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COAL HYDROGENATION AND HYDROCRACKING OF TARS

Professor G.C.A. Schuit

COAL HYDROCRACKING AND HYDROCRACKING OF TARS

INTRODUCTION

The history of coal hydrocracking can be divided into two periods.
The first (1920-1945) is entirely dominated by the German efforts to produce
gasoline out of coal (T.G. Farbin Ges. under the direction of M. Pier). This
period came to an end consequent to the discovery of the huge Middle East oil
fields because gasoline from coal could not compete in price with petroleum
derived gasoline. However, a considerable amount of "know how" in the field
of catalysis found application in the petroleum industry.

The beginning of the new period started about 1974 when price
differences became smaller, and crude oil reserves threatened to diminish so
that coal hydrocracking became interesting again. It is therefore worthwhile
to reconsider the German technology.

Fig. 1 compares German coal hydrocracking with modern petroleum
technology. The information about the former is derived from Donash et al [1]
but in particular from Weisser and Landa [2]. There are differences but also
similarities. Introduction of hydrogen was of primary importance for coal conversion,
but far less so for petroleum operations. The main efforts in the latter field
were directed at the removal of sulfur from the sulphur rich Middle East crudes.
Sulphur removal is less pressing for coal conversion where removal of N and O is
more pressing.

HYDROCRACKING OF
COAL

PETROLEUM REFINING

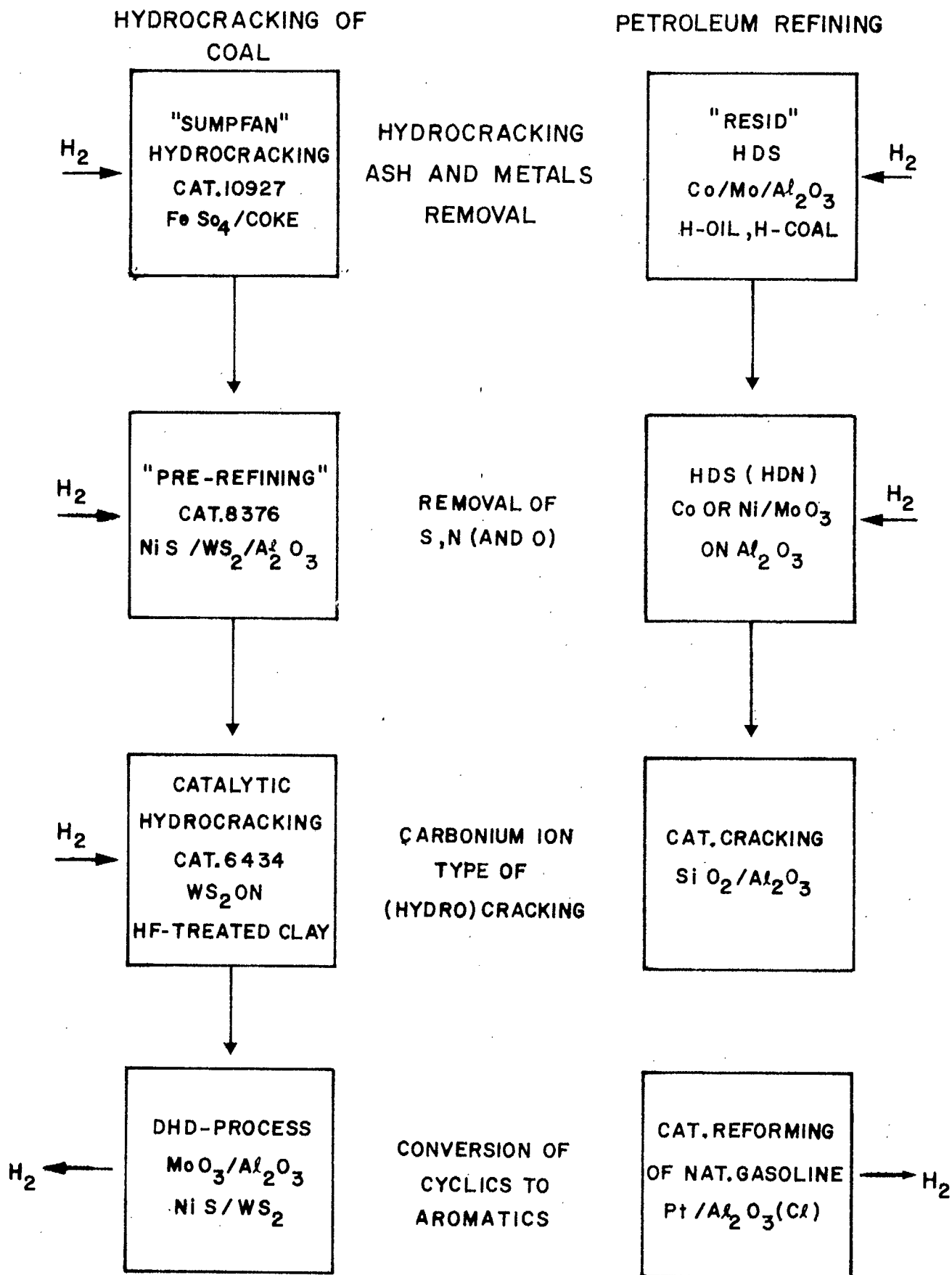| HYDROCRACKING OF COAL		PETROLEUM REFINING
$H_2 \rightarrow$ "SUMPFAN" HYDROCRACKING CAT.10927 Fe So$_4$/COKE	HYDROCRACKING ASH AND METALS REMOVAL	"RESID" HDS Co/Mo/Aℓ_2O$_3$ H-OIL, H-COAL $\leftarrow H_2$
$H_2 \rightarrow$ "PRE-REFINING" CAT.8376 Ni S /WS$_2$/A$_2$O$_3$	REMOVAL OF S,N (AND O)	HDS (HDN) Co OR Ni/MoO$_3$ ON Aℓ_2O$_3$ $\leftarrow H_2$
$H_2 \rightarrow$ CATALYTIC HYDROCRACKING CAT.6434 WS$_2$ON HF-TREATED CLAY	CARBONIUM ION TYPE OF (HYDRO) CRACKING	CAT. CRACKING Si O$_2$/Aℓ_2O$_3$
$H_2 \leftarrow$ DHD-PROCESS MoO$_3$/Aℓ_2O$_3$ Ni S /WS$_2$	CONVERSION OF CYCLICS TO AROMATICS	CAT. REFORMING OF NAT. GASOLINE Pt /Aℓ_2O$_3$(Cℓ) $\rightarrow H_2$

