



Energy, Mines and
Resources Canada

Énergie, Mines et
Ressources Canada

CANMET

Canada Centre
for Mineral
and Energy
Technology

Centre canadien
de la technologie
des minéraux
et de l'énergie

CHEMISTRY OF IRON SULPHATE-COAL CATALYSTS EMPLOYED IN THE HYDROCRACKING OF BITUMEN

D.J. PATMORE AND B.B. PRUDEN

SEPTEMBER 1977

ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
REPORT ERP/ERL 77-72 (TR)

ERP/ERL 77-72 (TR) c.2

01-7988590 c.2

CHEMISTRY OF IRON SULPHATE-COAL CATALYSTS
EMPLOYED IN THE HYDROCRACKING OF BITUMEN

by

D.J. Patmore* and B.B. Pruden**

ABSTRACT

A discussion of the chemistry of iron under the conditions prevailing during the hydrocracking of bitumen and heavy oils is presented. From an examination of the literature and an analysis of reaction equilibria, it is concluded that Fe_{1-x}S ($x = 0.07-0.1$) is the stable phase, possibly mixed with vanadium and nickel sulphides derived from the bitumen. A summary of the reported use of iron containing catalysts in hydrocracking processes is given, and the role of mineral matter in the prevention of reactor fouling is briefly discussed.

* Research Scientist and * Project Leader, Bitumen Processing Section, Synthetic Fuel Research Laboratories, Energy Research Laboratories, Canada Centre for Mineral and Energy Technology, Dept. of Energy, Mines and Resources, Ottawa, Canada.

INTRODUCTION

One of the objectives of CANMET (Canada Centre for Mineral and Energy Technology) is to develop an economical process for upgrading bitumen and heavy oils. This is in keeping with the Energy Research Program of the Department of Energy, Mines and Resources and its policy of ensuring the effective use of Canada's mineral and energy resources. The thermal hydrocracking process has been developed at the Energy Research Laboratories as a method of upgrading Athabasca bitumen.

This bitumen contains 51.5% by weight of pitch (material boiling above 524°C) and about 0.6% by weight of ash, as shown in Table 1. In converting this pitch to distillable material, there is a tendency to form coke deposits, leading to fouling of equipment such as the reactor and the downstream hot vapour-liquid separator. This necessarily affects operation of the system and generally leads to lower efficiency and eventual shut-down because of plugging. It is therefore highly desirable to provide a means for inhibiting or materially reducing coke formation in the reactor and thus increasing operability and on-stream time.

The presence of particulate solid matter in the hydrocracking reactor has been found to play an important role in the reduction of coke formation during the hydrocracking of bitumen and heavy oils (1,2). Bitumen which contains essentially 0% ash deposits coke over 100 times as fast as a similar feed with 0.6% ash under the same reaction conditions. It has also been found that addition of finely divided coal to the feed further reduces coke formation (3). Both coal and ash contain appreciable amounts of iron which is known to act as a hydrocracking catalyst. Indeed experiments have shown that addition of FeSO_4 supported on coal causes an even greater reduction in coke formation during hydrocracking than the use of coal alone (4).

The purpose of this report is to explore the chemistry of iron under the conditions prevailing in the reactor, and to attempt to predict the most stable iron phase that would be present. This will aid in the selection of the most appropriate catalyst systems from an economic point of view, and will ultimately help to understand in more detail the role played by iron in the reduction of coke formation during the hydrocracking process.

DISCUSSION

1. Initial Catalyst Composition

The catalyst was prepared by air drying an aqueous slurry of FeSO_4 and a high volatile A bituminous coal at 60°C to give a material with 31 wt % FeSO_4 .

