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(54) Improvements for reducing coke deposition in thermal upgrading processes.

(57) In a hydrocracking process, a feed mixture comprising a heavy oil containing asphaltenes and sulfur moieties, an oil−soluble metal compound additive (e.g. $Fe(CO)_5$) which will impede coalescence of coke precursors, and a hydrocarbon diluent which is a solvent for the asphaltenes, is mixed and heated to a mild temperature (e.g. 150 °C) to disperse the additive and associate it with the asphaltenes. The mixture is then further heated to hydrocracking temperature and reacted in a reactor wherein a prolific hydrogen flow is passed through the breadth and length of the charge to mix the charge and strip light ends. The combination of features results in impeding the evolution of coke precursors, so that a substantial proportion thereof remains in the agglomerate state, and in improving the conversion of the 504 °C$^+$ part of the feedstock.

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FIELD OF THE INVENTION

This invention relates to an improved hydrocracking process wherein inclusion of a combination of light ends stripping, addition of asphaltene – solubilizing diluent, and addition of an oil-soluble Fe, Ni or Co compound additive, which inhibits coalescence of coke precursors, results in improved conversion of the 504 °C$^+$ fraction and reduction of adhesive coke deposition.

BACKGROUND OF THE INVENTION

The present invention was developed in connection with hydrocracking of a heavy hydrocarbon feedstock particularly high in content of asphaltenes and sulfur moieties. More particularly, the feedstock tested was vacuum tower bottoms produced from distillation of bitumen. The invention is not limited in application to such a feedstock; however, it will be described below with specific respect to it, to highlight the problems that required solution.

Bitumen contains a relatively high proportion of asphaltenes. When the bitumen or its vacuum tower bottoms is hydrocracked, the asphaltenes produce coke precursors, from which solid coke evolves. The coke deposits on and adheres to the surfaces of the reactor and downstream equipment. In addition, since part of the feedstock is consumed in the production of coke, the conversion of the feedstock to useful products is reduced.

The present assignee is an Alberta government research agency which has been given a mandate to foster improvements in the upgrading of bitumen and other heavy oils. Realizing the conversion limitation and operating problems that coke deposition inflicts, it initiated a research project to investigate the mechanisms of coke formation and to look for improvements that might be applied commercially.

The present processes were generated as a result of this work. The research involved a progression of concepts and experimental discoveries that came together to yield several distinct process modifications that can be usefully applied individually or as sub-combinations. In addition, an overall process combination has been developed that is capable of providing a high order of conversion coupled with reduced deposition of adhesive coke and reduced production of coke.

Searches and prosecution of the parents of this application have identified the following relevant prior art:

U.S. 4,294,686 (Fisher et al) teaches that, when liquid hydrogen donor oil is used along with hydrogenation in connection with hydrocracking of bitumen vacuum tower residua, coke deposition is allegedly eliminated.

However the present assignee and the assignee of the above cited patent jointly conducted a large scale hydrocracking test on bitumen residue using a liquid hydrogen donor process. This test encountered serious coke production problems. It appears that hydrocracking high asphaltene content feed such as bitumen residue requires more than the presence of liquid hydrogen donor oil alone.

U.S. 4,455,218 (Dymock et al) teaches use of $Fe(CO)_5$ as a source of catalyst for hydrocracking heavy oil in the presence of H_2. The reaction is allegedly characterized by elimination of coking.

U.S. 4,485,004 (Fisher et al) teaches hydrocracking heavy oil in the presence of hydrogen, hydrogen donor material, and catalyst comprising particulate Ni or Co on alumina.

U.S. 4,134,825 (Bearden et al) teaches forming solid, non-colloidal catalyst in situ in heavy oil using trace amounts of Fe added in the form of an oil-soluble compound such as iron carbonyl. The metal compound may be added to the oil and heated to 325-415 °C in contact with hydrogen to convert it to a solid, non-colloidal, catalytic form. This catalyst is then used in hydrocracking the oil and it is stated that coke formation is inhibited.

SUMMARY OF THE INVENTION

In one aspect of the research work underlying the present invention, coke was produced by hydrocracking a mixture of diluent and bitumen vacuum tower bottoms ("VTB") and the coke composition was studied microscopically. It was found that at progressive stages of the evolution of the coke precursors into adherent solid coke, there were present different species of isotropic and anisotropic submicron and micron-sized spheroids. Some of the figures forming part of this specification illustrate these various species, which we have identified with the following labels:

- isotropic sphere; (Figures 1 and 6)
- basic isotropic particle; (Figure 1)
- isotropic agglomerates; (Figure 3)

- anisotropic spheres; (Figures 2 and 5)
- basic anisotropic particles; (Figure 2)
- anisotropic fine mosaic particles; (Figure 4)
- anisotropic coarse mosaic particles; (Figure 4) and
- anisotropic agglomerates (Figure 4).

It was further experimentally discovered:

- That the evolution of the coke precursors into coke involved a coalescence process from the minute isotropic species to the larger species; (Figures 5 and 6) and
- that if the coalescence process was inhibited with the major portion of the precursors remaining in the isotropic and anisotropic agglomerate state, then the deposition of adherent and solid coke was significantly reduced and even virtually eliminated.

These recognitions led to seeking out and identifying a compatible additive and a compatible diluent that would interfere with the coalescence process and assist in reaching an end where, if any coke was present, it would be present predominantly in the form of agglomerate species, preferably in the isotropic state. It was postulated that a well dispersed oil-soluble metal compound might be used to react in situ with sulfur moieties of the bitumen VTB to produce a colloidal dispersion having wetting characteristics that would enable the colloidal moieties to collect at the surfaces of the precursor spheroids and prevent the spheroids from coalescing. Furthermore, it was postulated that an appropriate diluent might be used to disperse this additive.

It was experimentally determined that if an oil-soluble metal compound additive, decomposable at hydrocracking temperatures and selected from the group consisting of Fe, Ni and Co compounds, most preferably iron pentacarbonyl ($Fe(CO)_5$), was mixed, at an elevated temperature less than the decomposition temperature of the compound, with diluent and bitumen VTB and the mixture was then heated to hydrocracking temperature and underwent hydrocracking, then the postulated mechanism appeared to take place. Stated otherwise, the inclusion of the additive in the reaction mixture undergoing hydrocracking did have the desired effect of greatly reducing the deposition of adherent solid coke. Examination of cooled solid samples after hydrocracking showed that the major portion of this coke was in the form of isotropic agglomerates. It is believed that at reactor temperature this coke would have taken the form of minute spheroids of coke precursor. Chemical analysis of the sample coke indicated that additive metal sulfide was associated therewith in a significant amount and that most of the metal sulphides were of dimension of the order, 1 nanometer.

In summary, it is believed that if an oil-soluble, decomposable metal compound is firstly well dispersed at moderate elevated temperature (e.g. 150 ° C) in the heavy oil and becomes associated with the asphaltenes, and if the mixture is then subjected to hydrocracking temperature, colloidal metal sulfide moieties are produced which are thought to accumulate at the surfaces of spheroids rich in coke precursors and interfere with their coalescence. Upon completion of hydrocracking it is believed that the coke precursors were largely transformed into isotropic agglomerates. It is found that the deposition of adhesive solid coke is significantly reduced.

Turning now to a second approach that was explored, it was well known that asphaltenes precipitate when pentane is added. Upon considering this known fact, applicants conceived the notion of emphasizing the removal of light ends during hydrocracking to determine the effect on coke formation. Experimental work was therefore initiated to determine the effect of stripping light ends (Boiling point ("B.P.") <220 ° C) from the hydrocracking zone. The experiment showed that coke formation was reduced when the light ends were consistently removed during hydrocracking. To improve this, it appeared desirable to apply mixing to the mixture during hydrocracking. Mixing would have the further attribute of maintaining dispersion of the additive metallic component.

To further elaborate on the foregoing, it had been noted that coke formation is associated with phase separation. It was postulated that, if the coke precursors became richly concentrated in a distinct phase, then the coke formation process would proceed rapidly and quantitatively. To impede this, it appeared desirable to strip the light ends.

Therefore, as a second preferred aspect of the invention, a tube reactor is used, preferably substantially free of internals, and the hydrogen flow through the reactor is prolific and is arranged to achieve mixing throughout the length and breadth of the reaction zone. The prolific hydrogen flow functions to strip light ends from the zone. More preferably, mixing and stripping is accomplished by ensuring that the hydrogen flow is sufficient to provide the following Peclet Number ("P.N.") regime in the reactor chamber:

Liquid:

axial P.N. = less than 2.0, preferably less than 1.0, most preferably about 0.2

Gas:

axial P.N. = more than 3.0.

In another thrust at reducing phase separation, a diluent for solubilizing the asphaltenes was added to the reaction mixture. The diluent was a hydrocarbon fraction having a B.P. of about 220 – 504 ° C, preferably 220 – 360 ° C. It was hoped that the diluent would in addition function usefully as a liquid hydrogen donor and, in combination with the metal sulfide (which is catalytic in nature) and the plentiful hydrogen, would create a regime that would be favourable to high conversion of the 504 ° C^+ fraction and low coke deposition. Experimental runs indicated that when the combination of diluent addition, light ends stripping with hydrogen, and well dispersed additive addition was practised in the context of hydrocracking of heavy oil containing asphaltenes and sulfur moieties, exceptionally high conversion of the 504 ° C^+ hydrocarbons could be achieved, together with virtually no adhesive coke deposition. When the diluent was omitted from the combination, or the diluent was not a good solvent of asphaltenes or when stripping of light ends was not sufficient, experimental runs showed significant coke deposition.

Dispersion is preferably achieved by preheating the heavy oil plus additive plus diluent mixture to a mild temperature (.e.g 150 ° C) that is significantly less than hydrocracking temperature, to reduce the viscosity of the oil, and mixing the three components, prior to heating the mixture to elevated temperature for hydrocracking and introducing it into the hydrocracking reactor.

In a broad form therefore, the invention is an improvement of heavy oil hydrocracking comprising:

- mixing an oil – soluble Fe, Ni or Co compound, heavy oil and a solvent for asphaltenes, preferably at a temperature that is sufficiently elevated to reduce the oil viscosity but less than hydrocracking temperature, to achieve substantially uniform dispersion of the compound in the oil in association with the asphaltenes;
- and then further heating the mixture sufficiently for hydrocracking to proceed and introducing the heated mixture into the reaction zone of a hydrocracking reactor;
- temporarily retaining the charge of mixture in the reactor chamber, passing hydrogen through the breadth and length of the charge and removing unreacted hydrogen and entrained light ends from the reactor;
- whereby hydrocracking is achieved in conjunction with inhibition of coke production, inhibition of deposition of adherent solid coke and improvement of conversion of the 504 ° C^+ fraction; and
- whereby the evolution of coke precursors is arrested sufficiently so that the major portion of said precursors remains in the agglomerate state.

