⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 396 384 A2**

⑫ **EUROPEAN PATENT APPLICATION**

㉑ Application number: **90304719.9**

(51) Int. Cl.^{5}: **C10G 47/00**

㉒ Date of filing: **01.05.90**

㉚ Priority: **02.05.89 CA 598440**
09.05.89 US 349527

㊸ Date of publication of application:
07.11.90 Bulletin 90/45

(84) Designated Contracting States:
DE FR GB IT

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(54) Hydrocracking of asphaltene-rich bitumen residuums.

(57) A process is provided for selectively converting the asphaltene-rich fraction of a hydrocarbon residuum to a refinery treatable product. The bitumen residuum is concentrated to provide an asphaltene-rich feedstock. The feedstock is admixed with a thermally decomposable catalyst precursor and preheated to a temperature of between about 200°C - 300°C under ambient conditions to convert said precursor to an active colloidal catalyst. The mixture is reacted with hydrogen under hydrocracking conditions at a temperature of between 420°C-490°C to thereby selectively hydrocrack the asphaltene fraction.

HYDROCRACKING OF ASPHALTENE-RICH BITUMEN RESIDUUMS

The present invention relates to a catalytic process for the hydrocracking of the asphaltene-rich fraction of bitumen residuums to produce a refinery treatable product.

Hydrogenation processes for the upgrading of heavy cretaceous crude oil and bitumens are well known. Upgrading processes are normally carried out to remove or reduce the contaminants in the oil and to convert the heavier components of the oil into lower boiling point hydrocarbon products.

Current commercial upgrading processes typically involve the use of heterogeneous catalyst, exemplary of which would be cobalt, molybdenum or nickel metals deposited on an alumina substrate. Deleteriously, the higher molecular weight components of the heavy oils tend to accumulate on the catalyst pellet surfaces, clogging the pore system and thus reducing the rate of hydrogenation. Ultimately, the deposition of coke and metals on the pellet surface will despoil the catalytic performance. This becomes a serious operational problem when feedstocks such as bitumen, which are high in asphaltenes are hydrocracked.

The types of reactor employed in hydrocracking may typically be a tubular reactor containing a fixed bed of catalyst or a fluidized bed of catalyst. The disadvantages common to both types of reactor are that they are easily plugged by coke and the hydrodynamics involved are complex.

It is well known in the art that upgrading processes which may be applicable to heavy crude oils from the Middle East or the like cannot be extrapolated to bitumens such as are recovered from the oil sands of regions of Northern Alberta, Canada. Generally the major portion of such crude oils is refinery distillable. However, with bitumen feedstocks only approximately 45% of the total is distillable and the remainder is non- distillable. The non-distillable fraction, namely that having an initial boiling point (IBP) above +525°C, is referred to as pitch.

In typical commercial operations, a bitumen feedstock is usually subjected first to an atmospheric distillation step followed by a vacuum distillation step. The overhead or fractions having an IBP below approximately 430°C are passed to a refinery for conventional treatment. The fractions having an IBP above 430°C, termed, the bitumen residuum are usually treated in a coker or simply burned.

The composition of pitch is chemically complex, containing different fractions which are identifiable by their solubility, or otherwise, in various organic solvents. One such class is termed the asphaltenes. Asphaltenes are known to be difficult to treat. Additionally, it is known that a correlative relationship exists in hydrocracking operations between the percentage of asphaltene conversion and the formation of coke. Stated otherwise as the asphaltene conversion increases the coke formation increases proportionately therewith.

By asphaltene conversions is meant :

$$\underline{\text{ASPHALTENE CONVERSION}} = \frac{\text{Asphaltene(In)}-\text{(Asphaltene+Coke)(Out)} \times 100}{\text{Asphaltene (In)}}$$

Pitch conversion, as used hereinafter, is defined as:

$$\underline{\text{PITCH CONVERSION}} = \frac{+525^{\circ}\text{C FRACTION(In)}-(+525^{\circ}\text{C) FRACTION (Out)} \times 100}{+525^{\circ}\text{C Fraction (In)}}$$

It is known that when thermal cracking of pitch predominates the total asphaltene conversion will not be high but coke formation is significant.