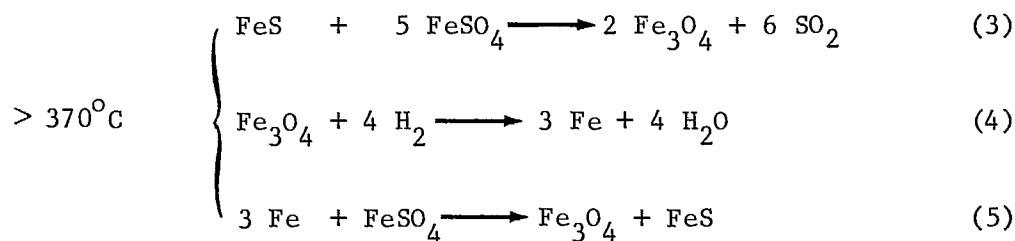
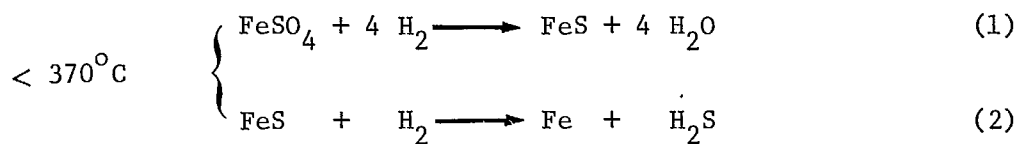
The iron can be present in the coal in several phases: (a) discrete $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$ microcrystals; (b) FeSO_4 adsorbed on the coal surface; and (c) iron chemically bound to various functional groups which might be present in the coal, e.g., $-\text{CO}_2\text{H}$ and R_3N (i.e., the coal can act as an iron exchange medium as well as an electron pair donor). Schafer (5) has studied organically bound iron in brown coals in which cations such as Fe^{2+} can be reversibly bound to carbonyl groups and can be exchanged for other cations. Such chemically bound iron was found to be very easily oxidized by air, although coal itself was able to reduce Fe^{3+} to Fe^{2+} in an acid medium at elevated temperature. In the present case one can thus expect some of the organically bound iron to be oxidized to Fe^{3+} during the air drying of the catalyst. The free FeSO_4 in the catalyst could also be partially oxidized.

2. Reactions of the FeSO_4 /Coal Catalyst During Hydrocracking

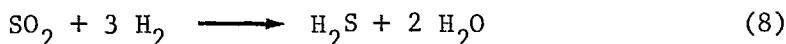
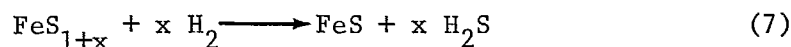
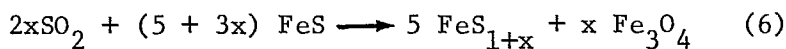
During the hydrocracking process the bitumen is mixed with 1 to 2% FeSO_4 /coal catalyst and the slurry then fed at the bottom of the tubular reactor (held at 450°C) together with a gas mixture consisting initially of 91 atm H_2 , 0.5 atm H_2S and 14 atm methane and other hydrocarbons. As the feed progresses up the reactor, hydrogenation takes place and the gas stream is depleted in H_2 and enriched in H_2S and hydrocarbons. At the top of the reactor the gas composition is typically 88 atm H_2 , 4 atm H_2S and 43 atm hydrocarbons, although these values can vary according to reaction conditions; the values quoted are typical of runs with about 70-80% pitch conversion. Hydrogen and H_2S mole percentages can vary from 50 to 80% and from 1 to 6% respectively.

The loss of water from $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ under 1 atm H_2 (or CO) begins at 200°C and is complete at 300°C (6,7,8). Also any Fe^{3+} present will begin to

be reduced. When the temperature reaches about 400°C it has been shown that appreciable reduction can occur to give a mixture of FeS and Fe⁰ in the presence of pure hydrogen (6,7,8,9). This reaction was investigated by the use of thermogravimetric analysis combined with chemical analysis, X-ray diffraction and Moessbauer spectroscopy (6,7,9). The following reaction scheme was proposed for the reduction of FeSO₄ by a stream of H₂ at 1 atm (6,7).

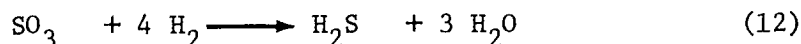
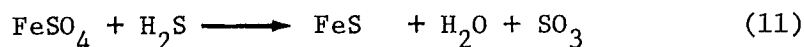
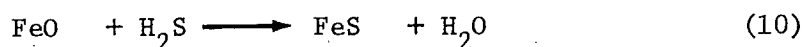
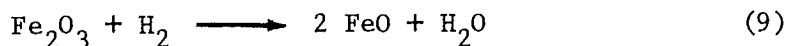


accompanied by:



In the present case not all of these reactions need be considered owing to the presence of H₂S. For Eq 2 the equilibrium constant is 7.8×10^{-5} at 450°C (10,11,12), i.e., $(\text{H}_2\text{S})/(\text{H}_2) = 7.8 \times 10^{-5}$ at equilibrium, thus when $(\text{H}_2) = 91$ atm the concentration of H₂S will be 7×10^{-3} atm. This means that FeS is the stable phase provided the partial pressure of H₂S is greater than .007 atm which is the case at all times during the thermal hydrocracking process. Iron metal is, therefore, very unlikely to be present which means that reactions such as Eq 5 can be ignored.

Hydrogen sulphide can also react directly with iron compounds to give FeS



The equilibrium constant for Eq 9 and 10 combined is $\sim 6 \times 10^7$ at 450°C which requires a steam pressure of ~ 1100 atm at equilibrium. The reaction thus lies completely to the right under the present conditions. The rate of Eq 9 and 10 was found to proceed very rapidly at 450°C (13,14,15,16). It is also possible that iron compounds can react directly with R_2S from the bitumen to form FeS.

