50,000 hours of process evaluation and optimization in bench scale and process development units. While the H-Coal Process development is in an advance stage in most respects, catalyst evaluation and development has not kept pace with overall program progress. A proposal for improving the current Co-Mo catalyst has been submitted to the Energy Research and Development Administration. It is anticipated that an approval from ERDA will be received soon.

CATALYST DEACTIVATION

Critical examination of available analytical data on fresh and used catalysts has disclosed that three common causes for catalyst deactivation, namely, carbon deposition, sintering, and metal deposition contributed to the deactivation of the Co-Mo catalyst. Their relative detrimental effects on the catalyst vary with the rank of coal being processed and the processing conditions.

Catalyst deactivation curves in terms of hydrogen consumption and sulfur content of fuel oil are presented in Figures 1 & 2. These curves were derived from HRI's recent PDU operation with Illinois No. 6 coal from Burning Star Mine and were included in a paper presented at the 68th AICHE Meeting, November, 1975.[1] The deactivation curves are characterized by a steep initial deactivation followed by a gradual decline. The shape of the curve is typical of most catalyst deactivation curves.

A discussion is given below with respect to the magnitude of carbon deposition, sintering, and metal deposition on the Co-Mo catalyst and the relative importance of these three factors in contributing to catalyst deactivation.

CARBON DEPOSITION

The used catalysts contained 10 to 35% carbon. In operations in the normal range of conditions the used catalyst contained 10 to 20% carbon. No consistent trend has been observed between the magnitude of carbon deposition on catalyst and the rank of coal feed. Although the lower rank coals (e.g. Wyodak Coal) and lignites tend toward the lower end of the range, while higher rank coals (e.g. Pittsburgh Seam Coal) tend toward the higher end of this range. For purposes of illustration, Table 1 summarizes the carbon content of used catalyst from a number of bench unit experiments on Pittsburgh Seam Coal. The extent of carbon deposition reaches a certain level within a few days time and does not increase with further operations. Low pressure operations at 800 psi hydrogen pressure or lower invariably yielded carbon deposition of over 22% on used catalyst. Experiments carried out with catalyst after regeneration indicate that carbon deposition contributes significantly to initial catalyst deactivation.

Table 1

CARBON CONTENT OF USED CATALYSTS

Coal Feed	--------- Pittsburgh Seam ----------				
Coal Processed, Lb.	760	102	805	2246	2602
Catalyst Age, Hours	503	59	463	1474	263
Hydrogen Partial Pressure, psig	800	----------1800----------			
Used Catalyst, % C	26.5	19.0	13.6	20.7	20.0

SINTERING

The Co-Mo catalysts used in the majority of experiments are supported on gamma alumina. Gamma alumina is thermally unstable, particularly in the presence of steam. Literature data are available on the effect of steam on sintering of alumina. For the purpose of illustration, the effect of temperature and steam on the sintering of a nickel on gamma alumina catalyst[2] is shown in Figure 4. The presence of steam not only causes an initial drop in surface area during the first sixty hours but also enhances the long term slow rate of decline.

An examination of the available analytical data on fresh, used, and regenerated catalysts indicates that catalyst sintering occurred after an extended run of thirty days using Illinois No. 6 coal wherein the $H_2O : H_2$ in the reactor outlet gas is about 1 : 8. An eleven day operation under similar conditions did not cause any noticeable sintering of catalyst. Sintering was quite pronounced after a forty nine day operation using partially dried coal containing 20% moisture, resulting in a $H_2O : H_2$ ratio of 1 : 2 in reactor outlet gas. Catalyst sintering could be the cause for the observed high deactivation rate of the wet Wyodak coal operation in comparison to a similar experiment using more completely dried Wyodak coal containing only 2% moisture.