By conversion is meant the thermal cracking of the feedstock to a distillable fraction.

U.S. Patent 2,091,831 issued to E.V. Pongratz et al. described a batch hydrocracking process wherein a catalyst comprising a hydrocarbon oil soluble molybdenum salt of a naphthenic acid is utilized. It will be noted that under the reaction conditions, the salt is not entirely decomposable. The treated feedstock comprises specifically a light oil.

U. S. Patent 4,226,742 issued to R. Bearden, Jr. et al. teaches a slurry hydrocracking process for converting a carbonaceous feedstock into useful oil in the presence of hydrogen. The feedstock in admixture with a catalyst or catalytic precursor is reacted with a hydrogen-containing gas, specifically H_2S, under hydrocracking conditions. The heavy oil portion to which the metal-containing solids report is then separated from the hydrocracked oil product and gasified to produce a metal-ash. The metal is recovered from the ash as an oxalic-acid extract and recycled as the catalyst precursor. Testing indicated that the active catalytic metal was present in a solid, non-colloidal form. The tubular reactor used in the process provides for the volatiles and liquids to leave the vessel at approximately the same residence times. The optimum conversion obtained was of the order of 90%.

At the time of the present invention, therefore, there existed the need for a process which would:
- selectively convert the asphaltenic fraction of the pitch with minimal coke formation;
- augment the rate of conversion; and
- operate with a more simplified reactor design.

In accordance with the present invention there is provided a process for selectively converting the asphaltene-rich fraction of a hydrocarbon residuum to a refinery treatable product.

The process is based on the discovery that if a thermally decomposable catalyst precursor in admixture with an asphaltene-rich feedstock is first preheated within a specific temperature range to convert it to an 'active' colloidal catalyst prior to the conventional hydrocracking step, the asphaltenes are preferentially converted to maltenes or volatile products with concomitantly reduced coke formation. Without being bound by the same it is believed that the 'active' colloidal catalyst is preferentially associated with the asphaltene molecules in the preheat stage, thereby rendering that fraction selectively more amenable to the subsequent hydrocracking step.

More specifically the process involves:
- concentrating the bitumen residuum to provide an asphaltene-rich feedstock;
- admixing the feedstock with a thermally decomposable catalyst precursor;
- preheating the catalyst and feedstock mixture to a temperature of between about 200°C - 300°C under ambient conditions to convert said catalyst precursor to an active colloidal catalyst;
- reacting the mixture with hydrogen under hydrocracking conditions at a temperature of between about 420°C-490°C to thereby selectively convert said asphaltenic fraction; and
- recovering the reaction products.

By colloidal catalyst is meant a catalyst having a particle size within the colloidal range. By catalyst precursor is meant a thermally decomposable compound comprising an oil-soluble compound of the group VIA metals for the group VIIIA metals. In its most preferred embodiment the catalyst precursor is molybdenum naphthenate.

Preferably the asphaltene-rich feedstock would have an asphaltene fraction content of at least about twenty-five percent.

Preferably the hydrocracking process is conducted in a tubular upflow reactor on a continuous basis with sufficient turbulence as is necessary to maintain the catalyst as a colloidal dispersion, and sufficient hydrogen flow to strip the volatile components from the reactor. Under reactor conditions, the volumetric flow of hydrogen must be greater than twenty times the liquid flow therethrough.

By using the process of the present invention it is possible to obtain a 98% conversion of the feedstock. Additionally, the use of a reactor of complex design is essentially eliminated. It has been found that because of the selectivity of the asphaltene conversion, the process may be operated under less severe operating conditions.

Broadly stated the invention comprises a process for selectively hydrocracking the asphaltenic fraction of bitumen residuum to a refinery treatable product which comprises admixing the asphaltenic feedstock with a thermally decomposable catalyst precursor; preheating the catalyst precursor and feedstock mixture to a temperature of between 200°C - 300°C under ambient conditions to convert said catalyst precursor to an active colloidal catalyst; reacting the mixture with hydrogen under hydrocracking conditions between a temperature of about 420°C and 490°C to thereby selectively convert said asphaltenic fraction; and recovering the reaction products.

The invention will now be further described, by way of Example, with reference to the accompanying drawings.