Formation of FeS_2 is not likely as pyrites is thermodynamically unstable at 450°C and a high $\text{H}_2:\text{H}_2\text{S}$ ratio (17).

Provided all the above reactions have time to reach equilibrium, we would expect FeS to be the predominant iron-containing phase present under thermal hydrocracking conditions.

It should be noted that iron monosulphide is usually non-stoichiometric and can have iron vacancies randomly distributed throughout the crystal lattice. It should thus be written as Fe_{1-x}S where $x = 0$ to 0.125 . There is also a sulphur deficient phase known, FeS_{1-x} where $x = 0$ to 0.11 , as well as Fe_3S_4 .

Various authors have studied the phases in equilibrium with $\text{H}_2\text{S}/\text{H}_2$ gas mixtures at temperatures above 670°C . According to the data of Turkdogan (18) and Rosenquist (17) the phase in equilibrium with a mole ratio of $\text{H}_2\text{S}/\text{H}_2 = 5 \times 10^{-3}$ is $\text{Fe}_{0.988}\text{S}$ and for a ratio of 5×10^{-2} is $\text{Fe}_{0.966}\text{S}$. These ratios represent the average gas compositions at the bottom and top of the reactor respectively. At lower temperatures, higher sulphur content would be expected. Thus the composition of the iron sulphide would depend to some extent on the position from which samples are taken from the reactor.

The above predictions of the most stable phase present are consistent with the experimental work carried out by several authors. Kawa et al.

(12) investigated the reactions of several iron compounds with $\text{H}_2\text{S}/\text{H}_2$ gas mixtures at elevated temperatures as summarized in the following table:

Compound	H_2S , atm	H_2 , atm	Temp $^{\circ}\text{C}$	Products
Fe^0	1	510	400	35% $\text{FeS}_{1.05}$:65% Fe^0
Fe_3O_4	1	150	250	4% $\text{FeS}_{1.1}$:96% Fe_3O_4
Fe_2O_3	1	150	255	72% $\text{FeS}_{1.1}$:28% Iron Oxide
FeSO_4	1	185	400	43% $\text{FeS}_{1.1}$:18% Iron Oxide plus 38% FeSO_4

As they used insufficient H_2S to react with all of the iron compounds and kept the reaction at operating temperature for zero time, their reaction products do not represent equilibrium mixtures. They identified the various phases by X-ray crystallography.

More recently, Amberg and Chang (19) reported the use of an iron sulphide catalyst in the hydrodesulphurization of thiophene and benzothio-
phene. They treated $\text{Fe}_2\text{O}_3/\text{clay}$ systems with $\text{H}_2/\text{H}_2\text{S}$ mixtures at 400°C to obtain an active catalyst. Preliminary studies using X-ray diffraction indicated the presence of Fe_7S_8 . When they sulphided the $\text{Fe}_2\text{O}_3/\text{clay}$ catalyst with $\text{H}_2/\text{thiophene}$ mixtures instead of $\text{H}_2/\text{H}_2\text{S}$ mixtures, the product spontaneously oxidized in air and had a lower catalytic activity. It is tempting to explain this by the formation of some organosulphur iron compound from the reaction of thiophene with iron oxide under reducing conditions. A similar interaction with organo sulphur compounds should not be completely ruled out in the present case.

So far, no account has been taken of the presence of other metals in the system, in particular, V and Ni. These metals can be present up to several hundred ppm as complexes with porphyrins and other ligands. Under thermal hydrocracking conditions some or all of these complexes may decompose in the presence of H_2S to form sulphides. Vanadium forms a range of sulphides,

the most stable one under our conditions being VS_x ($x = 0.8$ to 1.8) (14). In the range $VS_{1.00} - VS_{1.16}$ it has the NiAs structure, thus there is the possibility of substitution of V for Fe in $Fe_{1-x}S$. VS_x is known to be a desulphurization catalyst (20). Similarly, in the case of nickel the stable form will probably be either $Ni_{1-x}S$ (with the same NiAs structure as VS and FeS) or NiS_{1-x} . Again there is the possibility of substitution of Ni in $Fe_{1-x}S$. NiS_{1-x} is claimed to be a desulphurization catalyst (21).

These sulphides will probably be associated with the mineral matter present in the coal after the coal has been completely hydrogenated. Ash from the $FeSO_4$ /coal catalyst had the following analysis: 17% SiO_2 , 9.5 % Al_2O_3 , 52% Fe_2O_3 , 8.1% CaO , 0.6% TiO_2 , 1.5% MgO , 8.6% SO and $\sim 0.2\%$ alkali metals, thus iron compounds form about 50% of the total amount of mineral matter.