METAL DEPOSITION

Some typical analysis of coal ash composition and major catalyst contaminants are shown in Tables 2 and 3. Table 4 presents a semi-quantitative analysis of a typical used catalyst by emission spectrometry. The relative level of metal contaminants on the catalyst was not in the ratio characteristic of the ash composition of the coal. Metal contaminants act as a physical barrier between the reactants and active sites of the catalyst. When any metal contaminant increases with catalyst age, it usually is the prime factor in causing catalyst deactivation. The common metal contaminants on the used catalyst are titanium, iron, calcium and sodium. Bituminous coal, such as Pittsburgh Seam and Illinois No. 6, deposits appreciable amounts of titanium and low amounts of calcium and sodium; subbituminous coal, such as Wyodak, usually deposits higher amounts of sodium and similar amounts of calcium in comparison to the bituminous coal. The range of iron deposition is similar from various ranks of coal.

Table 2

COMPOSITION OF COAL ASH

Coal	Wyodak	Illinois No. 6
Ash, W %	9.73	9.95
Composition of Ash, W %		
Phosphorus Pentoxide	0.61	0.06
Silica	33.64	45.74
Ferric Oxide	3.80	16.18
Alumina	17.08	18.95
Titania	1.16	0.95
Calcium Oxide	18.50	9.50
Magnesium Oxide	4.70	0.94
Sulfur Trioxide	18.04	4.52
Potassium Oxide	0.71	1.79
Sodium Oxide	0.80	0.43
Undetermined	0.95	0.94

Table 3

CONTAMINANTS ON USED CATALYSTS

Coal Feed	Wyodak	Illinois No. 6
Catalyst Age, lb. Coal/lb. Catalyst	781	2644
Oil-Free Catalyst, Analyses, W %		
Carbon	13.67	10.9
Sulfur	5.13	4.6
Iron	1.73	1.5
Titanium	0.03	5.11
Sodium	1.46	0.42
Calcium	1.04	0.24

Table 4

EMISSION SPECTROMETRY ANALYSIS OF A TYPICAL USED CATALYST

Analysis of Oil-Free (Benzene-Extracted) +20 Mesh Extrudates

Element	Approximate W % Metal
Aluminum	10
Antimony	0.02
Arsenic	0.2
Barium	Not detected
Beryllium	0.01
Boron	0.7
Calcium	0.3
Chromium	0.05
Cobalt	1
Copper	<0.01
Gallium	0.05
Germanium	0.3
Iron	1
Lead	0.01
Magnesium	0.2
Manganese	0.08
Molybdenum	5
Niobium	~0.01
Nickel	0.3
Silicon	0.2
Titanium	3
Vanadium	0.2
Zinc	0.1
Zirconium	0.05

It is observed that among the metal contaminants identified so far, titanium deposition from the bituminous coal increased with catalyst age. Recent analyses of benzene-insoluble and benzene-soluble components of the residua derived from Illinois No. 6 coal show that the benzene-insoluble portion of the residuum contains about the same amount of titanium as present in the M.A.F. coal, 900 ppm, and the benzene-soluble portion of the residuum contains only about 5% of the titanium as present in the coal. Thus it is quite logical to deduce from these data that titanium exists in a form of organometallic complex in the bituminous coal. This deduction is further supported by the knowledge that titanium is just below vanadium with respect to the strength of the ligand-metal bonds and stable vanadium prophyrin exists in petroleum. It should be noted that very little titanium was deposited on the catalyst when Wyodak coal was processed, even though Wyodak coal contains about the same amount of titanium as Illinois No. 6 coal. Further work is needed to establish whether the benzene-insoluble residuum from the Wyodak coal contains any significant amount of

titanium. It is also observed that only about one-twentieth of the titanium present in the Illinois No. 6 bituminous coal deposited on the catalyst.

Scanning electron micrograph of spent catalysts showed that titanium penetrated to a depth of approximately 10% of the radius of the 1/16" extrudate, and iron was found in clusters on the surface of the extrudate. The way that titanium deposition concentrates in the periphery of the catalyst extrudate is expected to be more detrimental in reducing the effective diffusion of "coal molecule" into the catalyst pore than if the titanium were distributed uniformly throughout the whole extrudate.

When bituminous coal, such as Illinois No. 6, was processed and was liquified, metal deposition appeared to cause the gradual but steady deactivation of catalyst.