Figure 1 is a schematic flow plan of a first embodiment of the process.

Figure 2 is an alternative schematic flow plan for the process.

Figure 3 is series of IR spectra demonstrating the effect of the preheat step on the composition of the catalyst precursor.

Figure 4 is a plot of asphaltene conversion versus pitch conversion.

Having reference to the accompanying drawings, there is provided a hydrocracking process which is generally applicable to the asphaltene-rich fraction of bitumen residuum.

Such an asphaltene-rich feedstock may be obtained by the conventional distillation of bitumen. As shown in Figure 1, bitumen is introduced into a vacuum tower 3 via a line 2. The overheads are withdrawn via a line 4. The residuum leaving the vacuum tower 3 via a line 5 forms the feedstock for the process of the present invention.

Alternatively, solvent extraction of the bitumen by pentane, ligroin or other light petroleum fractions may be used to obtain the asphaltenic fraction in a higher concentration.

As illustrated in Figure 2 the asphaltenic fraction may otherwise be concentrated by introducing bitumen residuum via a line 6 into a deasphalting unit 7. The overheads leave the deasphalting unit 7 and are then treated further as shown by conventional methods. The asphaltene-rich residuum leaves the deasphalting unit 7 via a line 8 where it is passed to a heater 9. The feedstock leaves the heater via line 10.

The feedstock obtained from the above-described asphaltene concentrating processes would contain at least 25% asphaltene.

Characteristics data of a typical vacuum bottoms from bitumen would be as given in Table 1 below:

TABLE 1

Distillation Wt.%	IBP = 430°C
IBP - 525°C	24.0
+525°C	76.0
Elemental Composition Wt.%	
Carbon	83.6
Hydrogen	9.7
Nitrogen	0.8
Sulfur	5.9
Oxygen	--
H/C	1.4
TLC/FID Class Composition, Hydrocarbons	75.0
Asphaltene + Preasphaltene	25.0

The API gravity of such feeds would be in the range of -10° to +12°.

The process steps for the alternative embodiments shown in Figures 1 and 2 are identical from the feedstock in line 5 of Figure 1 and line 10 of Figure 2 respectively.

A catalyst precursor is added to the feedstock in lines 5 or 10 via line 11 to a metal concentration of between 50 to 500 ppm. Most preferably the metal concentration would be in the range of about 70 to 150 ppm.

The precursor may comprise the oil-soluble metal compounds of the group VIA or group VIIIA metals including molybdenum naphthenate, cobalt naphthenate, nickel naphthenate.

The preferred catalyst would comprise molybdenum naphthenate.

The catalyst precursor and feedstock in admixture are introduced via line 12 into a surge tank 13 where the mixture is subjected to a preheat stage. The mixture is heated to a temperature in the range of between about 200°C - 300°C under ambient conditions. During the preheat stage the catalyst precursor is converted to what is believed to be an active colloidal catalyst.

The evidence for the conversion of the catalyst precursor specifically molybdenum naphthenate, over this specific temperature range is provided by the IR spectra illustrated in Figure 3.

It is believed then the catalyst associates with the asphaltene molecules to preferentially predispose the latter to maltene and other volatiles formation during hydrocracking rather than coke formation.

Figure 3 which is a plot of asphaltene conversion versus pitch conversion over a broad range of operating conditions, is included to illustrate the selectivity of asphaltene conversion in the presence of colloidal catalyst.

It is seen that under reaction conditions which provide low pitch conversion, for example 53% conversion of pitch, the addition of catalyst precursor to the feedstock increases asphaltene conversion from 25% to 59%.

Under reaction conditions which provide high pitch conversion, for example 85%, addition of the catalyst precursor to the feedstock permitted the hydrogen partial pressure to be reduced from 23.8 MPa to 17 MPa, and the hydrogen flow to be significantly reduced from 40 to 14 slmp. It should be noted that the selectivity of the catalyst for the conversion of asphaltene is greatest under the conditions which provide for low pitch conversion.

From the surge tank 13, the mixture is passed via line 14 and through a pump 15. Hydrogen gas is introduced via line 16 into the line 14 and the mixture is then introduced into the tubular upflow reactor 17.