3. Use of Iron Containing Catalysts for Hydrogenation and Hydrodesulphurization

(a) Hydrogenation of Coal

Various accounts of the use of iron compounds used in the catalysis of coal hydrogenation have appeared. A comparison (22) of iron oxides with MoO_3 , WO_3 , Na_2S_4 , $\text{Sn}(\text{COO})_2$ and iron sulphate indicated that Mo oxides are best followed by WO_3 and Fe_2O_3 . Ferrous sulphide and mixtures with Mo sulphide were reported to give improved degrees of hydrogenation in the hydrogenation of solid coal at $360^\circ\text{--}430^\circ\text{C}$ for 2.5 hours with 100 atm H_2 (23). A similar study on the use of various iron containing materials as catalysts (24) indicated the following order of activity: hematite = magnetite = mill-scale = $(\text{SnS}_2 + \text{NH}_4\text{Cl}) > \text{FeSO}_4$ and blast furnace slag; impregnating coal with FeSO_4 increased the conversion. More recently the catalytic effect of mineral matter on the hydrogenation of coal has been studied (25). These authors found that Fe and Ti have a catalytic effect, and that "pyritic as well as organic sulphur appears to be responsible for formation of catalytically active form of iron sulphide". They found that the per cent of conversion increased as the atomic ratio of iron to total sulphur in the system increased. Previous work had shown that iron sulphide was capable of acting as a hydrogenation catalyst (26). The use of $\text{Fe}(\text{OH})_3$ for coal hydrogenation has been described (27).

The Gelsenberg coal hydrogenation (28) plant operating during the war used a catalyst at 1.2% FeSO_4 , 1.5% Bayer Masse and 0.3% Na_2S .

(b) Oil

The use of a lignite/ FeSO_4 (10%) catalyst in hydrogenation of crude naphtha is described in a German patent (24); a clay-based sulphided mixed catalyst containing iron has also been described (30). Heavy oils can be catalytically hydrocracked with 100–350 atm H_2 at 450–530 atm using 10% FeSO_4 on coke (31). Iron sulphate supported on a finely divided carbonaceous powder is used in the German Combi process. Herrmann and Bowles (32) evaluated a number of iron-based catalysts for hydrogenation of refinery vacuum residue and tar sand bitumen. They found an iron oxide residue from the Sherritt Gordan Mines, a lignite impregnated with Fe_2O_3 , and commercial FeS to give satisfactory yields and degree of desulphurization coupled with

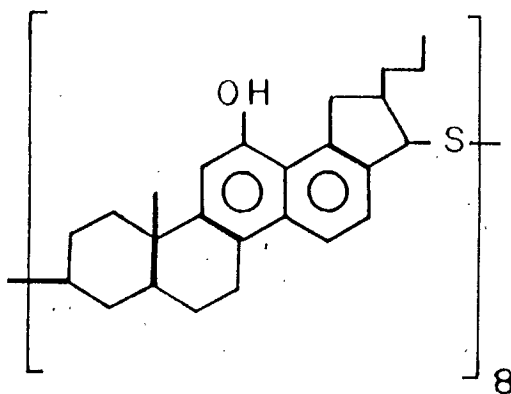
absence of coke formation. However, use of synthetic FeS caused coke formation.

Recently the use of iron oxide/ Na_2CO_3 mixture has been reported for the hydrodesulphurization of RSH and CS_2 , but would not remove thiophene (23).

Reports on the use of aluminum-iron-molybdenum oxide catalysts have also appeared (34,35,36).

4. The Role of Mineral Matter in the Reduction of Reactor Fouling

During the hydrocracking of bitumen, varying amounts of coke are produced depending on the reaction conditions. It has been generally found that coke from asphaltenes is more abundant in the reactor than that from the heavy aromatic oil fractions (37). Thus in order to fully understand the coking process a detailed understanding of the chemical composition and structure of asphaltenes is essential. Although this is a long way from being fully realised at the present time, certain structural aspects have been elucidated by various authors. On the basis of acetylation, silylation and infrared studies (38,39), it has been shown that the majority of oxygen is present as phenolic hydroxyl groups. It is also generally agreed that polynuclear aromatic groups are present in the asphaltene structure. O.P. Strausz and co-workers (39) have produced evidence to support their claim that asphaltene consists of smaller units of average MW, about 600, joined by sulphide bridges to form larger aggregates of MW = 3000 or more. They based this on the reduction in MW when asphaltene was reduced with K/naphthalene. They suggested the following average structure for asphaltene:

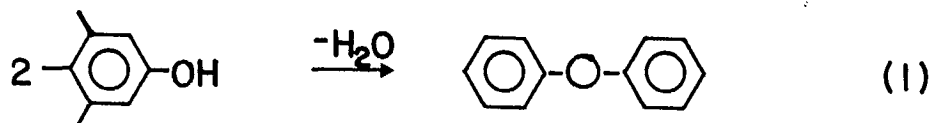


There will obviously be many other structural units present, e.g., S, N and O heterocycles, ethers, esters and more highly condensed aromatic systems. It is believed that the polar asphaltenes are held in solution in the far less polar oils by the peptizing action of resins which are intermediate in polarity and are soluble in the other less polar fractions of the bitumen. Resins possess ester groups which are able to hydrogen bond to phenolic OH groups on the asphaltene and in this way are able to hold the asphaltenes in solution. Based on the present knowledge of asphaltene structure, we can draw the following tentative picture of coke formation.

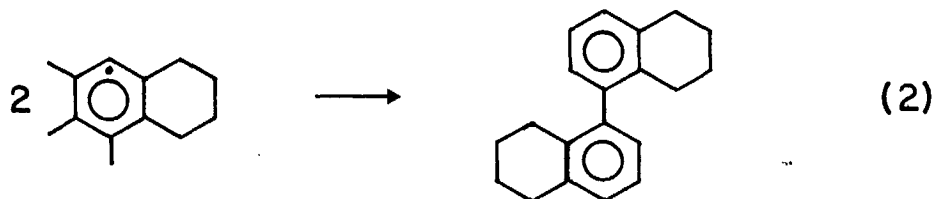
One of the initial reactions is presumably the precipitation of asphaltene due either to the decomposition (e.g., decarboxylation) of the protective resin or to an increase in light oil due to hydrocracking reactions. During or after this agglomeration of asphaltenes, various competing reactions can take place (40). These can be classified as follows:

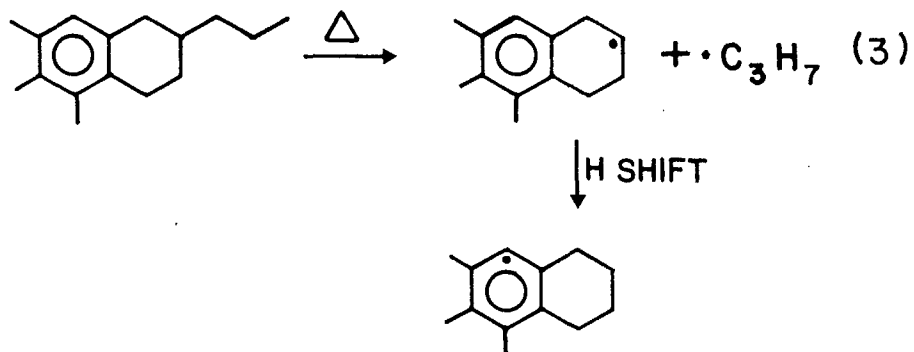
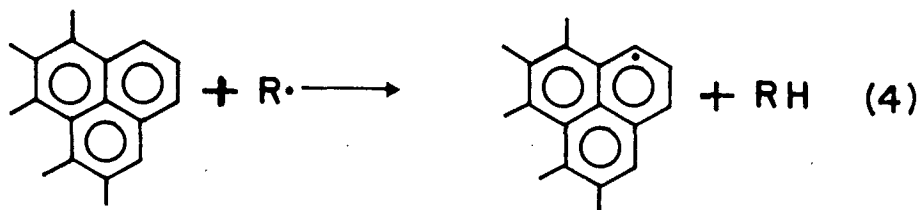
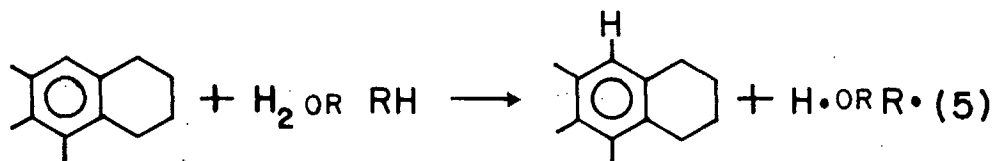
1. Condensation and Polymerisation Reactions

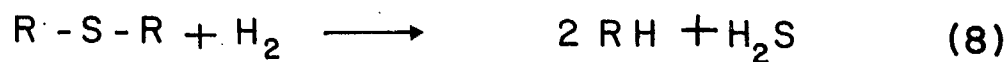
(a) Phenol Condensation



(b) Free Radical Combination



2. Hydrocracking Reactions(a) C-C Bond Scission(b) Hydrogen Abstraction(c) Hydrogenation

(d) Hydrogen Transfer3. Heteratom Removal

Coke formation is essentially a polymerisation and dehydrogenation reaction in which the carbon skeleton gradually approaches that of graphite. Thus the important reactions will be Eq 1 and 2, accompanied by Eqs 3, 4 and 7; i.e., steps involving free radical formation followed by C-C bond formation, C-O bond formation and aromatisation reactions. Obviously, the number

of individual reactions is very large and a detailed description is not feasible here. A more comprehensive discussion is given by Belinko and Denis (40).