Broadly stated, the invention is an improvement in a hydrocracking process wherein heavy hydrocarbon feedstock containing asphaltenes and sulfur moieties is heated to hydrocracking temperature and conveyed into the chamber of a reactor and reacted therein with hydrogen, whereby coke is formed as an undesired product. The improvement comprises: as a preliminary step, prior to heating to hydrocracking temperature and reacting, mixing and heating the feedstock, an oil – soluble metal compound additive and a hydrocarbon solvent for asphaltenes, said metal in the additive being selected from the group consisting of Fe, Ni and Co, to form a mixture having a mild elevated temperature that is less than hydrocracking temperature, said mixture having the metallic component substantially uniformly dispersed therein; then further heating the mixture to a sufficiently high temperature so that hydrocracking will take place in the reactor; introducing the heated mixture into the chamber of the reactor; temporarily retaining the charge of heated mixture in the chamber, continuously passing hydrogen through substantially the breadth and length of the charge, and removing unreacted hydrogen and entrained light ends from the upper end of the chamber, to effect hydrocracking and cause stripping of light ends from the charge; and removing the reaction products from the reactor.

DESCRIPTION OF THE DRAWINGS

Figure 1 is a photographic representation showing the nature of isotropic spheres(s) and basic isotropic particles (b), magnified 1650X;

Figure 2 is a photographic representation showing the nature of anisotropic spheres (s) and basic anisotropic particles (b), magnified 1650X;

Figure 3 is a photographic representation showing the nature of isotropic agglomerates (g) along with anisotropic solids (a) and iron sulfide particles (s), magnified 1650X;

Figure 4 is a photographic representation showing the nature of anisotropic agglomerates (a), anisotropic fine mosaic (f), and anisotropic coarse mosaic (c), magnified 1650X;

Figure 5 is a photographic representation showing anisotropic coke particles growing via the coalescence of smaller anisotropic spheres (c), magnified 1650X;

Figure 6 is a photographic representation showing isotropic coke particles growing via the coalescence of smaller isotropic spheres (s), magnified 1650X;

Figure 7 is a photographic representation of the reactor baffle after run CF-30;

Figure 8 is a photographic representation of the reactor baffle after run CF-9;

Figure 9 is a photographic representation of the reactor baffle after run CF-31;

Figure 10 is a bar chart setting forth coke composition for runs CF-9, CF-31 and CF-30;

Figure 11 is a photographic representation of the reactor baffle after run CF-A3;

Figure 12 is a bar chart setting forth coke composition for runs CF-A3 and FE-1;

Figure 13 is a photographic representation of the reactor baffle after run FE-1;

Figure 14 is a photographic representation of the coke particles from run FE-1, which were mostly isotropic agglomerates (A) associated with iron sulfides. Isotropic spheres (S) were trapped among the agglomerates;

Figure 15 is a photographic representation of the coke particles from run FE-1 showing isotropic spheres (s) which were effectively prevented from growing into basic isotropic particles by the iron derivative;

Figure 16 is a photographic representation of the reactor baffle after run CF-38;

Figure 17 is a plot showing nitrogen flowrate versus coke production for Example V;

Figure 18 is a phase diagram for Example V;

Figure 19 is a plot showing pressure profiles for runs involving different additives;

Figure 20 is a bar plot showing hydrogen consumed for various runs;

Figure 21 is a bar chart setting forth coke composition for a number of the runs;

Figure 22 is a photographic representation of coke from run CF-40, showing mostly a continuous sheet of basic isotropic particles (B), magnified 1650X; and

Figure 23 is a photographic representation of the reactor baffle after run CF-40.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The feedstock to the process is heavy oil. This term is intended to include bitumen, crude oil residues and oils derived from coal-oil co-processing that contain asphaltenes and sulfur moieties. A typical feedstock could be vacuum tower residues derived from Athabasca bitumen.

The feedstock is mixed with the oil-soluble compound additive, preferably $Fe(CO)_5$, and a solvent for asphaltenes, preferably a recycled stream having a boiling point in the range 220 °C - 504 °C. The amount of additive added is in the range 0.01-5 wt. % based on the weight of the feedstock. The weight ratio of diluent to feedstock is in the range 1:10 to 3:1. The preferred weight ratio range is 1:4 to 2:1.

Mixing may be accomplished by pumping the mixture from a storage tank, through a pre-heater and back to the tank. Preferably the mixture is preheated to a temperature, significantly less than hydrocracking temperature at which the oil viscosity is sufficiently low to permit uniform dispersal of the additive. This could be 150 °C.

The mixture is then heated to a temperature (e.g. 350 °C) which is sufficiently high so that hydrocracking temperature (e.g. 455 °C) will be achieved in the reactor when the mixture is contacted with hydrogen.

In the reactor, a Peclet Number regime, within the ranges previously described, is maintained to ensure that stripping of light ends using the hydrogen is achieved.

The development and background of the claimed invention is set forth in the following examples.

EXPERIMENTAL

The following examples are included to demonstrate the operability of the present process.

All the tests in examples I-V were performed in a 1 litre, baffled, stirred autoclave. The charge, comprising Athabasca vacuum tower bottoms (504 °C^+) as feedstock, solvent (otherwise referred to as "diluent") and catalyst (if used), was introduced into the autoclave. The autoclave was sealed, purged free of air, pressurized with nitrogen or hydrogen and heated to 430 °C. The reactor was stirred at 800 rpm, with a reaction temperature of 430 °C and a reaction time of 105 minutes.

Properties of the Athabasca vacuum tower bottoms (VTB) are given below.

	wt %
C	81.76
H	9.51
S	6.23
N	0.78

API @ 16 ° C: 2.43
IBP 504 ° C

Table 1 herebelow provides the composition (wt. %) of diluents used during the experimental procedures.

It is noteworthy that according to the relative content of condensed dicycloparaffins and benzocycloparaffins, diluent B has the most hydrogen donor capability and diluent C has the least.

TABLE 1

	Diluents		
Hydrocarbon Type	A	B	C
Paraffins	13.02	16.38	13.10
Uncondensed Cycloparaffins	7.32	6.29	5.51
Condensed Dicycloparaffins	5.20	13.03	3.80
Condensed Polycycloparaffins	0.49	1.27	0.15
Alkylbenzenes	18.07	15.25	11.50
Benzocycloparaffins	32.29	37.54	20.36
Benzodicycloparaffins	4.77	3.80	5.53
Naphthalenes	15.86	6.11	19.49
Naphthacycloparaffins	1.61	0.26	7.73
Fluorenes	0.82	0.00	6.21
Phenathrenes/Anthracene	0.61	0.00	6.18

EXAMPLE I

This example illustrates the effect of diluent. The autoclave was charged with 109 grams of bitumen and 220 grams of diluent A, B or C. A nitrogen overpressure of 0.55 MPa was applied and the contents were thermally cracked at 430 ° C for 105 minutes.

The results of the tests are shown in Table 2. The reactor was opened and Figures 7, 8 and 9 show the coke deposited on the baffles for experiments CF-30, CF-9 and CF-31, respectively.

It is noteworthy that experiment CF-31 produced as much coke as experiment CF-9 but that the coke was most easily dislodged from the baffles and reactor surfaces. Moreover, although experiment CF-31 produced nearly twice as much coke as experiment CF-30, the coke was most easily dislodged. The surfaces of the reactor and baffles of experiment CF-31 were least fouled.

The coke from the three experiments was examined microscopically and the results are shown in Figure 10. It was noted that when the agglomerate content (which was anisotropic) was relatively high (Experiment CF-31), the coke deposition and adhesion was least intense in spite of the fact that diluent C has the least hydrogen donor capability.

TABLE 2

Test conditions: 430°C, 105 min., 800 rpm, 0.55 MPa initial N_2 pressure

Diluent to Vacuum Tower Bottom ratio is 2:1

Experiment No.	CF-30	CF-9	CF-31
Diluent type	B	A	C
Yield (wt% vacuum tower bottom)			
H_2	0.21	0.07	0.08
C_1 - C_4	10.3	10.8	14.8
C_5 - 200°C	42.3	57.1	55.2
200 - 360°C	-8.6	-37.2	-43.5
360 - 504°C	22.8	26.5	30.6
504°C$^+$ (coke free)	26.3	33.8	34.6
Coke	4.3	7.7	7.7
Conversion to 504°C$^-$ & coke	73.7	66.2	65.4
Mass Balance	98.2	97.3	96.9

EXAMPLE II

This example illustrates the effect of hydrogen overpressure.

The experimental conditions and results are shown in Table 3. Experiment CF-A3 is compared with experiment CF-9.

Figure 11 shows coke deposited on the baffles for experiment CF-A3. Compared to Experiment CF-9 (Figure 8), the coke yield and deposition of Experiment CF-A3 was least.

Figure 12 shows results from a microscopic examination of the coke obtained from experiment CF-A3. It is to be compared with those results shown in Figure 10 for experiment CF-9. The results are similar.

In both experiments, over 80% of the coke components were of the anisotropic type. The agglomerate concentration for experiment CF-A3 was not significantly more than that of experiment CF-9.

This example teaches that abundance of hydrogen alone does not neutralize the adhesiveness of the coke precursors nor does it selectively modify the coke composition.

TABLE 3

	CF-9	CF-A3
Diluent	A	A
Yield (wt % VTB)		
H_2S	0.07	2.2
C_1 - C_4	10.8	11.6
C_5 - 200°C	57.1	44.0
200 - 360°C	-37.2	-18.0
360 - 504°C	26.5	30.1
504°C^+ (coke free)	33.8	27.7
Coke	7.7	3.1
Conversion to 504°C^- & coke	66.2	72.3
Mass Balance	97.3	98.5
Selectivity to C_5 - 504°C^-		77.6
Conditions: CF-9: 430°C, 105 min., 800 rpm, 0.55 MPa N_2 initial pressure, diluent: VTB ratio 2:1 Conditions: CF-A3 430°C, 105 min., 800 rpm, 6.8 MPa H_2 initial pressure, diluent: VTB ratio 2:1		

EXAMPLE III

This example illustrates that coke containing much agglomerate is not adhesive.

The results and conditions of experiments CF-A3 and FE-1 are shown in Table 4.

Figure 13 shows no coke deposited on the baffles for experiment FE-1. Compared to Experiment CF-A3 (Figure 11), the coke yield and deposition of Experiment FE-1 was least.

The coke from Experiment FE-1 was observed to be minute particles loosely settled in the bottom of the reactor.

TABLE 4

Test conditions: 430°C, 105 min., diluent/vtb = 2:1, 800 rpm

Experiment No.	CF-A3	FE-1
Diluent	A	A
Gas/Pressure (MPa)	H_2/6.8	H_2/6.8
Additive (metal, wt% vtb)	-	Fe/0.5
Yields on vtb, wt%		
H_2S		1.2
C_1 - C_4	11.6	6.6
C_5 - 200°C	44.0	37.7
200 - 360°C	-18.0	-9.1
360 - 504°C	30.1	31.2
504°C$^+$ (coke free)	27.7	31.4
Coke	3.1	1.6

Figure 12 shows results from a microscopic examination of coke obtained from experiments CF-A3 and FE-1. The results are very different. The coke from experiment FE-1 is over 80% isotropic agglomerate.

Figures 14 and 15 for Experiment FE-1 showed that solid particles were all loosely associated with one another. Coke composition showed that over 97% of the components were of the isotropic type - see Figure 12. Isotropic agglomerates accounted for 80% of the coke composition.

This data for experiment FE-1 indicated that the adhesiveness of the coke precursors was effectively neutralized by the highly dispersed iron compound. Where isotropic spheres were concentrated (see Figure 15), the isotropic agglomerates effectively prevented the spheres from coalescing into basic isotropic particles.