The tubular reactor 17, which could alternatively be described as a still-pot reactor with overflow, is operated on a continuous basis with sufficient turbulence as is necessary to maintain the catalyst as a colloidal dispersion and sufficient hydrogen flow to strip the volatile components from the reactor. Under reactor conditions, the volumetric flow of hydrogen must be greater than twenty times the liquid flow therethrough. The reactor may be described as well-mixed with liquid Peclet numbers much less than one. The gas Peclet numbers would be about ten times larger.

The hydrogen gas would comprise from between about 85 to 100 mole percent.

The temperature of the reactor in the hydrocracking zone would be from between about 420°C to 490°C. The preferred temperature range would be 450°C to about 485°C. The reactor pressure would be maintained between about 10.2 MPa to about 17.0 MPa. The overheads from the reactor as passed to a gas-liquid separator 18 and treated conventionally thereafter.

Examination of the pitch by scanning electron microscope demonstrated that the catalyst remained in the colloidal form. Thus it was suitable for recycle from the vacuum tower 19 to either the vacuum tower 3 of the first process option or the reactor 17 of the second process option.

Example I

An asphaltene-rich feedstock of Cold Lake vacuum residuum IBP greater than 430°C was charged to a 0.01 m^3 surge tank. 300 ppm of molybdenum, as molybdenum naphthenate was added to the tank which was equipped with a stirrer and recycle pump and mixed homogeneously therewith. The mixture was heated under a nitrogen blanket to 250°C. The mixture was then pumped to a preheater. Hydrogen was admixed with the feedstock and catalyst at the entrance to the preheater. The preheater consisted of a 2.9mm I.D. 6100mm long coil immersed in a fluidized sand bath at reactor temperature.

The gaseous heated mixture comprising 93 mole percent hydrogen was introduced into the bottom of the reactor at a rate of 330cc/h. The 328cc reactor has an I.D. of 25mm and was .670m. The reactor was manufactured by Autoclave Engineers, Erie, Pa. The LHSV was 0.9 to 1.2 h^{-1}. It usually required 4 - 6 h. for the reactor to reach steady state operating conditions. The hydrocracking took place at a temperature of 470°C and pressure of 17.0 MPa. The reactor effluent comprising a mixture of gases and liquids was fed to a hot separator where primary product separation took place.

Example II

The following example shown in Table II provides a comparison of two runs, one with catalyst and one without catalyst present, is included so as to demonstrate the effect of the catalyst.

TABLE II

Run No.	1	2
Catalyst	300 ppm Mo	None
Pitch Conversion, wt.%	53	53
Asphaltene Conversion, wt %	59	25
HDS, wt %	39	32
Yield, wt % on feed		
C_1 - C_4	2.9	3.5
C_5 - 195°C	3.3	4.8
195 - 350°C	19.9	22.1
350 - 525°C	35.3	31.4
C_5 - 525°C	58.4	58.3
Coke,	0.8	6.0

The above hydrocracking tests were conducted on Cold Lake vacuum bottoms. The pressure was 17.0 MPa. The liquid hour space velocity was 4 h^{-1}. The hydrogen gas rate was 28 slpm. The temperature was 455°C.

Example III

The following example shown in Table III herebelow demonstrates the effect of reactor temperature on pitch and asphaltene conversion.

TABLE III

Run No.	1	2	3	4
Temperature, °C	440	455	470	485
Pitch Conversion,wt%	63	85	98	97
Asphaltene Conversion,wt %	60	81	99	98
HDS, wt %	53	72	81	81
Yield, wt % on feed				
C_1 - C_4	4.4	7.5	10.6	13.3
C_5 - 195°C	4.3	6.1	14.1	14.7
195 - 350°C	23.3	36.7	39.5	40.2
350 - 525°C	36.3	31.2	27.8	25.0
C_5 - 525°C	63.9	74.0	81.4	79.9

The runs were conducted on a continuous basis in the above-described upflow reactor. The feedstock comprised Cold Lake vacuum bottoms IBP 430°C. The pressure was maintained at 17.0 MPa, the liquid hour space velocity was $1.2h^{-1}$. The hydrogen gas rate was 43 reactor volumes per minute at NTP. The catalyst concentration was 300 ppm Mo.