CATALYST ATTRITION

The magnitude of catalyst attrition in the ebullated bed reactor is well defined by the rotating drum attrition test developed by HRI. By applying this test, HRI has successfully chosen a commercial catalyst which showed satisfactory attrition resistance during recent PDU operations. Catalysts recoveries are summarized in Table 5. About 93 W % catalyst (by Mo balance) was recovered after 814 hours operation, processing 2,687 lb. coal/lb. catalyst. The increase in weight of the catalyst was consistently greater than the total weight of the major contaminants determined. These and other data obtained with different coal feeds indicate the possibility of the presence of other major contaminants. Deposition of alumina appears to be another major contaminant as shown by a few analyses comparing the Al to Mo ratio of fresh and used catalyst.

Table 5

CATALYST RECOVERY FROM PDU OPERATIONS

Run	A	B	C	D
Catalyst Age				
Hours	814	535	475	272
Coal Processed, Lb/Lb Catalyst	2687	3061	2451	1509
Catalyst Recovery, W %				
Gross Weight	139.0	140.6	133.8	156.4
Gross Weight less major Contaminants determined	103.5	102.3	100.0	112.2
Molybdenum Balance	92.7	96.8	96.4	97.6

SUMMARY AND CONCLUSIONS

Critical examination of available analytical data on fresh and used catalysts disclosed that three common causes for catalyst deactivation, namely, carbon deposition, sintering, and metal deposition, contributed to the deactivation of the Co-Mo catalyst used in the H-Coal® Process. Their relative deterimental effects on the catalyst vary with the rank of coal being processed and the process conditions.

The used catalyst contained 10 to 35% carbon. The extent of carbon deposition is affected more by process conditions than by either coal feed or catalyst age. Low pressure operations at 1000 psig or lower yielded high carbon deposition of over 22%.

The Co-Mo catalyst is supported on gamma alumina. The pronounced effect of steam on sintering of gamma alumina at temperatures below 1000°F is well known. Operations with subbituminous coal such as Wyodak coal caused much more pronounced catalyst sintering than those using bituminous coal such as Illinois No. 6 coal. The high oxygen and high moisture content of Wyodak coal (in the event of incomplete drying) give rise to a relatively high H_2O/H_2 ratio in the process gas, which caused rapid catalyst deactivation through sintering.

Major metal contaminants found on the catalyst are titanium, iron, calcium, and sodium, and in some cases also aluminum. The magnitude of titanium deposition on catalyst from bituminous coal feed increased with catalyst age. Titanium deposition was concentrated to a depth of approximately 10% of the radius of spent 1/16" extrudate, whereas iron was found in clusters on the extrudate surface.

It is concluded that the initial catalyst deactivation is caused by carbon deposition in the case of bituminous coal. Both carbon deposition and sintering contribute to the initial catalyst deactivation with subbituminous coal feed. Titanium deposition from the bituminous coal causes a gradual decline in catalyst activity.

Commercial Co-Mo catalysts have shown different magnitude of catalyst attrition in the ebullating bed reactor. HRI developed a rotating drum attrition test which defines the attrition resistance of the catalyst under H-Coal processing conditions. HRI successfully chose a commercial catalyst which showed satisfactory attrition resistance during recent extended PDU operations at gas and coal rates at the design values for the pilot plant being built at the present time.

ACKNOWLEDGEMENT

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REFERENCES

(1) Johnson, C. A., Chervenak, M. C., Comolli, A. G., Johanson, E. S., Kang, C. C., and Volk, W., "H-Coal Process Development", 68th AICHE Meeting, November, 1975.

(2) Williams, A., Butler, G. A., and Hammonds, J., "Sintering of Nickel - Alumina Catalysts", J. Catalyst 24, 352, (1972).