It is noteworthy also, that additive present as iron sulphide amounts to approximately 1/3 the weight of the coke but is not so evident.

EXAMPLE IV

This example further illustrates that the choice of diluent is important.

The experiment CF-38 was done according to the teaching of U.S.4,455,218 (Dymock et al). The experimental conditions were identical to those shown in Table 4 for experiment FE-1. Whole Athabasca bitumen was used instead of Athabasca VTB and no diluent was added. The whole bitumen contained about 60 wt. % hydrocarbon boiling at temperatures greater than 504°C. 0.5% (metal) of iron pentacarbonyl was added on the basis of equivalent 504°C$^+$ content in the bitumen.

The coke yield was 7.9% (504°C$^+$ basis) and this coke adhered very strongly to surfaces of the reactor and baffles. Figure 16 shows the coke deposited on the baffles.

EXAMPLE V

This example illustrates the effect of the rates of continuously removing highly volatile components from the reacting fluids.

The one liter autoclave was fitted with a dip tube for sparging N_2 or H_2 into the reacting liquid, an outlet permitting continuous flow of product gas, and cold trap condensers to remove volatile products from the gas stream before collecting the latter in a sample bag for analysis. Experiments were conducted in the above described reactor at 430 ° C for 105 minutes under 550 KPa pressure both without gas flow and with gas flowing continuously into and out of the reactor. In each experiment, 110 g of Athabasca 504 ° C$^+$ vacuum tower bottoms (VTB) and 220 g of a diluent were used. Table 5 presented herebelow gives the reaction conditions and experimental results.

TABLE 5

Autoclave Test Results

Experiment No.	1	2	3	4	5	6
Diluent Type	A	A	B	B	B	B
Nitrogen Flow Rate (l/min)	0.0	1.89	0.0	0.2	1.05	2.16
Yield (wt% VTB):						
C_1 - C_4	15.5	16.5	10.3	10.0	8.2	13.8
C_5 - 504^{0}C$^-$	42.3	38.1	56.5	56.5	56.6	51.4
504^{0}C$^+$ pitch (coke free)	34.6	38.8	26.3	27.0	30.0	29.7
Coke	7.9	3.8	4.3	3.8	3.4	3.1
Condensate recovered from purge gas (wt% VTB)	--	47.5	--	3.1	23.9	39.7

TABLE 6

imulated Distillation Results of Condensate from Experiment No. 5			
% Off	Temp ° C	% Off	Temp ° C
IBP	34	55	146
5	57	60	156
10	70	65	164
15	84	70	176
20	94	75	190
25	98	80	201
30	111	85	210
35	116	90	219
40	123	95	229
45	131	FBP	262
50	139	- -	- -

Figure 17 shows the amount of coke produced as a function of the rate of flow of nitrogen. As shown for diluents A and B the amount of coke nroduced decreased as the rate of flow of nitrogen was increased. At high rates of flow of nitrogen, the amount of coke produced for the experiment using diluent B (the best hydrogen donor solvent) was not very different from that for the experiment using diluent A (the worst hydrogen donor solvent).

It is noteworthy in Table 5, that for those conditions providing the least amount of coke, the amount of condensate recovered from the purge gas was highest. This was true for both diluents A and B.

Table 6 shows results of simulated distillation of the condensate from experiment 5. About 90% of this condensate boils at temperatures less than 220 ° C.

This example teaches that coke production is reduced if the low boiling products are removed continuously (stripped) from the reacting fluids. Moreover, it teaches that coke production is reduced if the low boiling products are removed from the diluent.

These observations are consistent with the model that has asphaltenes separate as another liquid phase from the reacting fluids. In analogy with the common experiment that has pentane added to bitumen to yield solid asphaltene as a precipitate at room temperature, such an experiment done at high temperature is expected to yield asphaltene as a separate liquid phase. Moreover, it is expected that this separate liquid phase will be rich in the asphaltenes that thermally crack to form coke.

This phase separation is shown schematically in Figure 18. The three components of this Figure are respectively labelled asphaltenic, aromatic and paraffinic and alicyclic to represent those fractions having boiling points 504 ° C^+, 220 – 504 ° C and 220 ° C, respectively. The arrow indicates the evolution of the composition of whole bitumen as might occur for Example IV.

EXAMPLE VI

This example illustrates the effect of using hydrogen for continuously removing highly volatile components from the reacting fluids.

A continuous flow system consisting of a preheater, a 2-litre stirred reactor and a product collection system was used. The baffles and stirrer were similar to those of the previous examples. A mixture of Athabasca VTB, diluent A and preheated hydrogen were pumped through the preheater into the bottom of the stirred reactor. Products were removed through a dip tube with its entrance set at 60% of the reactor's height.

The experimental conditions and results are shown in Table 7 for experiments 7, 8 and 9. In each experiment the hydrogen flow rate was 12 slpm. In experiment 7, the liquid hourly space velocity is twice that of experiment 8 and of experiment 9. The temperature of the reacting fluids is 20 ° C higher than that of experiment 8.

Noteworthy is that the amount of coke produced in experiment 8 was less than that of experiment 7 and that almost no coke at all was produced in experiment 9, in spite of the increased severity of hydrocracking from experiment 7 to 8 to 9. Such a result is expected if one considers that the highly volatile fractions of the reacting fluids are removed with increasing efficiency as conditions are changed from experiment 7 to 8 to 9. In experiment 9 the pipe connecting the reactor to the product collection vessel became plugged at the completion of the experiment.

In experiment 10, two one-litre reactors were placed in series with the entrances to the dip tubes adjusted a 50% and 70% of reactor height. The conditions and results are shown in Table 7.

TABLE 7

Continuous Bench Unit Test Results

Diluent Type : A

Pressure : 10 MPa

Experiment No.	7	8	9	10
Reactor 1 (l)	1.2	1.2	1.2	0.5
Reactor 2 (l)	--	--	--	0.7
Reaction Temperature (°C)	440	440	460	440
Liquid Hourly Space Velocity (hr^{-1})	1	0.5	0.5	1
Hydrogen Flow rate (slpm)	12	12	12	16
VTB Concentration in feed (Wt%)	63.10	65.02	45.53	47.3
Conversion (Wt% VTB to coke and 504°C-)	69.0	78.3	98.1	79.8
Yield, Wt% VTB C_1 - C_4	5.2	7.9	17.3	7.2
C_5 - 200°C	16.3	19.1	31.4	15.1
200°C - 360°C	23.4	31.1	43.1	24.2
360°C - 504°C	20.3	18.4	9.3	24.8
Coke	4.6	3.1	0.1	4.6
504°C$^+$ Pitch (coke free)	31.0	21.7	1.9	24.8
Total distillate C_5 - 504°C	60.0	68.6	83.8	64.7

It is noteworthy that the conversion was similar to that of experiment 8. This was expected given the different liquid hourly space velocities and different number of reactors. However, the amount of coke produced in experiment 10 was higher than that produced in experiment 8 in spite of the higher rate of flow of hydrogen of experiment 10.

This example teaches that hydrogen flow and reactor temperature may be used skilfully to remove (strip) low boiling products from the reacting fluids to reduce the amount of coke that is produced. Moreover it teaches that for one or more hydrocracking reactors in series, a configuration having one reactor only produces the least amount of coke. Moreover, it teaches that if several hydrocracking reactors are placed in series, then least coke is produced if volatile hydrocarbons are removed from the fluids as they pass from one reactor to the next.

EXAMPLE VII

This example illustrates that by skilful use of reactor configuration, severity of reaction, stripping of volatile components and additive, high conversions of VTB to distillate products can be obtained with acceptable production of coke and minimal fouling of the reactor.

The continuous flow system of experiments 7, 8 and 9 of Example VI was used. The additive was iron pentacarbonyl. The conditions and results of experiments 11 and 12 are shown in Table 8.

The conditions for experiment 12 were much more severe than those of experiment 11. Nevertheless, all surfaces in the reactor, pipes and collection vessel remained free of fouling by coke and the coke that was produced was a fine friable matter that settled in the product collection vessel.

The results of a microscopic examination of the coke produced in experiment 12 are shown in Table 9. 74% of the coke was in the form of agglomerates. 23% of the coke was in the form of isotropic spheres but these spheres were isolated and trapped in a matrix of agglomerates.

This example teaches that high conversions with minimal fouling of the reactor may be obtained when the coke that is produced is mostly agglomerates.

TABLE 8

Experiment No.	11	12
Reactor 1 (1)	1.2	1.2
Reactor 2 (1)	--	--
Reaction Temperature (°C)	450	450
Liquid Hourly Space Velocity (hr^{-1})	1.05	0.73
Hydrogen Flow rate (slpm)	8	12
VTB Concentration in Feed (wt%)	47.5	47.8
Catalyst (Wt% of Fe based on VTB)	0.5	0.5
Conversion (Wt% VTB to coke and 504°C+	67.8	82.1
Yield (Wt% VTB) C_1-C_4	5.2	9.4
C_5-200°C	19.1	22.9
200-350°C	19.9	27.6
350-504°C	21.9	21.1
Coke	2.4	2.8
504°C+ Pitch Coke free	32.2	17.9
Total distillate C_5-504°C	60.9	71.6

Note that if H_2 flow was not increased in experiment 12, one would expect that a 14% increase in conversion should be accompanied by much higher coke yield than the 0.4% recorded.

TABLE 9

Coke Composition of Run No. 12	
	Vol %
Basic Isotropy	3
Isotropic Spheres	23
Isotropic Agglomerates	42
Basic Anisotropy	0
Anisotropic Fine-Mosaic	0
Anisotropic Coarse-Mosaic	0
Anisotropic Spheres	0
Anisotropic Agglomerates	32

EXAMPLE VIII

This example also compares various additives and various metal compounds.

A series of tests using the following additives:

- fine, Alberta coal char,
- oil soluble nickel naphthanate,
- oil soluble cobalt naphthanate, and
- oil soluble molybdenum naphthanate were carried out to compare their relative effectiveness in preventing coke formation and deposition. Iron pentacarbonyl was used as the bench mark for comparison.

All tests were performed under a common reaction condition:

0.5 wt % (metal on vacuum tower bottoms) additive, Athabasca vacuum tower bottoms (33.3%), diluent (66.7%), 6.8 MPa initial hydrogen pressure, 800 rpm stirrer speed, 430°C, and 105 minutes reaction time. In the case of Alberta coal char, the amount added was equivalent to 4% of the vacuum tower bottoms.

Pressure profiles presented in Figure 19 and the hydrogen consumption results presented in Figure 20, showed the following observed order for hydrogen consumption:
molybdenum additive (CF-40) 68%
nickel additive (CF-41) 39%
cobalt additive (CF-41) 27%
iron additive (FE-1) 26%
and coal char (CF-43) 21%

Product distributions presented in Table 10 showed the following order of additive for:

- vacuum tower bottoms conversion
  molybdenum > iron > coal > char > nickel > cobalt
- selectivity to C_5 - 504°C
  nickel > iron > cobalt > molybdenum > coal char
- coke formation
  nickel < cobalt < coal char < iron < molybdenum.