EXAMPLE IV

This example shown in Table IV herebelow is included to demonstrate the effect of the presence of catalyst on the composition of the reaction products.

TABLE IV

Fraction	Pitch I		Pitch II	
	Yield %	Sulfur %	Yield %	Sulfur %
Maltenes	63.2	3.9	41.5	4.7
Asphaltenes	36.6	5.8	33.4	6.3
Preasphaltenes			16.3	6.2
Coke	0.2	--	8.3	6.7

The produced pitch has a composition of +525°C. Pitch I was derived from a run containing molybdenum naphthenate precursor. Pitch II was derived from a run which was conducted without the presence of a catalyst.

Claims

1. A process for selectively hydrocracking the asphaltenic fraction of bitumen residuum to a refinery treatable product which comprises;
- admixing the asphaltenic feedstock with a thermally decomposable catalyst precursor;
- preheating the catalyst precursor and feedstock mixture to a temperature of between 200°C - 300°C under ambient conditions to convert said catalyst precursor to an active colloidal catalyst;
- reacting the mixture with hydrogen under hydrocracking conditions between a temperature of about 420°C

to 490°C to thereby selectively convert said asphaltenic fraction; and
- recovering the reaction products.

2. The process as set forth in Claim 1 wherein said asphaltene feedstock is prepared by concentrating the bitumen residuum to thereby provide an asphaltene-rich feedstock.

3. The process as set forth in Claim 2 wherein said catalyst precursor is selected from the group comprising an oil-soluble compound of the group VIA metals or the group VIIIA metals.

4. The process as set forth in Claim 2 wherein said catalyst precursor comprises molybdenum naphthenate.

5. The process as set forth in Claim 4 wherein the temperature for hydrocracking is in the range of between about 450°C to about 485°C.

6. The process as set forth in Claim 5 wherein said hydrocracking process is conducted in a tubular upflow reactor on a continuous basis having a volumetric flow of hydrogen greater than twenty times the liquid flow therethrough under reactor conditions.

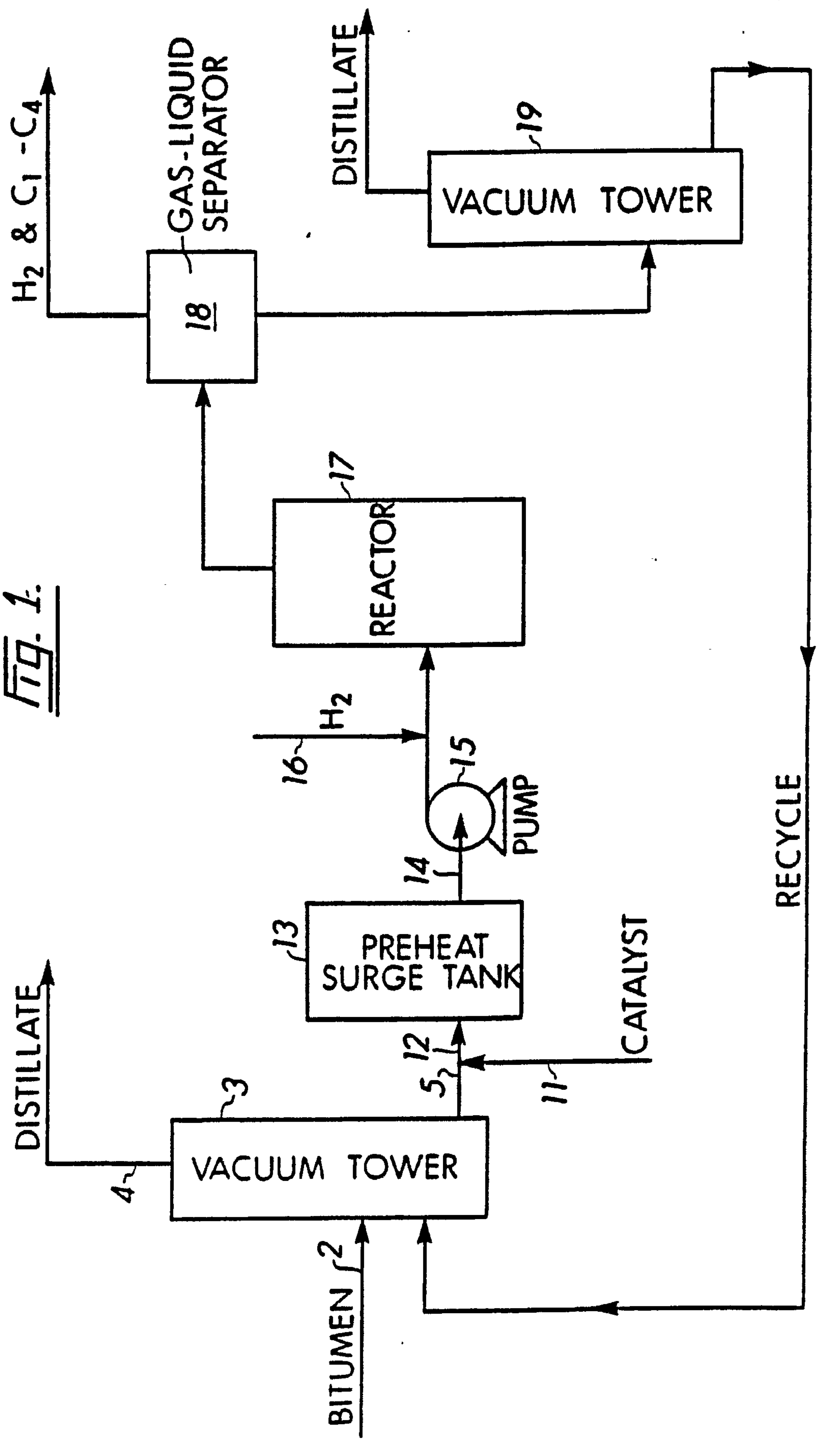
Fig. 1.
BITUMEN
2
VACUUM TOWER
3
4
DISTILLATE
5
12
CATALYST
11
PREHEAT SURGE TANK
13
14
PUMP
15
16
H2
REACTOR
17
GAS-LIQUID SEPARATOR
18
H2 & C1 -C4
VACUUM TOWER
19
DISTILLATE
RECYCLE