Fig 1
GERMAN COAL HYDROCRACKING OPERATIONS,
COMPARED TO PETROLEUM REFINING OPERATIONS.

If the conversion processes are directed to the production of motor-gasolines, it becomes necessary to adapt the structures of the organic molecules in the feed to the demands on the properties of the gasoline (volatility, ON). Saturated molecules should be branched and there should be aromatics present, necessitating the conversion of five-rings to six-rings. This is the task performed by solid acid-catalysts. Petroleum technology uses catalytic cracking and catalytic reforming for this purpose; German operation hydrocracking and the DHD - dehydrogenation process.

German operation starts with a process (Step I) in which hydrogen is added to the coal in a cracking operation. It also serves the purpose of getting rid of "ash" and metals. It turns out that the first step is not sufficient to add enough hydrogen; so there is need for another operation (step III) in which hydrogenation and acid-cracking is combined. Since nitrogen compounds poison ·the acid-catalyst, they have to be removed by a refining operation (step II) before the feed goes to step III.

A survey of the German catalysts is given in fig.2. It is noteworthy that with the exception of the ultimate catalyst for step I, they are all derived from WS_2.

The final step in the German operations (DHD, step IV) is basically a dehydrogenation. operation to convert saturated ring structures into aromatics, once the feed has the boiling range of a gasoline. Since the catalytic reforming of the oil industry is far superior, step IV is not particularly interesting and it will not be discussed.
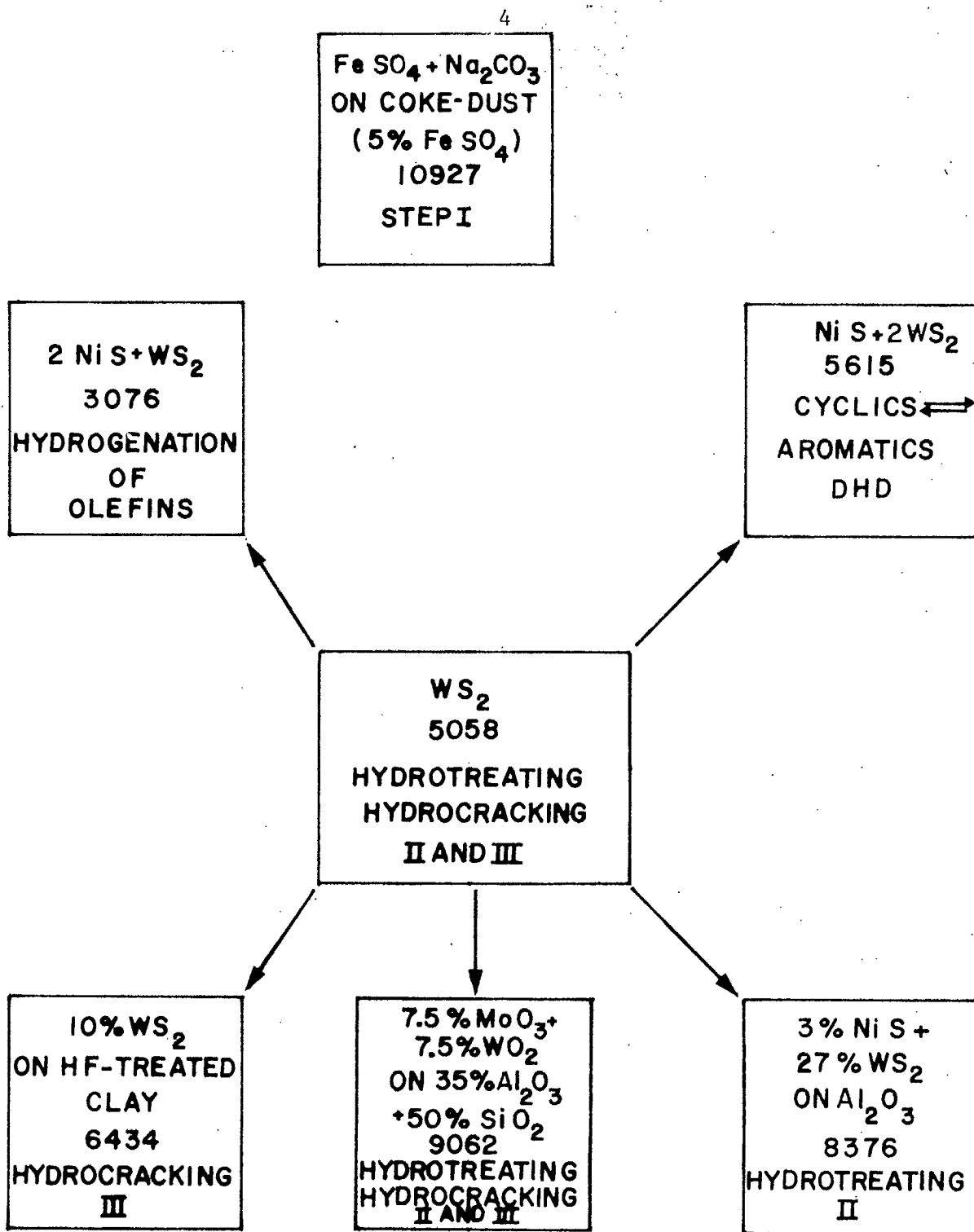
FIGURE 2

GERMAN CATALYSTS

The discussions in the coal hydrocracking meetings during the months of October and November 1977 set out to clarify the basic elements of the various processes. The participants represented different disciplines viz. :

Chemical Engineering – Denis, Logie, Patmore, Ranganathan

Coal structure   – Belinko

Organic Chemistry   – George, Sawatzky

Catalysts   – Furimsky, Kriz, Ternan , Hardin

Coal hydrocracking   – Kelly

General programming   – Hardin

Preparation of subject–Schuit.

The subjects discussed were

1) Mechanisms of thermal hydrocracking, hydrogen donor action and the influence of catalysts;

2) Catalytic hydrocracking and catalytic cracking based on acid – catalysts;