Figure 21 shows the effectiveness of the various additives in converting the coke precursors to form the non-depositing isotropic agglomerate coke particles. Although experiments using additives containing molybdenum consumed the highest amount of hydrogen, over 90% of the coke was basic isotropic particles. In Figure 22, coke from CF-40 appeared as a continuous sheet of basic isotropic particles. The coke from CF-40 was evidently more densely packed than the coke from FE-1 using the iron additive (Figures 14 - 15).

As pointed out earlier, it was discovered that, to prevent the coke from depositing on the reactor walls, the additive must selectively transform the coke precursor spheres into isotropic agglomerates. The lack of isotropic agglomerates in coke from experiment CF-40 suggested an explanation for the deposition of adherent coke on the reactor baffles (Figure 23). In contrast, the reactor baffles in experiments which iron pentacarbonyl (Figure 13) did not have any adherent coke.

This example teaches that appropriate selection of additive may inhibit coke production and may inhibit deposition of adherent coke provided that an appropriate diluent is used. Such an additive will maximize the fraction of coke that is in the form, isotropic agglomerate. Oil soluble additives containing iron or cobalt or nickel or combinations of these are preferred.

TABLE 10

Test Conditions: 430°C, 6.8 MPa H_2 initial pressure, 105 min, 800 rpm

additive added = metal concentration of 0.5 wt% vtb

Diluent/vtb = 2:1

Experiment No.	CF-A3	CF-43	FE-1
Additive	-	Coal char (4%)	Fe
Diluent type	A	C	A
H_2 consumed (wt% initial H_2)	21	21	26
Yield, wt% vacuum tower bottom H_2S	2.2	2.3	1.2
C_1 - C_4	11.6	9.8	6.6
C_5 - 200°C	44.0	36.6	37.7
200 - 360°C	-18.0	-7.7	-9.1
360 - 504°C	30.1	24.4	31.2
504°C$^+$ (coke free)	27.7	33.8	31.4
Coke	3.1	1.1	1.6
Conversion to 504°C$^-$ & coke	72.3	66.2	68.6
Selectivity to C_5 - 504°C$^-$	77.6	80.5	87.0
Mass Balance	98.5	99.0	98.1

Experiment No.	CF-41	CF-42	CF-40
Additive	Ni	Co	Mo
Diluent type	C	C	C
H_2 consumed (wt% initial H_2)	39	27	68
Yield, wt% vacuum tower bottom H_2S	2.0	1.9	3.3
C_1 - C_4	6.1	8.0	8.5
C_5 - 200°C	34.6	36.4	42.4
200 - 360°C	-2.3	-8.9	-11.8
360 - 504°C	24.9	27.3	29.6
$504^\circ C^+$ (coke free)	34.8	35.3	28.2
Coke	0.4	0.9	1.8
Conversion to $504^\circ C^-$ & coke	65.6	64.7	71.8
Selectivity to C_5 - $504^\circ C^-$	87.2	84.7	83.8
Mass Balance	99.6	99.5	98.9

Claims

1. A hydrocracking process wherein heavy hydrocarbon feedstock containing asphaltenes and sulfur moieties is heated to hydrocracking temperature and conveyed into the chamber of a reactor and reacted therein with hydrogen, characterised in the steps of: –

i) prior to heating to hydrocracking temperature, mixing and heating to an elevated temperature that is less than hydrocracking temperature:

a) the feedstock;

b) an additive comprising an oil – soluble metal compound; and

c) a hydrocarbon solvent for asphaltenes;

said metal in the additive being selected from the group consisting of Fe, Ni and Co, to form a mixture having the metallic component substantially uniformly dispersed therein;

ii) further heating the mixture to a sufficiently high temperature so that hydrocracking will take place in the reactor;

iii) introducing the heated mixture into the chamber of the reactor;

iv) temporarily retaining the charge of heated mixture in the chamber, continuously passing hydrogen through substantially the breadth and length of the charge, and removing unreacted hydrogen and entrained light ends from the upper end of the chamber, to effect hydrocracking and cause stripping of light ends from the charge; and

v) removing the reaction products from the reactor,

whereby formation of coke as an undesired product is inhibited.

2. The process of claim 1 wherein the process is controlled by adjusting any of additive addition, solvent addition and hydrogen addition to ensure that at least 30% of the coke produced in the reactor is in the form of agglomerates, whereby the deposition of adhesive solid coke is inhibited.

3. The process of claim 1 or claim 2 wherein the additive is iron pentacarbonyl and the solvent has a boiling point in the range 220 ° C to 504 ° C.

4. The process of any preceding claim wherein the hydrogen flow is sufficient to provide the following Peclet number ("P.N.") regime within the charge:
for liquid:
    axial P.N. is less than about 2, and
for gas:
    axial P.N. is more than about 3.

5. The process of claim 4 wherein the axial P.N. for liquid is less than about 1.0.

6. The process of claim 3 (or claim 4 or claim 5 as dependent on claim 3) wherein the amount of iron pentacarbonyl added is between about 0.01 and 5.0% by weight based on the feedstock.

7. The process of any preceding claim wherein the solvent/feedstock weight ratio is in the range 1:10 to 3:1.

8. The process of any preceding claim wherein mixing is conducted at an elevated temperature that is substantially less than hydrocracking temperature, whereby the viscosity of the feedstock is reduced to facilitate dispersion of the additive.

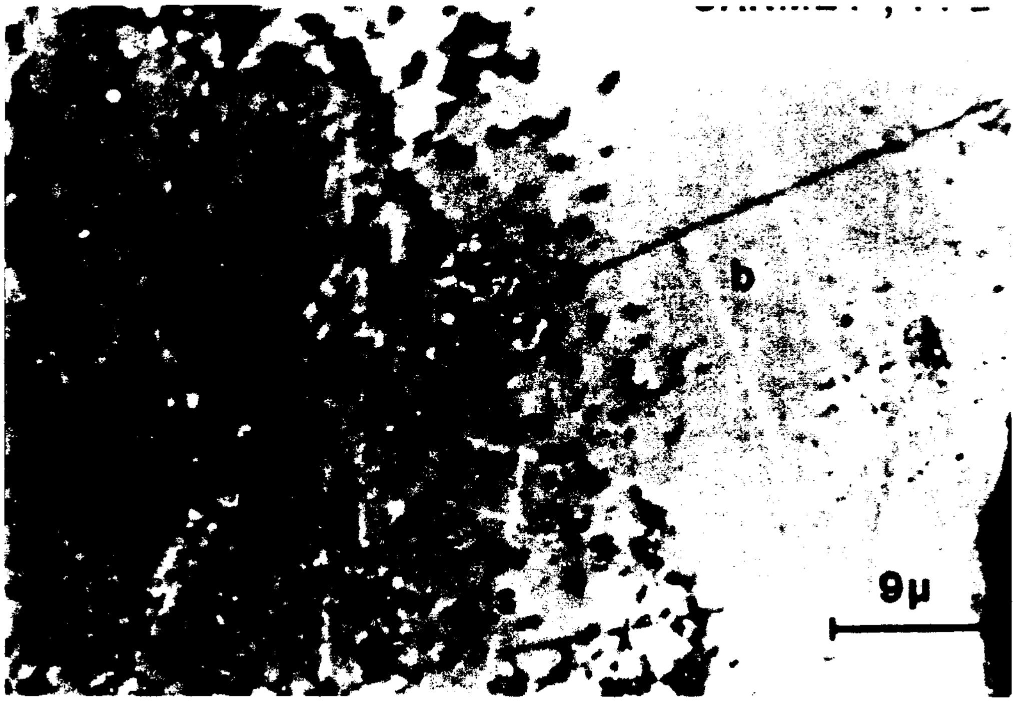


Figure 1. Isotropic Spheres (s) and basic isotropic particle (b). Magnification at 1650X.

Figure 2. Anisotropic Sphere (s)(and all the visible spheres) and basic anisotropic particle(b).Magnification at 1650X.

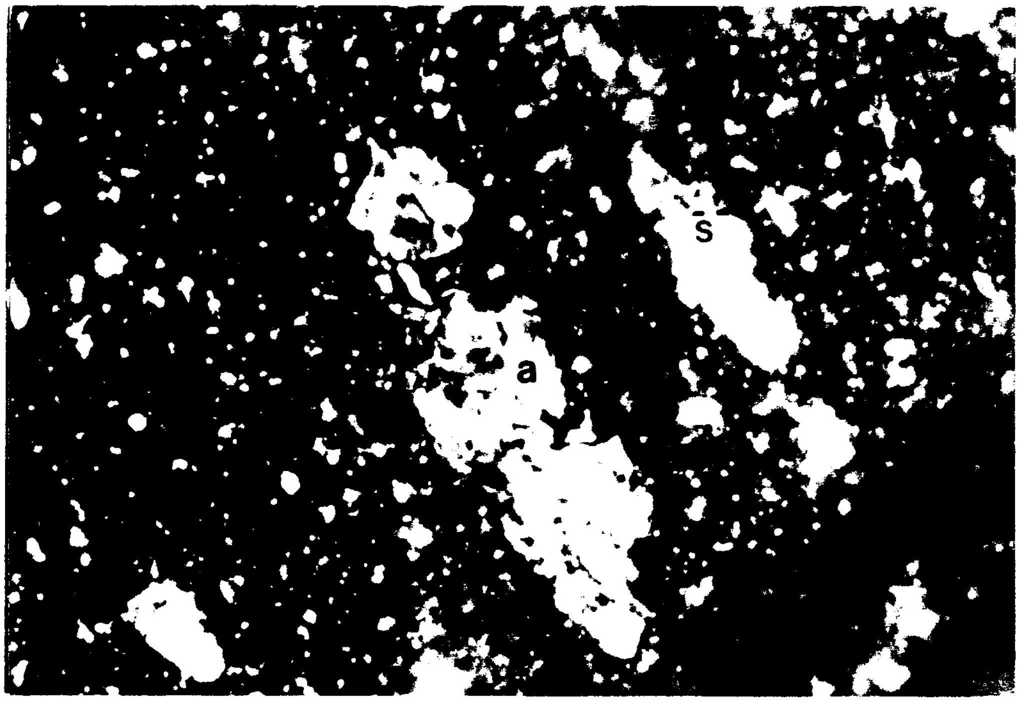


Figure 3 Isotropic agglomerates (g) along with anisotropic solids (a) and iron sulfide particles (s). Magnification at 1650X.