Reactions which will tend to inhibit coke formation include hydrogenation reactions 5 and 6 which remove free radical intermediates and unsaturated systems as well as reactions which will tend to break up the asphaltene structure into smaller units such as Eq 3, as well as Eqs 8 and 9. These reactions will be speeded up with an increase in H_2 partial pressure. Asphaltene fragmentation will separate otherwise reactive centres which can crosslink via the coking reactions mentioned above. If the asphaltene agglomerates into large particles before significant fragmentation can occur, the effective hydrogen partial pressure will be reduced and coking reactions will be emphasised. Thus an increase in hydrogen partial pressure and a decrease in the degree of agglomeration of asphaltene and associated material should decrease coke formation. Based on these arguments, we can now attempt to explain the efficiency of ash and other solid matter in the prevention of coke formation. In the presence of solid material, asphaltene will tend to deposit as thin layers on the surface of particles provided the total surface area is large enough. This will increase the availability of hydrogen and tend to inhibit coking reactions by increasing hydrogenation and hydrodesulphurization reactions. This process will be further enhanced if there are catalytic sites on the solid particles, which is probably the case for coal derived ash and other iron containing materials as outlined in the previous section.

It is therefore concluded that the effectiveness of $FeSO_4$ /coal for the prevention of coke in part involves deposition of asphaltene on particles of coal or coal ash containing FeS followed by hydrogenation and HDS partly catalysed by FeS and other minerals present. This fragments the asphaltene which can then re-dissolve to undergo further hydrocracking reactions. This is obviously a simplification of the situation, the mineral matter and coal are undergoing more or less rapid thermal and chemical reactions, and other non-asphaltene components will be undergoing reactions on the surface. This discussion also ignores the formation of coke from heavy oil, although similar reactions will also occur.

A complication to the above picture arises from attempts to use

Co-Mo catalysts supported on coal, one would expect such a system to be even more effective than the iron/coal catalyst, but in fact extensive coking does occur. However a lower melting point coal was used which may have caused the coal particles to agglomerate thus destroying its efficiency as a coke getter (43).

A purely mechanical scouring and scavenging action by solid particles is another important effect which must be considered. It is possible that coke does deposit on the solid material, but is carried out of the reactor along with the heavy ends thus preventing coke build-up. Solid particles would also tend to scour the walls and remove any deposits which tend to form. It should be noted that the amount of coke actually formed is only a few per cent of the total feed. Thus with a few per cent solid matter present, such a scavenging action would be quite a feasible process. The actual situation may in fact involve both processes to some extent. Previous workers have claimed that mechanical scavenging is the predominant process for prevention of coke build-up (2,41,42,43).

CONCLUSIONS

From a survey of information contained in the literature, together with a consideration of chemical equilibria using published values of equilibrium constants, it was concluded that Fe_{1-X}S will be the most stable phase present under the conditions prevailing in the hydrocracking reactor. It is possible that this material will be associated with nickel and vanadium sulphides derived from the bitumen. The conversion of iron compounds to iron sulphide under hydrocracking conditions is strongly indicated by the experimental work of various authors.

From a survey of the pertinent literature it was shown that iron sulphide and other iron compounds can act as hydrogenation and hydrodesulphurization catalysts. It was suggested that the catalytic activity of the iron sulphide may play some role in the ability of iron sulphate/coal coke getter to prevent coke build-up in the reactor.

PROPOSALS FOR FURTHER WORK

Determination of Iron Containing Species Present in the Reactor

It is proposed that reactor and heavy end samples be studied by various analytical techniques to establish the constitution of the solid phases present, and to determine the nature of the iron containing species. Suggested techniques include Moessbauer Spectroscopy, X-ray Diffraction and Electron Microprobe Analysis.

Using Moessbauer Spectroscopy, it is possible to distinguish between iron atoms in different chemical environments, and from comparison with spectra of known compounds it should be possible to identify iron sulphide and other iron compounds present in the reactor samples.

X-ray diffraction studies of these samples will give information on both iron containing compounds and other phases present, and will therefore give a more detailed picture of particle composition.

Details of Fe, Ni, V and S distribution in the particles can be obtained using electron microprobe analysis. From this it should be possible to determine how material builds up in the reactor and whether deposition of nickel and vanadium occurs.