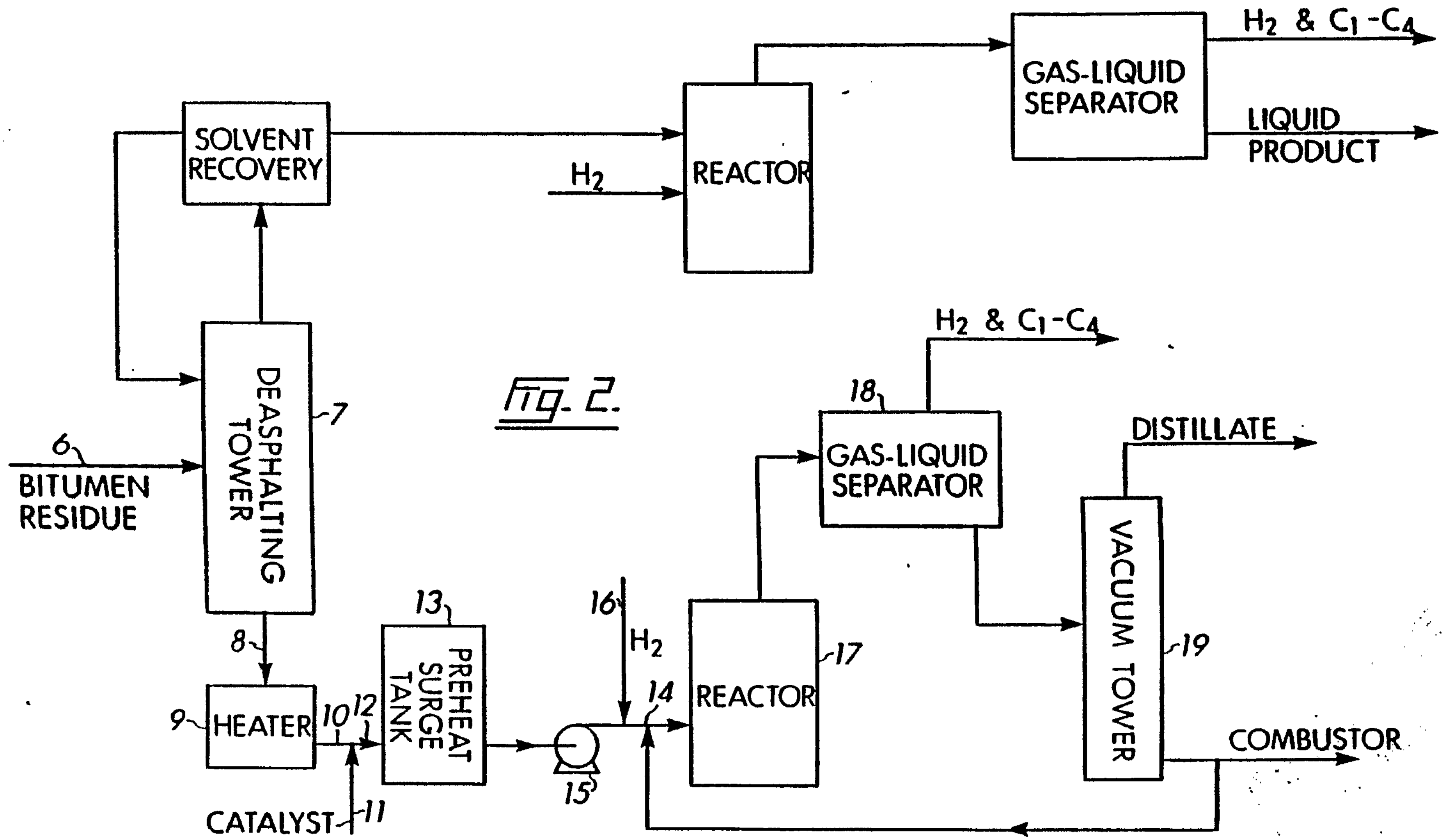
SOLVENT RECOVERY
REACTOR
H_2
GAS-LIQUID SEPARATOR
H_2 & C_1-C_4
LIQUID PRODUCT
6
BITUMEN RESIDUE
DEASPHALTING TOWER
7
8
9
HEATER
10
12
CATALYST
11
13
PREHEAT SURGE TANK
15
16
H_2
14
REACTOR
17
18
GAS-LIQUID SEPARATOR
H_2 & C_1-C_4
DISTILLATE
VACUUM TOWER
19
COMBUSTOR