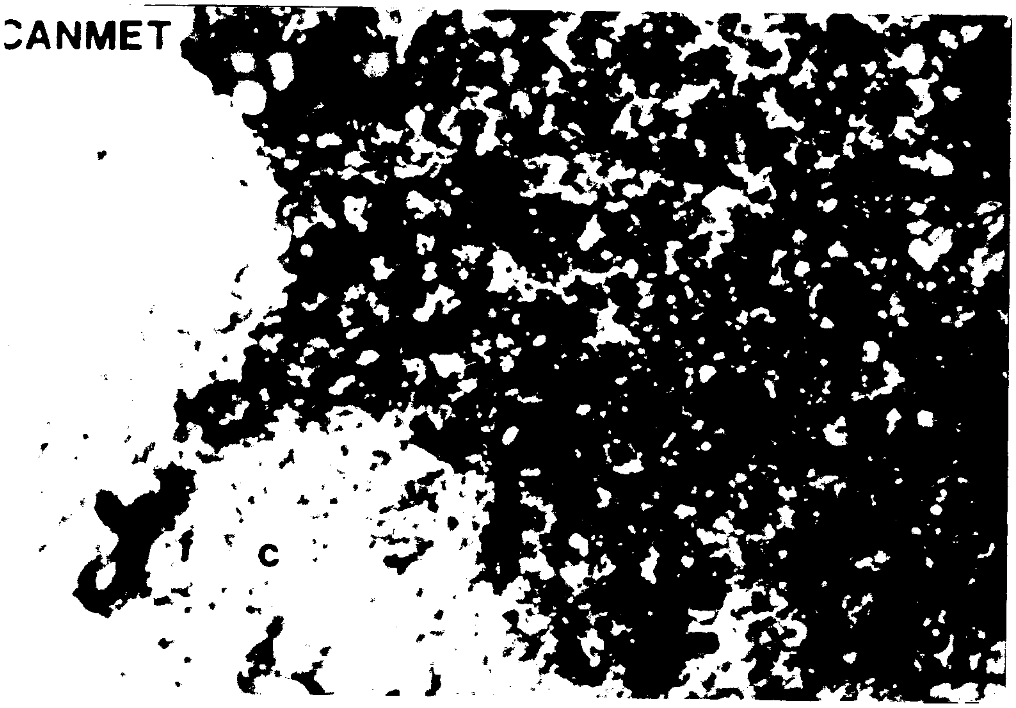


Figure 4 Anisotropic agglomerates (a), anisotropic fine mosaic (f) and anisotropic coarse mosaic (c). Magnification at 1650X

Figure 5 Anisotropic coke particles grow via the coalescence of smaller anisotropic spheres (c). Magnification at 1650X.

Figure 6 Isotropic coke particles grow via the coalescence of smaller isotropic spheres (s). Manification at 1650X.

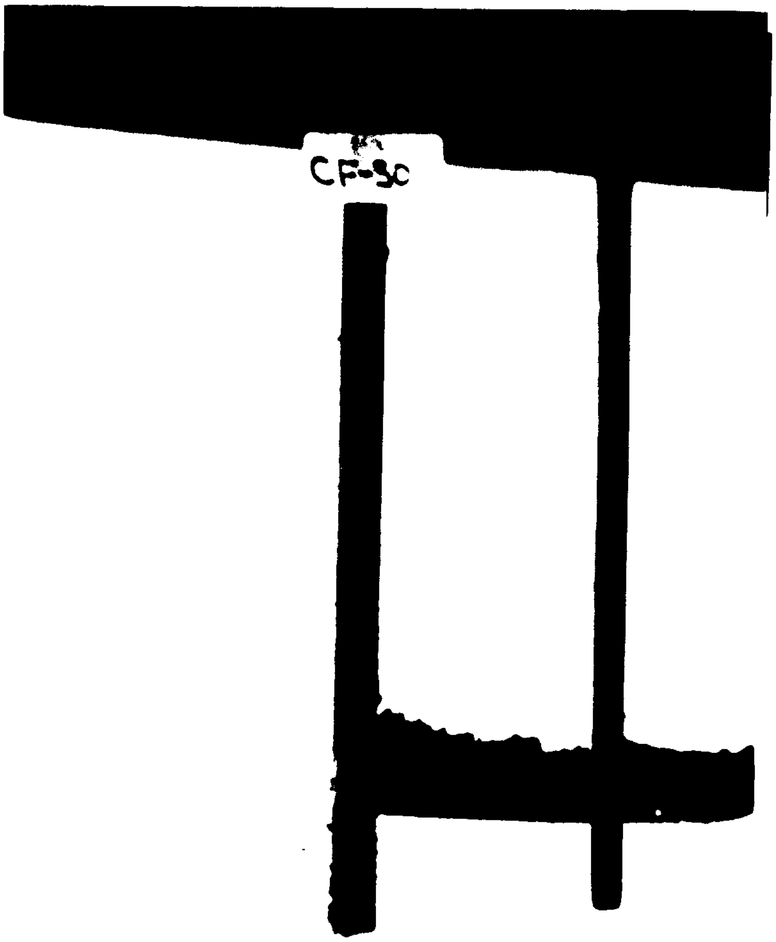


Figure 7 Coke deposition on baffles in test CF-30. (diluent B)

Figure 8 Coke deposition on baffles in test CF-9. (diluent A)

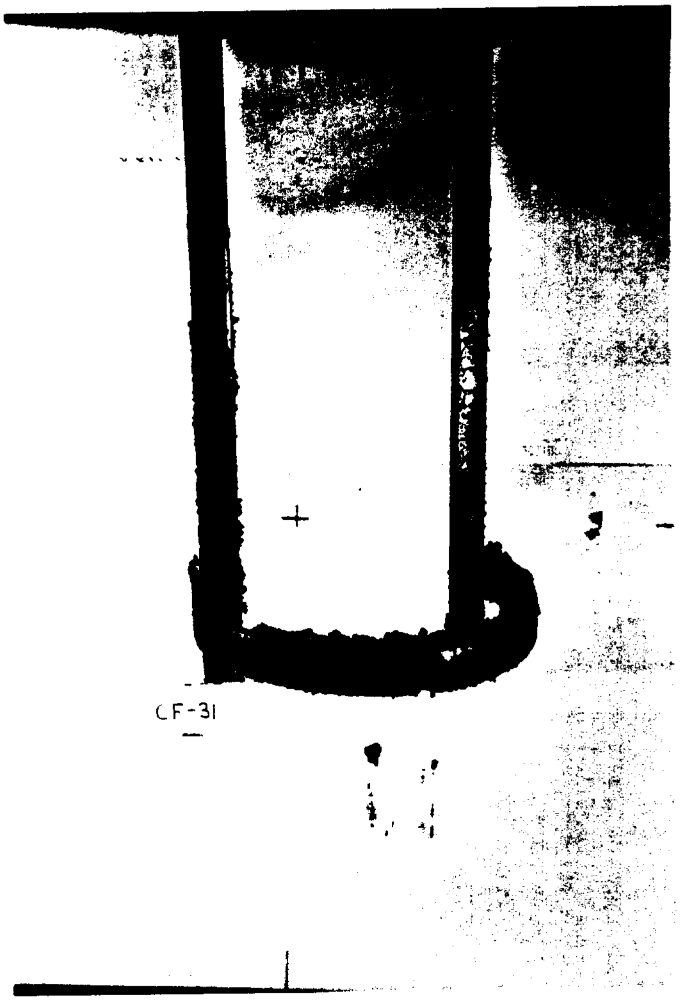


Figure 9 Coke deposition on reactor baffles in test CF-31 (diluent c)

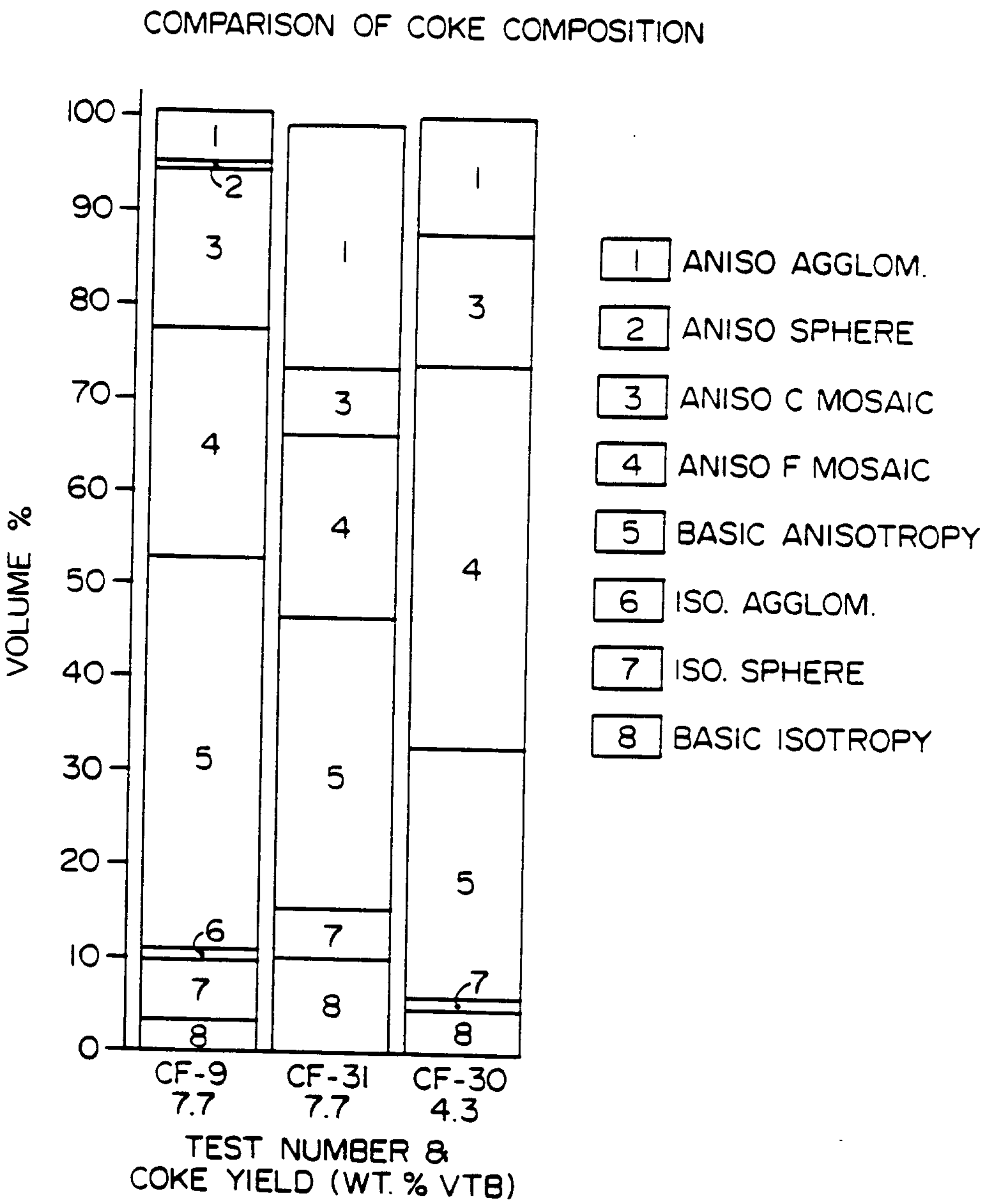

COMPARISON OF COKE COMPOSITION
VOLUME %
100
90
80
70
60
50
40
30
20
10
0
CF-9
7.7
CF-31
7.7
CF-30
4.3
TEST NUMBER &
COKE YIELD (WT. % VTB)
1 ANISO AGGLOM.
2 ANISO SPHERE
3 ANISO C MOSAIC
4 ANISO F MOSAIC
5 BASIC ANISOTROPY
6 ISO. AGGLOM.
7 ISO. SPHERE
8 BASIC ISOTROPY

Fig. 10.