3) Pre-refining, hydrodesulfurization (HDS), hydrodenitrification (HDN), and hydrodeoxygenation (HDO);.

4) Conclusions as to future research ;

and   5) Choice of expensive instrumental methods to investigate catalysts.

Since one of the main activities of the CANMET – Research is connected with the hydrocracking of Athabasca bitumen and this feed is somewhat intermediate in character between coal and heavy petroleum crudes, its hydrocracking often served as a lead for the approach of the more difficult coal hydrocracking.

I The first reaction

(A catalytic radical hydrocracking)

1) In the German process the catalyst was $FeSO_4$/coke and the process

served also to remove ash because the product was distilled after

the reaction. No efforts were made to recover the catalyst.

In the comparable H-coal process the catalyst is the convent-

ional $Co/Mo/A\ell_2O_3$ catalyst. Conversion to distillates is only

partial. The process is an operation in slurry phase, both catalyst

and coal particles being present as fine particles in an oil medium.

The slurry is thoroughly mixed by passing hydrogen bubbles through

the liquid. Part of the catalyst is continuously discarded and

replaced by fresh catalyst.

2) Operational models for the structures of tars, coals and coke

To rationalise the interactions of tars, coals and coke with H_2 we

need simplified models for their structures and structural components.

They are operational in a restricted sense because they do not

intend to account for the "structure" of the materials although they

should contain elements that might be used for extending the model

in that direction if so desired.

Extensive work at the CANMET labs in the groups of coal research

and organic chemistry are helpful in the construction of such models,

as for instance Belinko and Denis[3], Belinko, Nandi and Denis[4], and

George, Banerjee, Smiley and Sawatzky[5]. Guided by these results and

the theories advanced in the reports, three types of structural elements are adopted here:

1) Primary elements consisting of polyaromatic molecules. The bonds involved are aromatic C-C bonds including such as in diphenyl between two phenyl groups. The molecules may also contain N, O and S. Nitrogen will occur predominantly in six-ring structures by replacing a CH - unit by N as in pyridine. S and O will tend to be in five-ring structures as in dibensothiophene.