From the above studies a much better picture of particle composition and morphology can be obtained. This will lead to a greater understanding of the role played by various coke getters in the reduction of coke build-up in the hydrocracking reactor, and will materially aid in the choice of the most appropriate catalyst system.

REFERENCES

1. Ranganathan, R. "Literature survey of thermal hydrocracking processes" CANMET (Canada Centre for Mineral and Energy Technology, formerly Mines Branch, Department of Energy, Mines and Resources). Report in preparation.
2. Pruden, B.B., Logie, R.B., Denis, J.M. and Merrill, W.H. "Thermal hydrocracking of Athabasca bitumen - reduction of reactor fouling"; CANMET Research Report 76-33; Aug. 1976.
3. Ranganathan, R., Pruden, B.B. and Denis, J.M. "Thermal hydrocracking of Athabasca bitumen: 1. Effect of coal addition on pilot plant operation"; CANMET Report ERP/ERL 77-53 (R); June 1977.
4. Ranganathan, R., Pruden, B.B. and Denis, J.M. CANMET report in preparation.
5. Schafer, H.N.S. "Organically bound iron in brown coal"; Fuel; v. 56, p 45; Jan. 1977.
6. Pannetier, G. and Bugli, G. "Reduction par l'hydrogene du sulfate ferreux anhydre et reactions entre phases solides en resultant"; Compte. Rend. Acad. Sci. Paris; v. 261, groupe 8, p 156; July 1965.
7. Pannetier, G. and Bugli, G. "Etude de la reduction par l'hydrogene du sulphate ferreux anhydre et des reactions entre phases solides en resultant"; Bull. Soc. Chim. France; no. 7, p 2240; 1966.
8. Pechkovskii, V.V. and Ketov, A.N. "Characteristics of sulphide reduction by solid and gaseous reducing agents"; Sb. Nauchn. Tr. Permsk. Politckhn. Inst.; no. 10, p 3; 1961.
9. Huuska, M., Koskenlinna, M. and Niinisto, L. "Thermal decomposition of iron sulphates: 1. Thermogravimetric study of $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ in carbon monoxide and hydrogen atmospheres"; Thermochimica Acta; v. 13 p 315; 1975.
10. Ienciu, M. "Thermodynamics of reduction reactions of sulphide-natural gas mixtures"; Bul. Inst. Poiteh. "Georghe Gheorghiu-Dej" Bucuresti; v. 33, no. 3, p 133; 1971.
11. Ienciu, M. "Thermodynamics of the iron sulphide-methane gas system"; Metalurgia (Bucharest); v. 22, no. 4, p 221; 1970.
12. Kawa, W., Hiteshue, R.W., Anderson, R.B. and Greenfield, H. "Reactions of iron and iron compounds with hydrogen and hydrogen sulphide"; U.S. Dept. of Interior, Bureau of Mines report of investigations 5690; pp 1-16; April 1960.

13. Shrodt, J.T., Hilton, G.B. and Rogge, C.A. "High temperature desulphurization of low-CV fuel gas"; Fuel; v. 54, p 269; Oct. 1975.
14. Bada, R.U. and Sage, W.L. "Desulphurizing Fuel via metal oxides"; Am. Chem. Soc. Div. Fuel Prepr; v. 14, p 121; 1970.
15. Reeve, L. "Desulphurization of coke-oven gas at Appleby-Frodingham"; Journ. Inst. Fuel; v. 31, p 319; July 1958.
16. Abel, W.T., Shultz, F.G. and Langdon, P.F. "Removal of hydrogen sulphide from hot producer gas by solid absorbents"; U.S. Dept. of Interior, Bureau of Mines report of investigations 7947; 23 pp; 1974.
17. Rosenqvist, T.A. "A thermodynamic study of the iron, cobalt, and nickel sulphides"; Journ. Iron and Steel Inst.; v. 176, p 37; 1954.
18. Turkdogan, E.T. "Iron-sulphur system; Part 1: Growth rate of ferrous sulphide on iron and diffusivities of iron in ferrous sulphide"; Trans. Metallurg. Soc. AIME; v. 242, p 1665; Aug. 1968.
19. Amberg, C.H. and Chang, J.R. "Research study on the catalytic hydrodesulphurization of organo sulphur compounds"; Report on research agreement No. 1 SU 76-00019; pp37; 1977.
20. Ranney, M.W. "Desulphurization of petroleum"; Chem. Technology Rev. 44; Noyes Data Corp.; p 81; 1975.
21. Ranney, M.W. "Desulphurization of petroleum"; Chem. Technology Rev. 44; Noyes Data Corp.; p 99; 1975.
22. Szucs, M. "Hydrogenation of Hungarian coals in oil suspension"; Magyar Tudomanyos Akad. Kem Tudomanyok Osztalyanak Kozlemenyei; v. 6, p 375; 1955.
23. Petrik, G.K. and Zabramnyi, D.T. "Primary destructive hydrogenation of coals"; Doklady Akad. Nauk. Uzbek. S.S.R.; no. 9, p 29; 1954.
24. Bose, S.K., Basak, N.G. and Lahiri, A. "Hydrogenation of Assam coal. II Development of indigenous catalysts"; J. Sci. Ind. Res. (India); v. 18B, p 255; 1959.
25. Mukherjee, D.K. and Chowdhury, P.B. "Catalytic effect of mineral matter constituents in a North Assam coal on hydrogenation"; Fuel; v. 55, p 4; Jan. 1976.
26. Mukherjee, D.K., Sama, J.K., Chowdhury, P.B. and Lahiri, A.; Proc. Symp. Chemicals and Oil from Coal, Central Fuel Res. Inst. India; p 116; 1972.
27. Morita, M. and Sato, S. "Liquefying coal and ligning by hydrogenation and thermal cracking"; Japan Kokai 76 13,803 (cl. C10G); Feb. 1976, Appl 74 85,074; July 1974; pp5;