Figure 11 Coke deposition on reactor baffles in test CF-A3 (6.8 MPa initial hydrogen over diluent A)

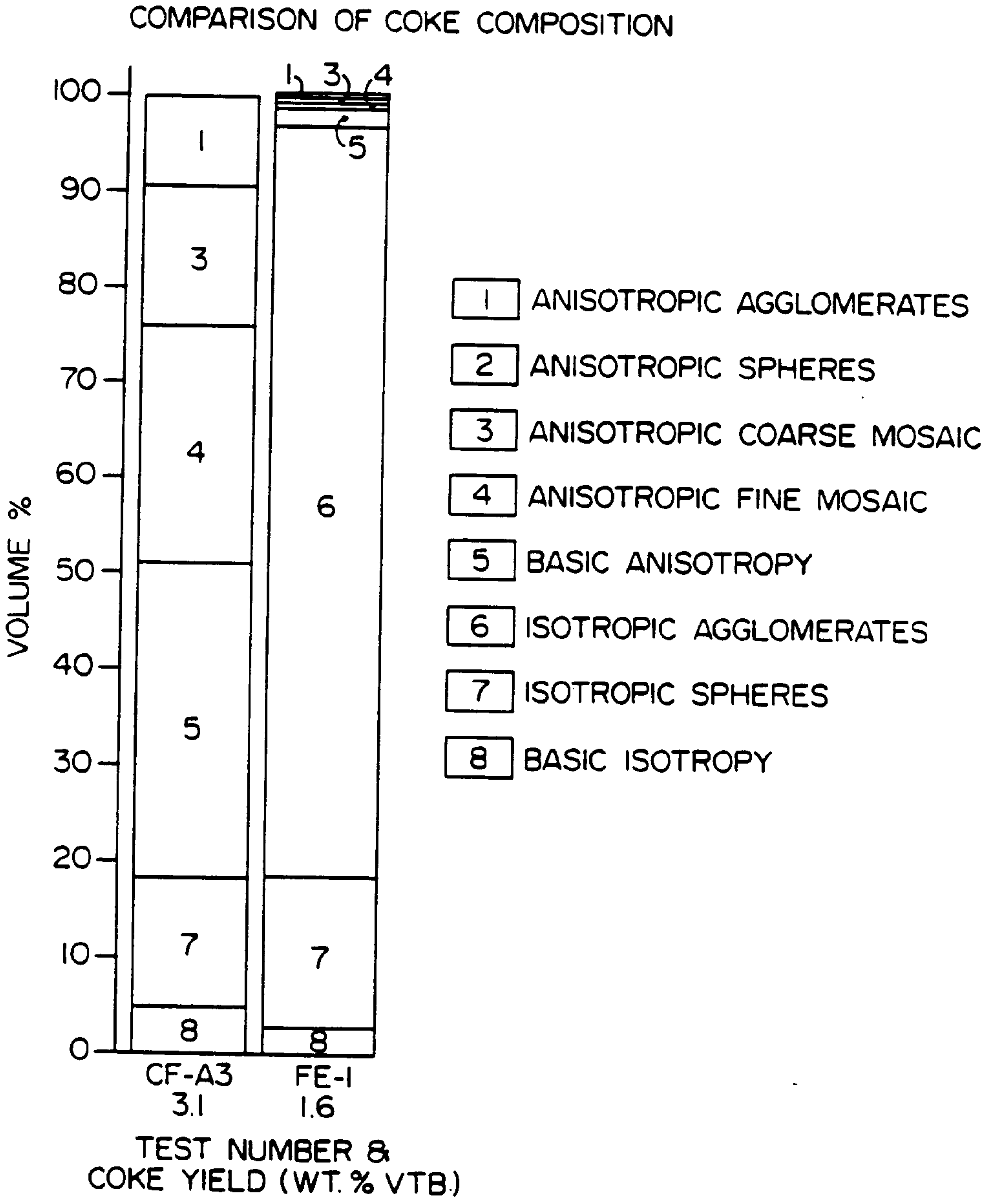

COMPARISON OF COKE COMPOSITION
VOLUME %
100
90
80
70
60
50
40
30
20
10
0
1
3
4
5
7
8
1
3
4
5
6
7
8
CF-A3
3.1
FE-1
1.6
TEST NUMBER &
COKE YIELD (WT. % VTB.)
1 ANISOTROPIC AGGLOMERATES
2 ANISOTROPIC SPHERES
3 ANISOTROPIC COARSE MOSAIC
4 ANISOTROPIC FINE MOSAIC
5 BASIC ANISOTROPY
6 ISOTROPIC AGGLOMERATES
7 ISOTROPIC SPHERES
8 BASIC ISOTROPY

Fig. 12.

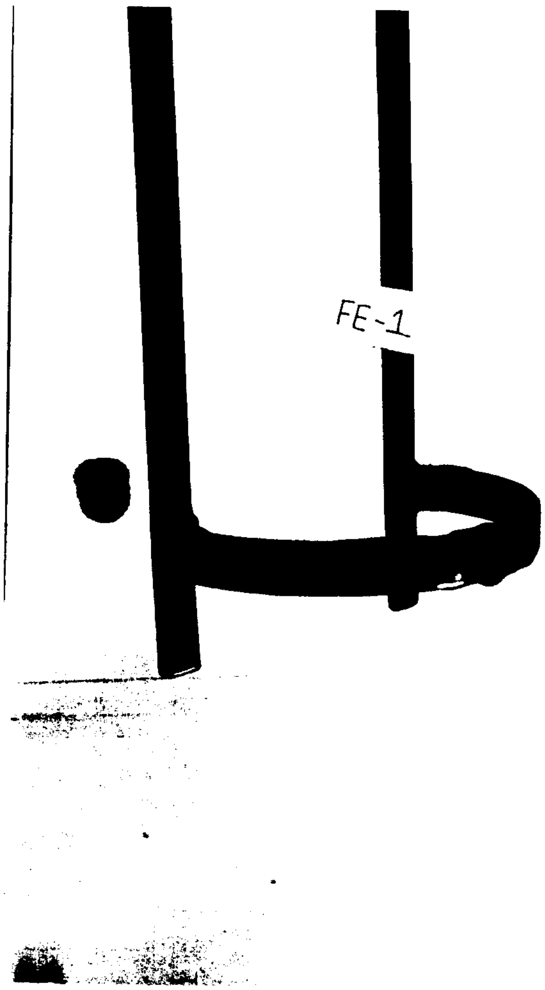


Figure 13. Reactor baffles in test FE-1

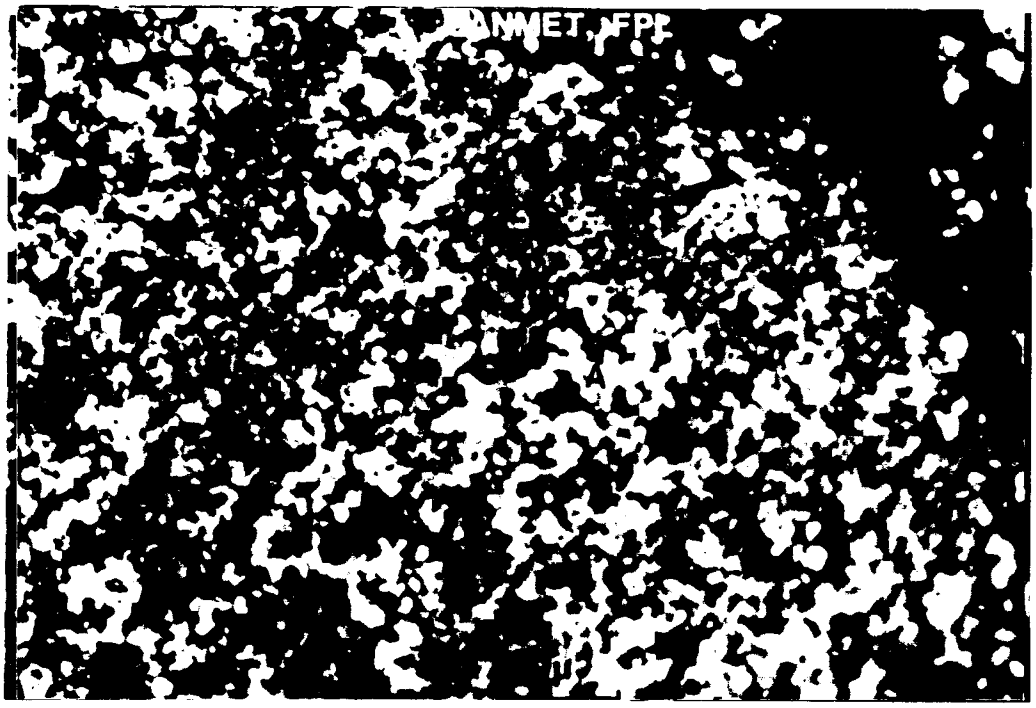


Figure 14 Coke particles in FE-1 were mostly isotropic agglomerates (A) associated with iron sulfides. Isotropic spheres (s) were trapped among the agglomerates.

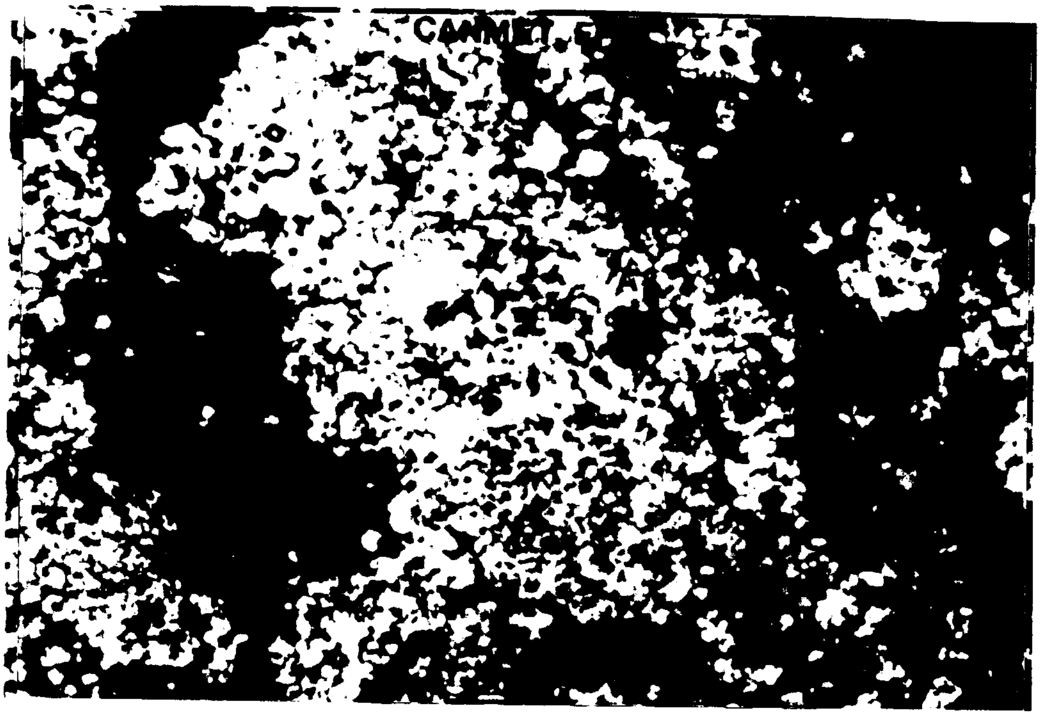


Figure 15 Isotropic spheres (s) were effectively prevented from growing into basic isotropic particles by the iron derivative in FE-1