2) Secondary structures formed by bridges between the primary units. Bridges can be $-(CH_2)_n-$ chains (n=1,2 ch), O, S and NH groups (isoelectronic with $-CH_2-$). The bridges are saturated, but not all saturated side chains are bridging so we may find side chains such as OH, SH, NH_2, C_nH_{2n+1}, etc. There are reasons to assume that the hydrocarbon side chains are cyclic, at least in Athabasca bitumen; George et al [5] find them to be so in feed and products from thermal hydrocracking of Athabasca bitumen.

3) Tertiary units. The secondary units contain polar groups (OH, SH), but also polarizable molecules such as the polyaromatics. These allow a multitude of polar interactions such as acid - base, H - bonding, dipole - dipole, and dipole - induced dipole modes. They are probably of great importance for defining long distance structures such as liquid crystals observed by Belinko and the curious selectivity in asphaltene-resin interactions (see report 77-43, p.8). We shall

consider them for the moment as of less importance where hydro-
cracking is concerned, although this is definitely one of the
more drastic simplifications in the model.

The important elements that vary in going from tar to coals,
to coke, and ultimately to graphite are: 1) the size of the poly-
nuclear primary elements (increasing in that direction); 2) the
number of saturated side chains; and 3) the fraction thereof
that are bridging (decreasing). The difference between asphaltenes
and maltenes is assumed to be primarily given by the ratio of poly-
aromatic to saturated elements. In the first instance the average
molecular weight and H/C ratio are indicative for the position of
the particular feed material in the sequence given above.

3) <u>Thermal cracking and thermal hydrocracking</u>*

Thermal cracking is usually assumed to start with the breaking of
a single -c-c- bond (initiation of the chain reaction). Cracking
of the bond in β - position - c - c - c. - - C. + CH_2 = CH_2) etc,
CH_2 = CH_2 as main product if the hydrocarbon chains are straight.
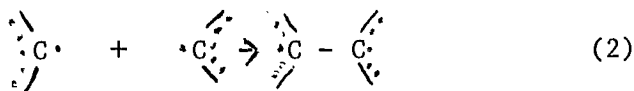If they are branched, branched olefins may be produced

$$- c - \overset{\overset{\textstyle c}{\diagdown}}{c} - c . - - c . + \overset{\overset{\textstyle c}{\diagdown}}{c} = c \qquad (7)$$

$$- - c - c = c + c.$$
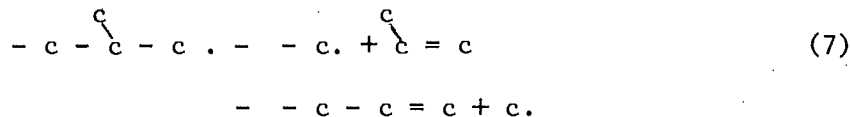
The disintigration of the bridging chains ends with the formation
of radicals such as $\overset{\diagdown}{\underset{\diagup}{\cdot C}} .$ or $\overset{\diagdown}{\underset{\diagup}{\cdot C}} - \overset{H}{C} .$
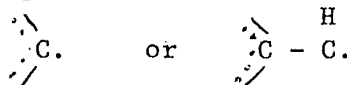
* Belinko and Denis[3]

Recombination of these radicals (chain termination) causes the

production of greater polyaromatic clusters,

$$\overset{\cdot}{\underset{\cdot}{\diagdown}} C \cdot \quad + \quad \cdot C \overset{\diagup \cdot}{\diagdown} \quad \rightarrow \quad \overset{\cdot}{\diagdown} C - C \overset{\diagup \cdot}{\diagdown} \qquad (2)$$
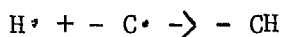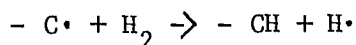
etc.

Thermal cracking therefore tends to eliminate side chains under

the formation of larger primary units (greater polyaromatic clusters),
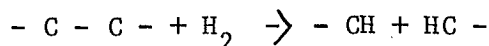
i.e. coking.

If H_2 is present in sufficient quantities, i.e. under a high pressure,

a chain transfer reaction is supposed to occur, viz.

$$- C - C \cdot + H_2 \quad \rightarrow - C - C - H + H \cdot , \quad (3)$$
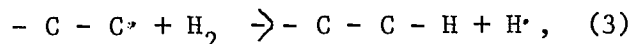
i.e. Cracking of the side chains is suppressed. If the side chains

are bridging, the secondary clusters tend to fission into primary

elements: this is what gives rise to hydrocracking. The ratio of

"coking" to "hydrocracking" is in the first instance determined by

the rate of the fission reaction (7) and the chain transfer reaction (3).

However, the overall - rate is only dependent on the number of potential

centers ($-CH_2-CH_2-$) and their specific rate of forming radicals.