Fig. 2.

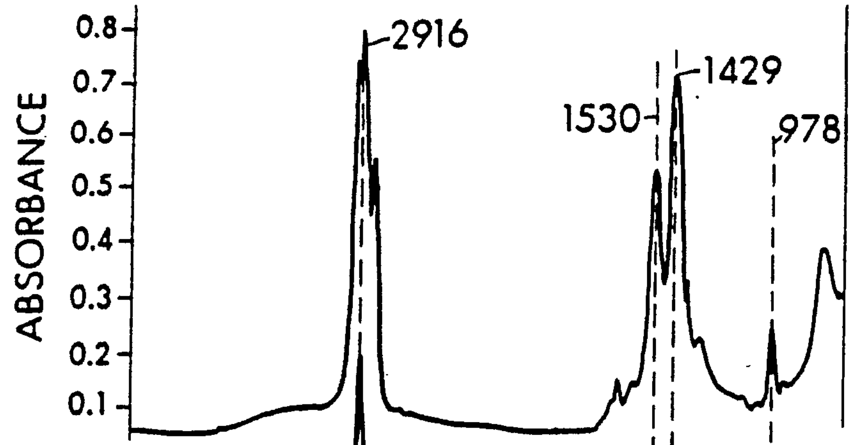

Fig. 3a.