Figure 16. Coke deposition on reactor baffles of test CF-38

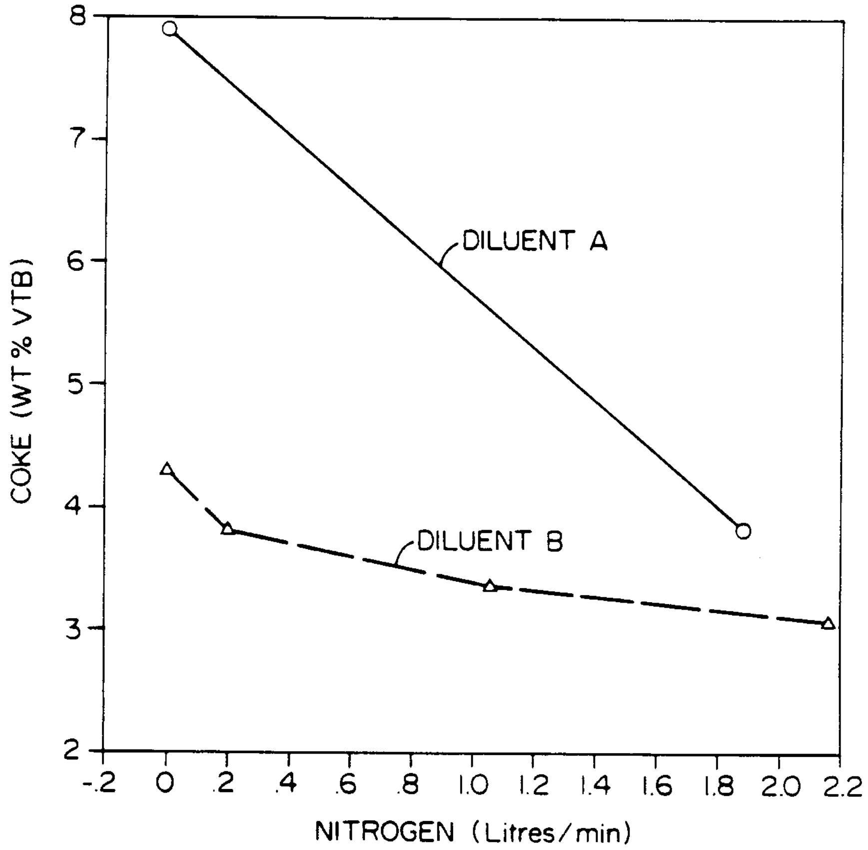

COKE (WT% VTB)
8
7
6
5
4
3
2
-.2
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
NITROGEN (Litres/min)
DILUENT A
DILUENT B

Fig. 17.

Fig. 18.

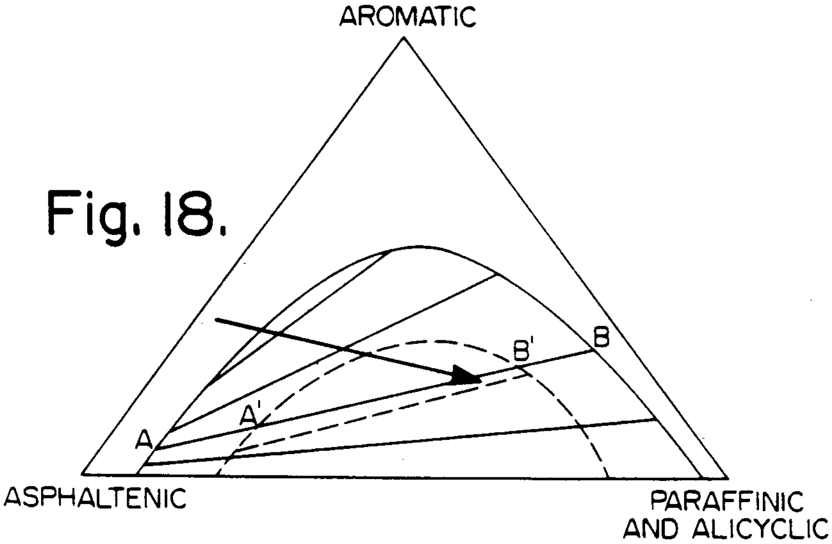
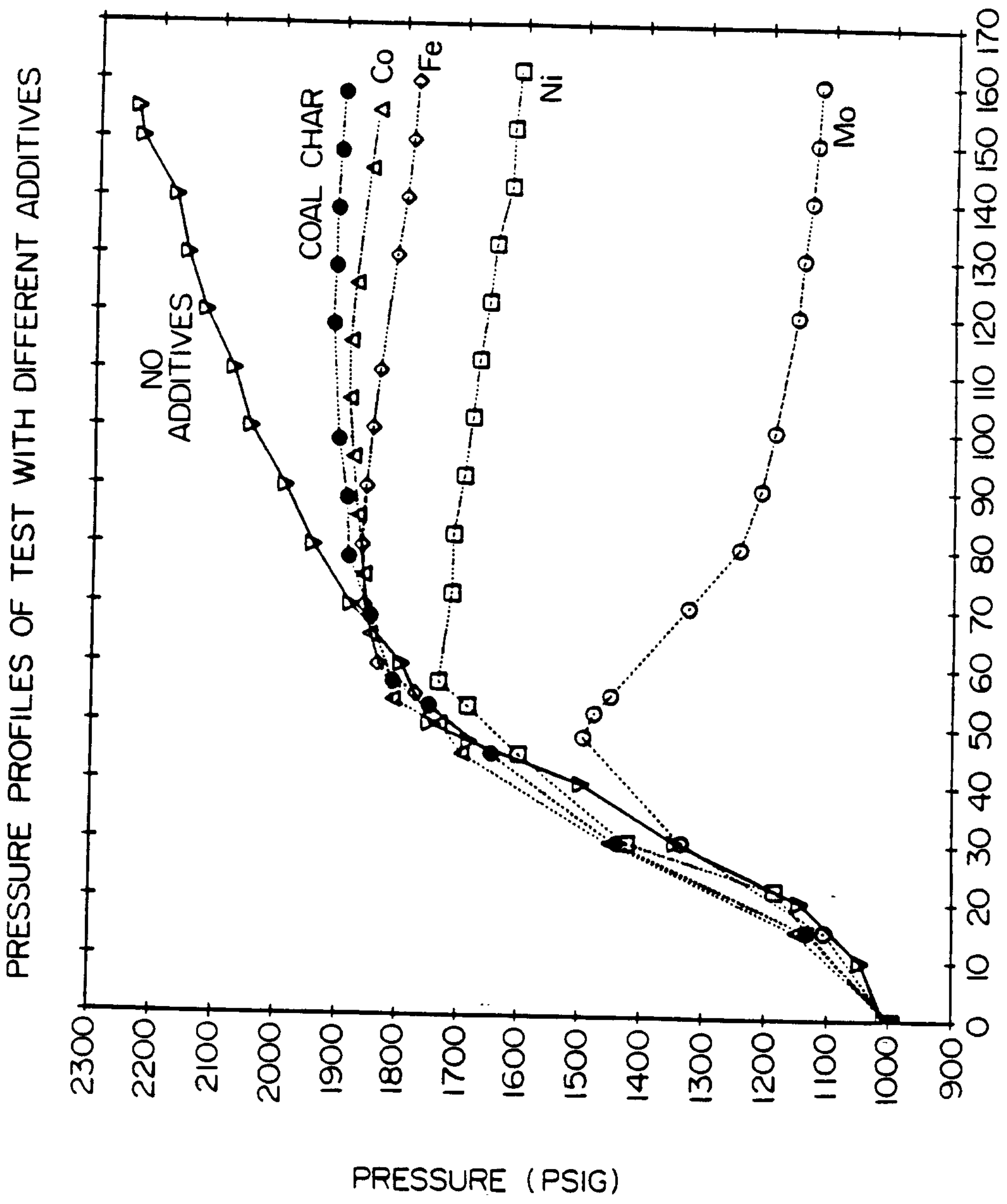

AROMATIC
ASPHALTENIC
PARAFFINIC AND ALICYCLIC
A
A'
B
B'

Fig. 19.


PRESSURE PROFILES OF TEST WITH DIFFERENT ADDITIVES
NO ADDITIVES
COAL CHAR
Co
Fe
Ni
Mo
PRESSURE (PSIG)
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
TIME (MINUTES)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