The rate of (3) evidently depends on the hydrogen concentration, i.e.

on the hydrogen pressure. If the partial pressure of H_2 is very

high, the overall reaction is in principle.

$$- C - C - \quad \rightarrow \quad 2 - C \cdot$$

$$- C \cdot + H_2 \quad \rightarrow \quad - CH + H \cdot$$

$$H \cdot + - C \cdot \quad \rightarrow \quad - CH$$

hence,

$$- C - C - + H_2 \quad \rightarrow \quad - CH + HC -$$

"Conversion", if considered as the rate of reaction of large molecules to smaller molecules (i.e. high boiling species to lower boiling products), then needs only small amounts of H_2. Merrill et al. [6] and Pruden et al. [7] indeed find that the first 50% of the Athabasca bitumen hydrocracking occurs with only small hydrogen consumption. Above that level however H_2 consumption increases. George et al [5/] show that this is accompanied by a conversion of polyaromatics to di- and even monoaromatics (see their fig.2 p.17)

Figure 3
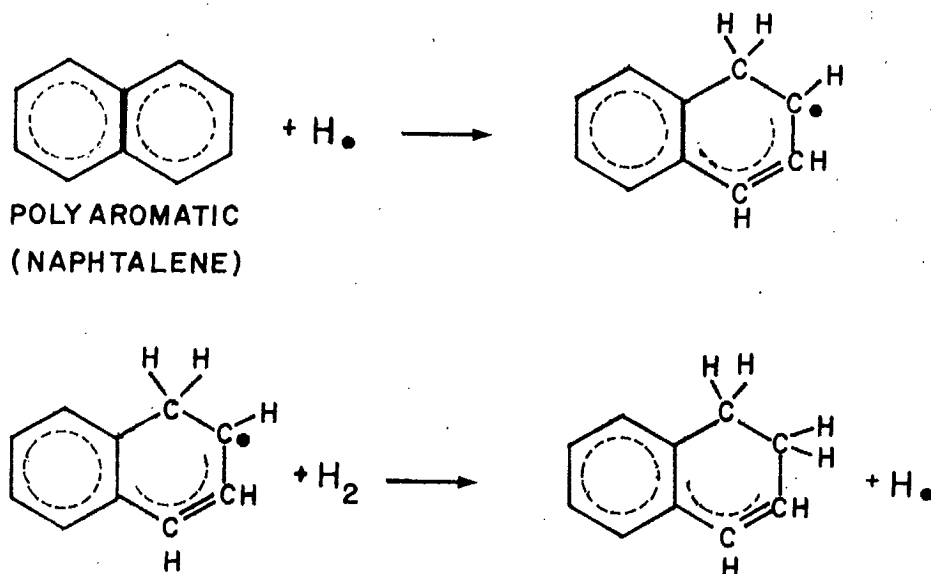
Conversion of polyaromatics to partially hydrogenated species in radical chain reactions.

This indicates that side chain fission is not the only reaction occurring. Evidently, during the hydrocracking also the primary (polyaromatic) elements are attacked. A simplified model (with naphtalene as the polyaromatic) is given in fig. 3,

$$\text{(5)}$$
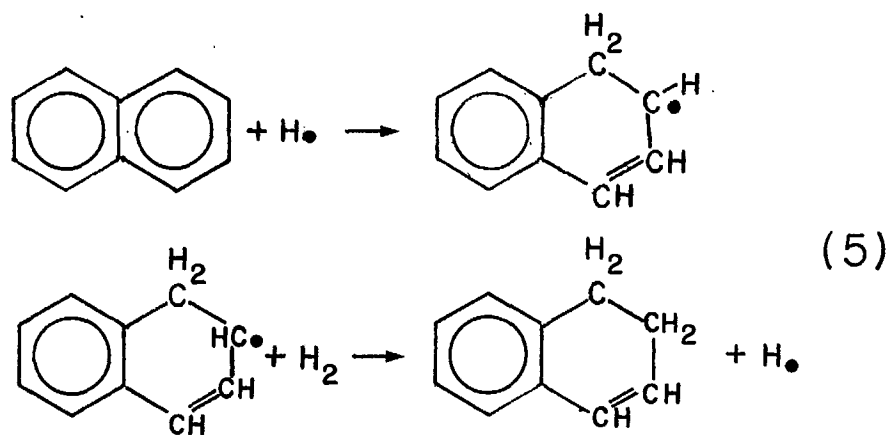
The hydrogenation of the polyaromatic systems needs more H_2 and the H_2 - consumption therefore increases with conversion.

There might be still another factor that is involved. As seen in Fig.3, ring hydrogenation is connected with the formation of a new - CH_2 - CH_2 configuration, i.e. with creation of a new potential center for chain initiation. If the chain, once started, produces "n" new potential centers and if each center has a chance α of producing a new chain, then ($n\alpha$ - 1) is the number of new chains produced from the original one. If this is greater than 7, the chain is branching. The speed of H_2 consumption then slowly increases with time.