28. Cockram, C. "Visit to Gelsenberg hydrogenation plant"; Combined Intelligence Objectives Sub-Committee, Item No. 30, File No. XXX-105; 39 pp; H.M. Stationery Office, London; Aug. 1945.
29. Oettinger, W. and Gohre, O. "Low-boiling hydrocarbons by catalytic hydrogenation of crude naphtha"; Ger. 829,344; Jan. 1952.
30. Rossmanith, G., Sander, H. and Sander, W. "Catalyst for hydrogenation-cracking of middle oils and heavy residues"; Ger. (East) 12,202; Oct. 1956.
31. Pier, M., Urban, W., Schmidt, P. and Oettinger, W. "Refining of heavy oil"; Ger. 933,648; Sept. 1955.
32. Herrmann, W.A.O. and Bowles, K.W. "An evaluation of catalysts for the liquid phase hydrogenation of refinery vacuum residuum"; Mines Branch Report R280; 52 p; Dec. 1973.
33. Mazumdar, M.M., Kaushik, V.P., Kumar, K.N. Prasad, K. and Dutta, B.K. "Desulphurization of petroleum feedstocks using alkalinized iron oxide"; Technology (Sindri, India); v. 11, no. 1, p 33; 1974.
34. Abidova, M.F., Rakhmatullaev, N. and Samigov, K.A. "Study of an aluminum-iron-molybdenum oxide catalyst for hydrocracking of high-sulphur raw material"; Uzb. Khim. Zh.; v. 19, no. 6; p 32; 1975.
35. Talipov, G.Sh., Khakimov, U.B., Samigov, K.A., Abidov, M.F. and Rakhmatullaev, N.; Tr. Inst. Khim Nefti, Priir. Solei, Akad Nauk Kaz. S.S.R., v. 6, p 22; 1973.
36. Trifiro, F., Villa, P.L., Pasquon, I., Iannibello, A. and Berti, V. "Residual oil hydrodesulphurization on four component catalysts"; Chim. Ind. (Milan); v. 57, no. 3, p 173; 1975.
37. Belinko, K., Nandi, B.N. and Denis, J.M. "The distribution of coke precursors in the reactor during thermal hydrocracking of Athabasca bitumen"; CANMET Report ERP/ERL 76-186 (OP); 16 pp; April 1977.
38. Moschopedis, S.E. and Speight, J.G. "Oxygen functions in asphaltenes"; Fuel; v. 55, p 334; Oct. 1976.
39. Strausz, O.P. "Some aspects of the chemistry of Alberta oil sand bitumen"; Am. Chem. Soc. Div. Petrol. Chem. Preprints; v. 21, no. 3, p 456; Aug. 1976.
40. Belinko, K. and Denis, J.M. "A review of some chemical aspects of the formation of coke during thermal hydrocracking of bitumen"; CANMET Report 77-43; 13 pp; Sept. 1976.

41. Schuman, S.C. "Heavy oil conversion with low coke formation"; U.S. Patent 2,875,150; Feb. 24, 1959.
42. Khulbe, C.P., Pruden, B.B., Denis, J.M. and Merrill, W.H. "Pilot plant thermal hydrocracking of GCOS (Great Canadian Oil Sands) bitumen: 1. The effect of heavy oil recycle on the plant operation"; CANMET Report 76-28; June 1976.
43. Khulbe, C.P., Pruden, B.B. and Denis, J.M. "Hydrocracking of Athabasca bitumen: Effect of coal-base catalyst on pilot plant operation"; CANMET Laboratory Report ERP/ERL 77-3(R); Jan. 1977.