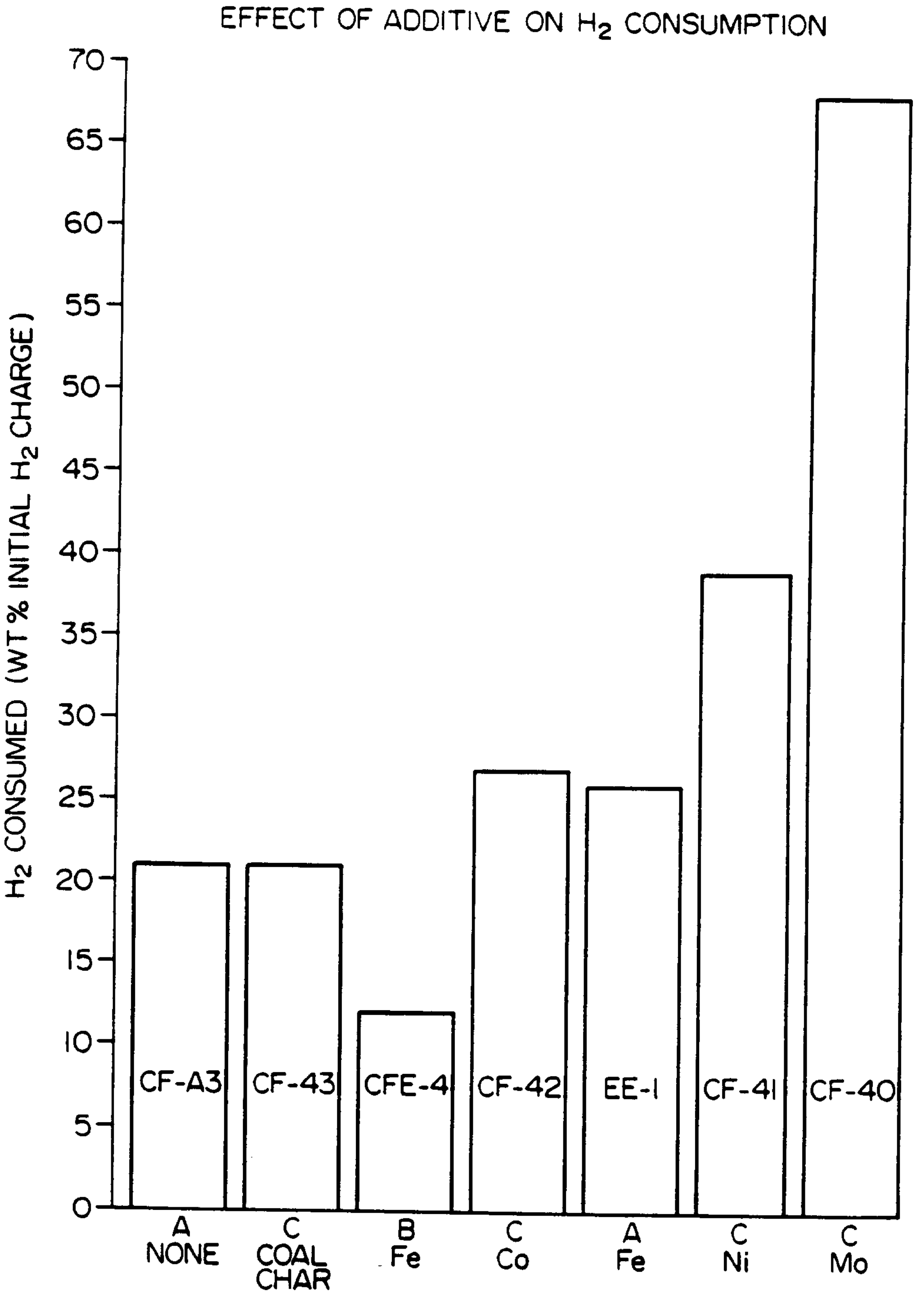
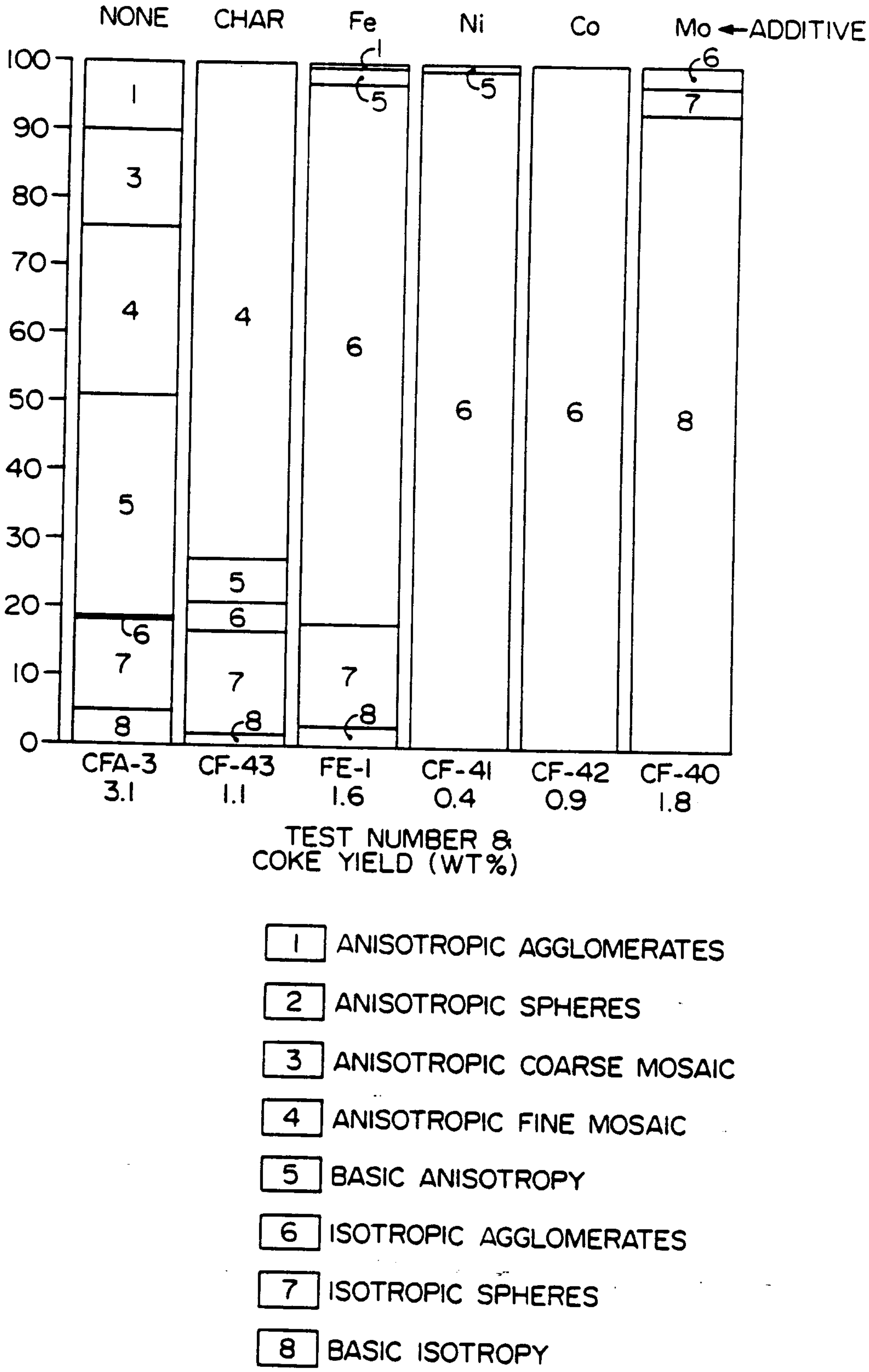

EFFECT OF ADDITIVE ON H2 CONSUMPTION
H2 CONSUMED (WT % INITIAL H2 CHARGE)
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
CF-A3
CF-43
CFE-4
CF-42
EE-1
CF-41
CF-40
A NONE
C COAL CHAR
B Fe
C Co
A Fe
C Ni
C Mo
DILUENT TYPE & ADDITIVE

Fig. 20.

Fig. 21.

EFFECTS OF ADDITIVE ON COKE COMPOSITION



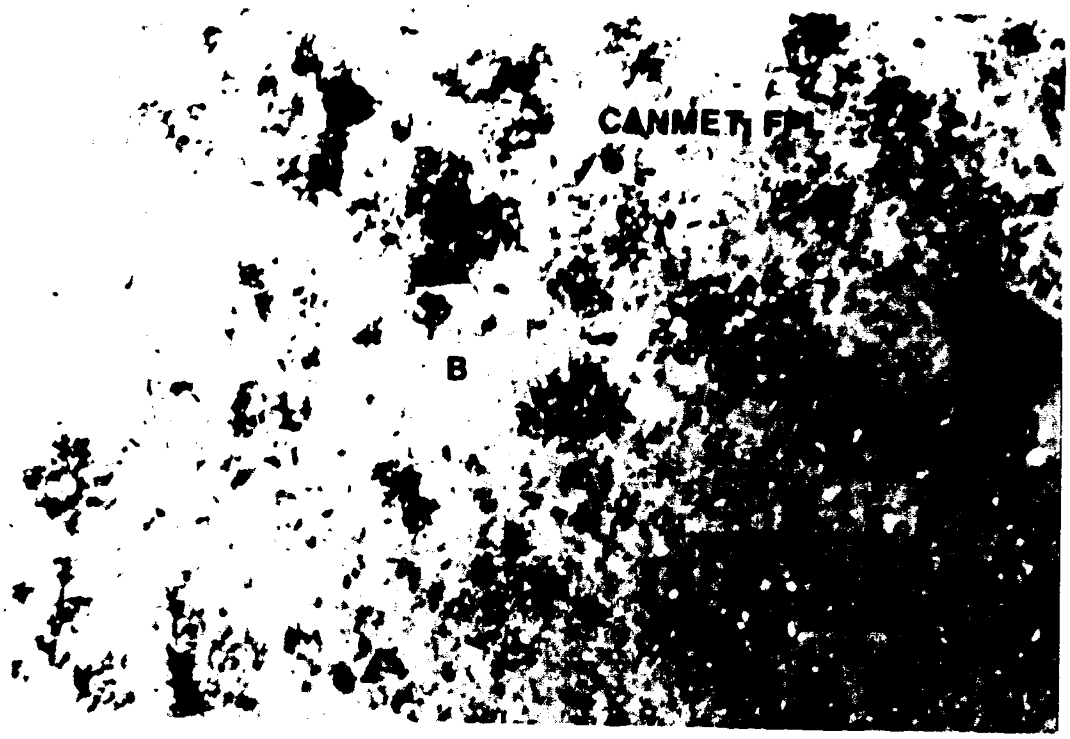


Figure 22 Coke in CF-40 were mostly continuous sheet of basic isotropic particles (B). Magnification at 1650X.

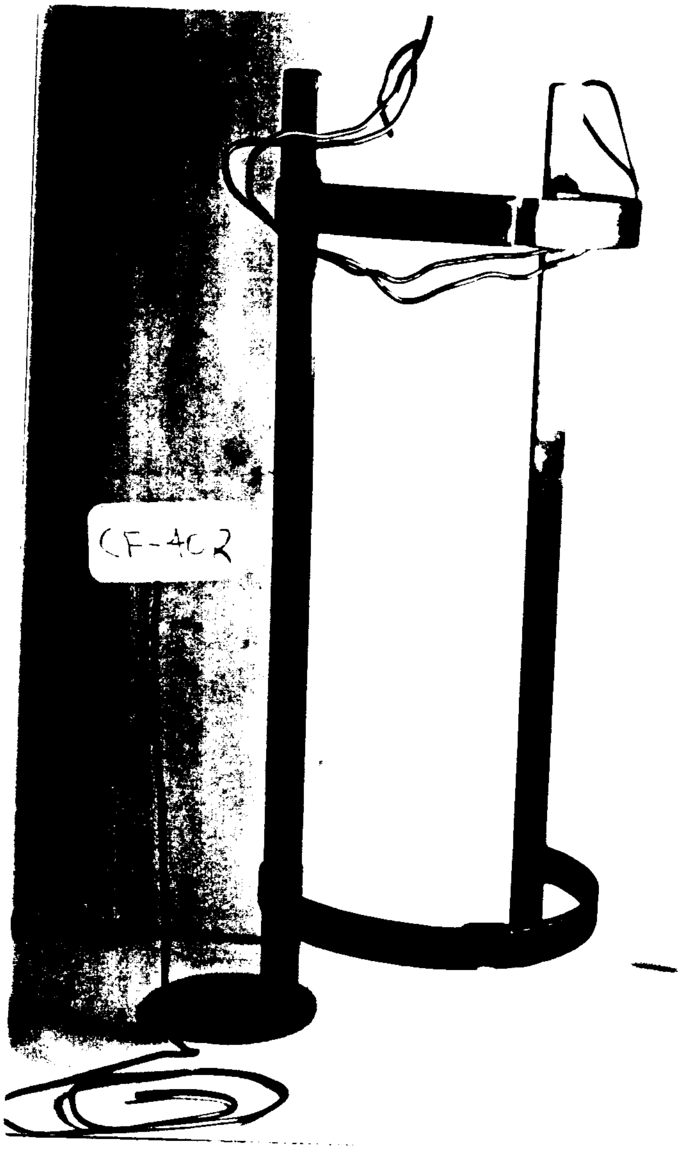


Figure 23 Coke deposition on reactor baffles of CF-40

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 31 0328

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	DE-B-1 034 302 (ESSO) * claims 1,3,4 * ---	1,3,7	C10G47/26 C10G47/00 C10G47/34
A	DE-C-696 083 (I.G. FARBEN) * claims 1,2 * * page 2, line 33 - line 61 * ---	1	
A	EP-A-0 396 384 (ALBERTA OIL SANDS TECHNOLOGY AND RESEARCH AUTHORITY.) * claims 1,3 * ---	1	
A	WO-A-9 112 297 (AMOCO) * claim 9 * -----	1,3	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
C10G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	08 JULY 1992	OSWALD DE HERDT

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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