In this connection hydrogen donors may be introduced. In first approximation the hydrogen donor (further named DH_2) may be considered as a reactive form of H_2, giving rise (in reactions similar to (3) and (4)) to radicals and recombination agents. Neavel (8) describes the interaction of the hydrogen donor tetralin with coal. It is noteworthy from his observations that the tetralin consumption increases with coal converted to species soluble in the liquid. Most coals show an initial reactivity with hardly any hydrogen consumption, just as athabasca bitumen does, only the amount is much lower, being 20% instead of 50%. Neavel proposes that this 20% is due to some form of coal based hydrogen donor system.

It is interesting in this connection that Doyle[5] finds that tetralin can convert dibenzothiophene to diphenyl + H_2S. The data on the athabasca bitumen also show that desulfurization is occurring predominatly in the later stages of the reaction. According to what has been said above that is where the radical concentration is highest. There is also a difference: tetralin at temperatures below $400^{\circ}C$ does not attack N-hetroaromatics, but thermal hydrocracking ($> 400^{\circ}C$) does give rise to hydrodenitrification.

4) <u>Thermal hydrocracking in the presence of a hydrogenation catalyst</u>

It is not very well known how solid sulphides, acting as hydrogen catalysts, can accelerate hydrocracking although there seem good reasons to assume that they do. This catalytic mechanism may be entirely different from that of the homogeneous (thermal) process.

Hydrogenolysis and ring hydrogenation are well known reactions on metal surfaces, but there is not much evidence for hydrogenolysis on transition metal sulfide systems. Ring hydrogenation, however, is known to be catalysed by sulfides.

GAS-PHASE
(H_2 UNDER PRESSURE)

LIQUID MEDIUM

CATALYST PARTICLE
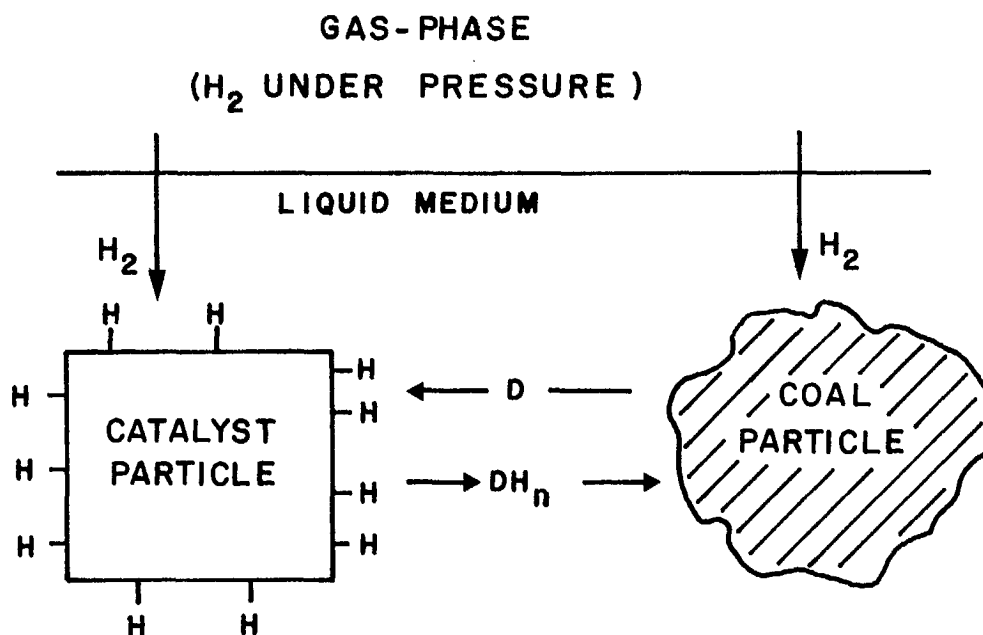
COAL PARTICLE

——— DH_n IS HYDROGEN DONOR, PARTIALLY HYDROGENATED AT CATALYST SURFACE.

——— D IS MOLECULE AFTER HAVING DONATED ITS H TO THE COAL PARTICLE.

Fig 4

HYDROGEN TRANSPORT FROM CATALYST
TO COAL PARTICLE VIA HYDROGEN DONORS
("SHUTTLE MECHANISM")

One might also consider the possibility that a catalyst, with its surface covered by hydrogen atoms due to a dissociative adsorption, acts as a chain transfer agent for the homogeneous chain reaction.

In summing up hydrogenation catalysts, the sulfides may be more versatile hydrogen donors than their organic counterparts. However, contrary to the hydrogen donors they are subject to poisoning.