EBULLATED BED REACTOR

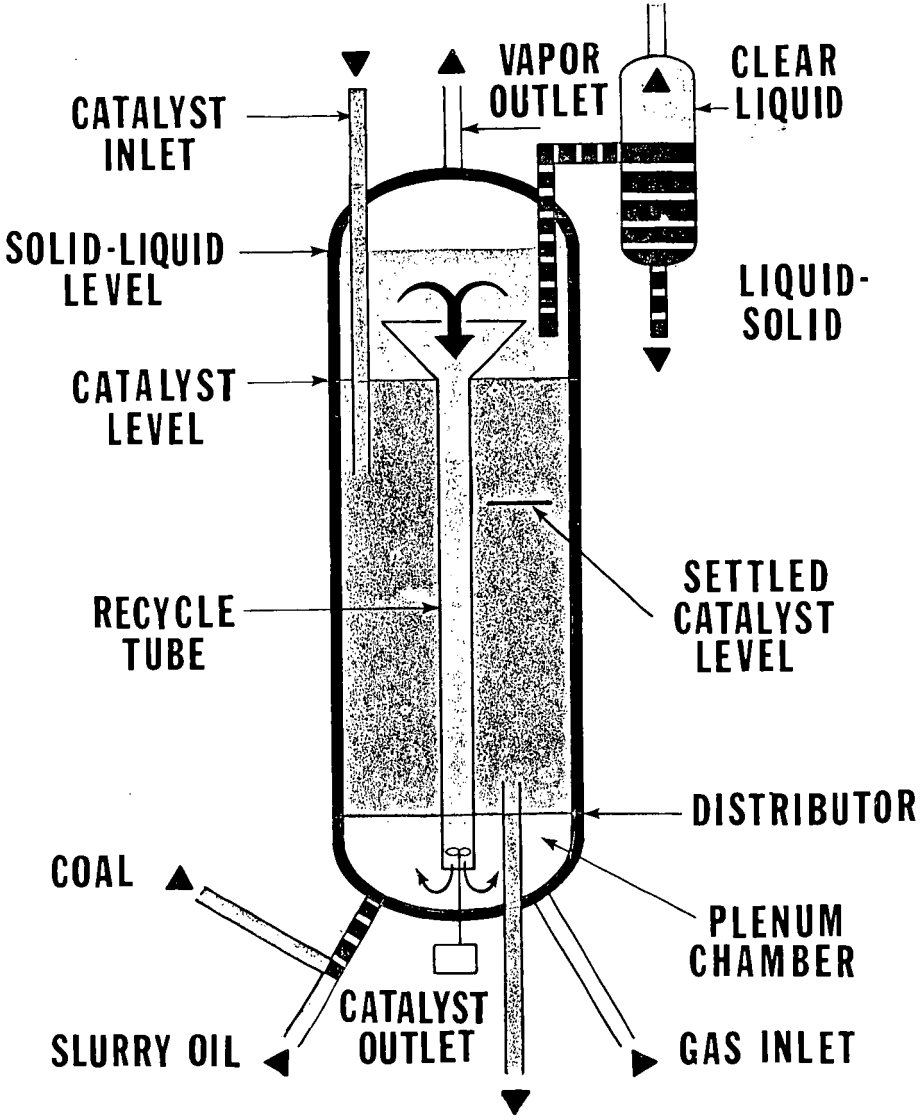


Figure 1

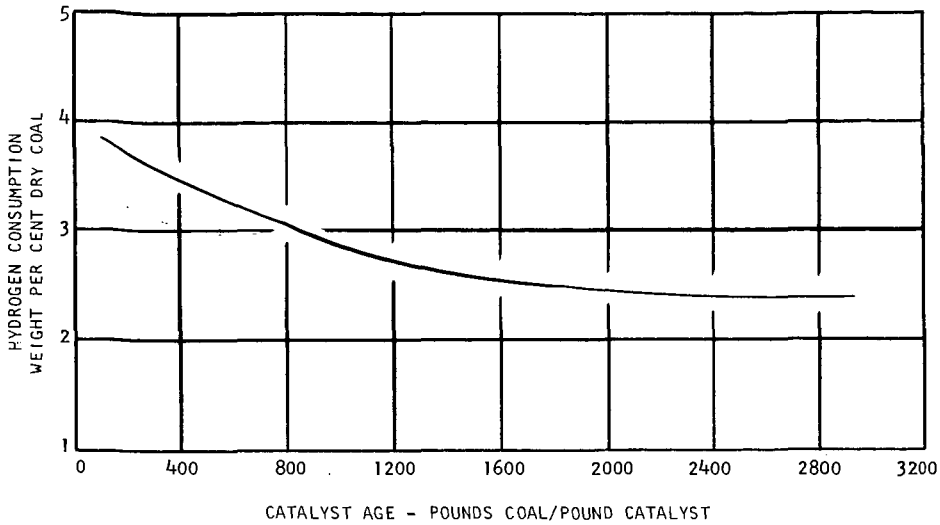


Figure 2 Decline in Hydrogenation Activity of Catalyst

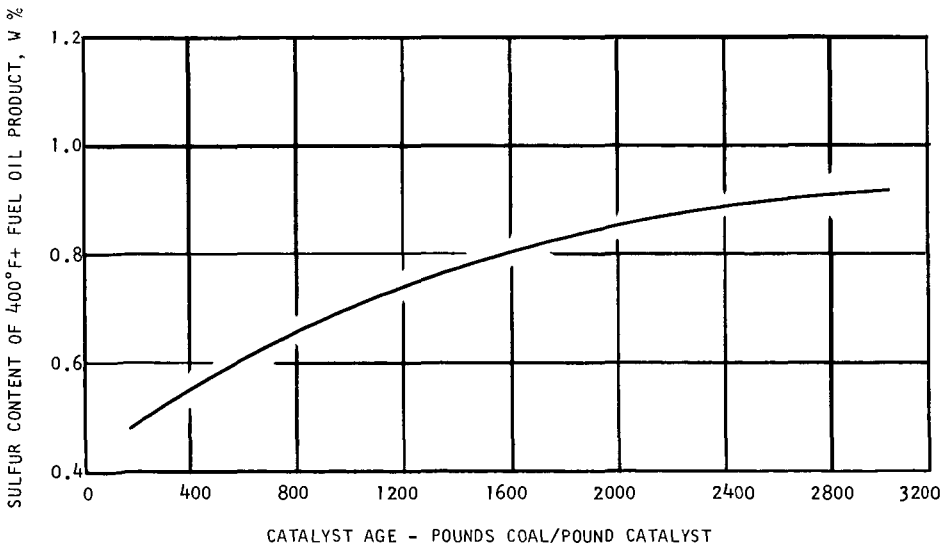
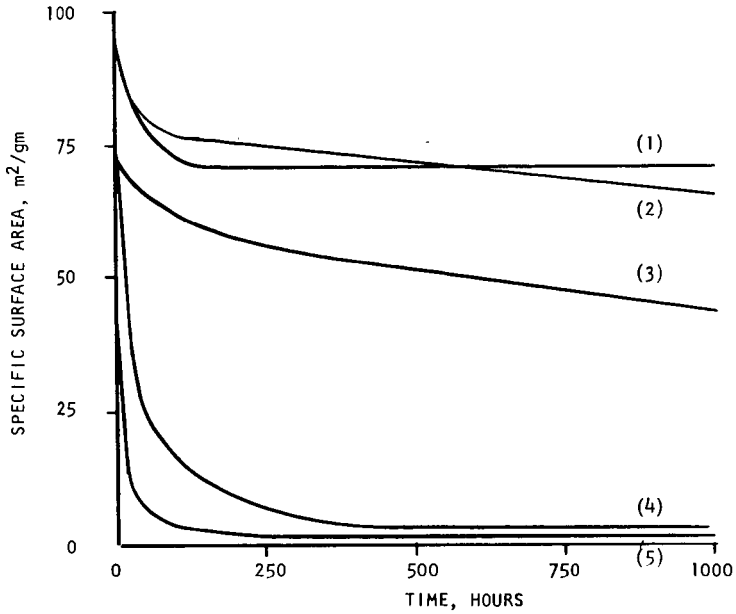


Figure 3 Decline in Desulfurization Activity of Catalyst



(1) 800°C, only H_2

(2) 400°C, $H_2O:H_2$ = 9:1

(3) 500°C, $H_2O:H_2$ = 9:1

(4) 600°C, $H_2O:H_2$ = 9:1

(5) 800°C, $H_2O:H_2$ = 9:1

Figure 4

Effect of Temperature and Steam

On Sintering of Gamma Alumina Catalyst