Leaving aside poisoning for the moment, the question now arises how do catalysts and macrocolecules suceed in interacting with each other so that the catalyst can interact with the thermal hydrocracking reaction developing in this macromolecule. If the latter are relatively small then the number of collisions would be frequent. However, for coal particles the collision frequency would be low and it is very doubtful whether during the few encounters there would be enough transport of hydrogen (atoms) from catalyst to coal particle.

There are, in principal, two manners to speed up the hydrogen transport. One is to assume that hydrogen donors act as transport agents for hydrogen. For instance, naphtalene can become hydrogenated to tetralin on the catalyst, desorb and diffuse to the coal particle, give off its hydrogen and return to the catalyst particle to obtain another load. This is called the "shuttle" mechanism. (fig.4)

The other possibility is to prolong the time during which

coal and catalyst particle remain in contact during a collision.

If they stick together for a considerable time, transfer of H

would be greatly enhanced provided the coal

Fig. 5   Hydrogen transport from catalyst
to coal particle in the case that
the coal particle remains attached
to the catalyst particle
("Sticking" Mechanism)

H_2 UNDER PRESSURE
IN GAS PHASE

LIQUID MEDIUM

H_2

H   H   H

H

H

CATALYST
PARTICLE

S

COAL
PARTICLE

H

H

H   H   H   H
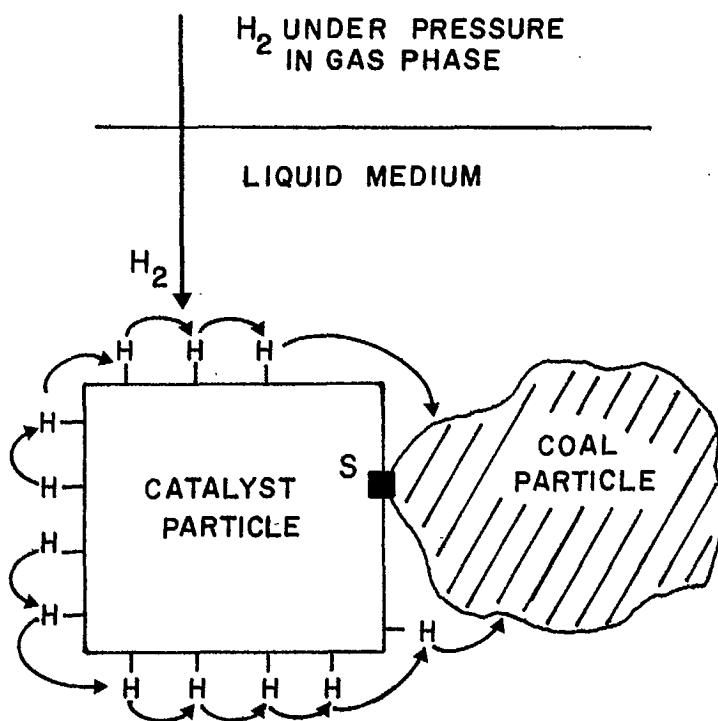
The arrows denote the direction of
migration of H-atoms over the surface
of the catalyst to the coal particle.
The latter is bonded to the catalyst
at site S. ("sticks" to the catalyst)
Note that H migration is essential for
the model.

particle does not block the catalyst particle for interaction with H_2. This is further called the "sticking" mechanism. (fig.5) It is noteworthy that both need mobile H-atoms.

As remarked by Furimsky (10), the shuttle mechanism, because it necessitates the simultaneous presence of catalyst and hydrogen transfer agent, can operate only within what is probably a narrow temperature range. At low temperatures, chain initiation, necessitating the breaking of a C-C bond of 83 kcal mole^{-1} strength, will be very slow. At temperatures in excess of 450°C, the donor agent, because of thermodynamic reasons, will not be able to become hydrogenated so the shuttle ceases to be operative. It is therefore understandable why the experiments of Aarts et al[11] failed to show any influence of hydrogen donor addition in the catalytic hydrodesulfurization of Athabasca bitumen.

The "sticking" mechanism does not seem entirely excluded a priori. It has been pointed out before that the internal, tertiary structure of the coal particles depends on polar interactions. Similar interactions might occur between the cations and anions of the catalyst and structural elements of the coal particles. Belinko[12] has found the structure of coke to be different if FeS was present or not. Furimsky[13] has shown that N-compounds in coke deposited on hydrodesulfurization are bonded to the catalyst. The writer[14] has found that $AlCl_3$ could be adsorbed in considerable quantities on activated carbon (Norit). It was bonded so strongly that even heating at 400°C did not suceed in separating it from the carrier: nevertheless it remained fully active for paraffin isomerization.

There are observations, both from the older German literature
and from more recent work on "H - oil" operation that "sticking"
of the catalyst and coal particles is not a relatively small
effect. It is actually so preponderant that it may lead to the
formation of large clusters. As will be shown later on, the
German application of the 10927 catalyst ($FeSO_4$ on coke) was
supposed to inhibit deposition of asphaltenes on the hydrogenation
catalyst proper. There are also rumours of difficulties in the
"H - oil" process caused by excessive clustering of catalyst and
asphaltenes for some residual oils. Under adverse circumstances
this led to "runaway" situations where exothermic reactions,
such as the formation of CH_4, occurred.

5) <u>Which catalyst to apply in the first step?</u>

This problem had the German scientists working for a long time
before they found what to them seemed a satisfactory solution.
Obviously the catalyst has to be a sulfide, presumably a transition
metal sulfide. Given the adverse conditions under which the catalyst
has to operate, and its consequent short life time, the catalyst has
to be either very cheap or active in such small quantities that it
can be discarded after a single pass. The search for an acceptable
catalyst only met with success when a special support was found, a
brown-coal semi-coke from dust of Winkler generators. According to
Weisser and Landa[2] (p. 295) it is "a support of unique properties
versus asphaltenes because it adsorbs these on the inner active
surface". Actual catalyst components used were (first) MoS_2 and
(later) $FeSO_4$. Presumably the latter was converted to FeS during
operation. (The final $FeSO_4$/coke catalyst is known as catalyst 10927).

Both FeS and the support come as a surprise. Not much is
known about the hydrogenating properties of FeS except that
it is certainly not an outstandingly active catalyst. Herrmann
et al [15] found that it increases the conversion during hydro-
cracking of Athabasca bitumen. Recent results in the pilot
plant tend to confirm its beneficial influence on coke formation.
However, it remains a remarkable observation that catalysts such
as WS_2 or $NiS.2WS_2$ (both undoubtedly superior as attraction agents
for H_2) were not used except in the early stages of the German
research and were then discarded later on. In fact NiW_2S_5, the
best hydrogenation catalyst known to the Germans, was never
seriously considered for actual operation in the first hydrocrack-
ing reaction. This situation led to lively discussions during
our meetings. Two opinions came to the fore. One is based on
the pragmatic argument that since FeS had been shown to be an
acceptable catalyst all efforts should be concentrated on its
optimal use. The other insists on further research with MoS_2 and
WS_2 catalysts operating from the idea that the availability of a
potentially superior hydrogenation catalyst should be a sufficient
reason to probe deeper in the causes that leads to its inapplic-
ability. Both opinions merit attention. In the opinion of this

author the best policy for the near future would be to start

with FeS as the catalyst and later on perform additional

research into the application of the potentially more active

catalysts.

The problem of the support seems even more pressing. It

has been argued above that asphaltene and coke deposits on

the catalyst are due to the strong "sticking" of these

materials on the catalyst. In fact, this is the major problem

in the application of the $Co/Mo/Al_2O_3$ catalyst that still

remains the petroleum industry's only catalytic tool in coal

hydrocracking. It is noteworthy that the underlying assumption

heretofore is that it is the best hydrogenation catalyst known

to the industry in the presence of S – containing compounds.

The means to improve its lifetime were sought in the direction

of modelling its pore structure starting from the assumption

that coke depositing could not be avoided anyhow but then should

be made to occur on sites different from those where the

catalytically active sites are, for instance on the outer

surface of the catalyst. Now, Weisser and Landa [2] report

that "other carriers (than the Winkler dust) agglomerate in the

course of the reaction to form clusters covered on the outer

side with asphaltenes", something that the carbonaceous carrier

apparently does not do. There is no information as to its

pore structure. However, if it has some similarity to that of the

best Al_2O_3 supports, it should have special advantages. The

inorganic catalyst systems might be screened from direct inter-

action with the asphaltenes while at the same time its outer

surface should have less tendency to adsorb asphaltenes with

consequent clustering of the catalyst particles. This kind

of thinking leads us to consider carbonaceous supporting

materials as potentially similar in pore architecture to

materials such as, for instance, Al_2O_3. Consequently, one

should not stay with the assumption that any coal should be

applicable as support for the catalyst; on the contrary precisely

as for alumina one should try to structure the support. A care-

ful research, starting with the literature, should be made to

ascertain which carbon carriers are available at the moment, what

is there structure and how do we have to operate to deposit the

inorganic catalysts components at the required places and as the

required catalyst structures. Since the CANMET laboratories have

done extensive work on the structures of coals and coke and have

the experience and instruments to investigate them they might

very well be the best place to originate such a research.

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    Calgary, Alberta 26-27 Oct. 1977.

12) K. Belinko, (private communication).

13) E. Furimsky, (private communication).

14) G.C.A. Schuit, (unpublished work 1937-1940 from

    the Shell Lab - Amsterdam).

            The catalysts were prepared by sublimation of

    $AlCl_3$ over Norit-activated carbon, the support adsorbing an

    amount of $AlCl_3$ equal to its own weight. The final product

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    and $ZnCl_2$-promoted Fe catalysts for hydrocracking of Athabasca

    bitumen",

    CANMET report 77-50.