CATALYST PRECURSOR

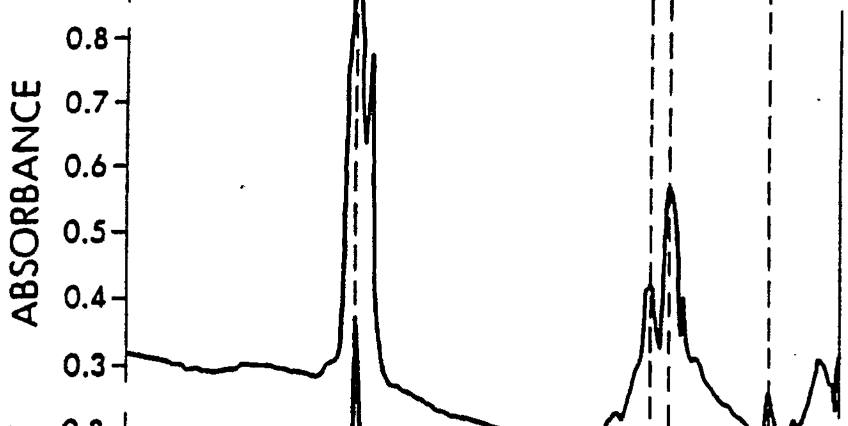

Fig. 3b.

FEED & CATALYST PRECURSOR AT 150 °C

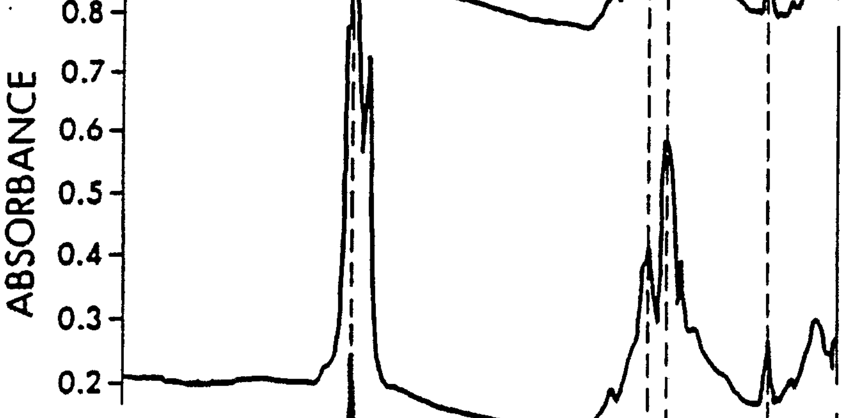

Fig. 3c.

FEED & CATALYST PRECURSOR AT 200 °C

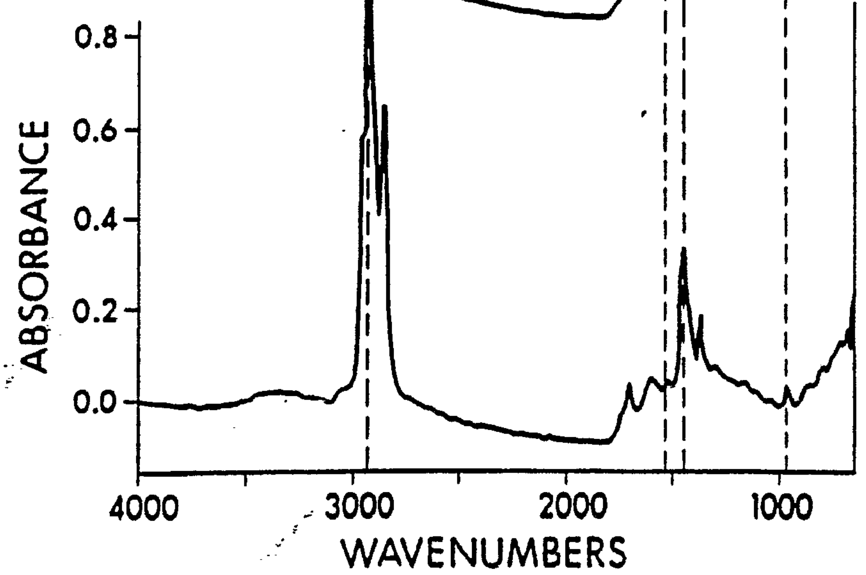

Fig. 3d.

FEED & CATALYST PRECURSOR AT 300 °C

Symbol	Catalyst (Mo)	Pressure (MPa)	LHSV (per hr.)	H_2 (slpm)	Temperature (°C)
●	None	23.8	1.2	40	455
■	None	17.0	4.0	28	455
□	300 ppm	17.0	4.0	28	455
○	300 ppm	17.0	1.2 - 4	13 - 28	440 - 485

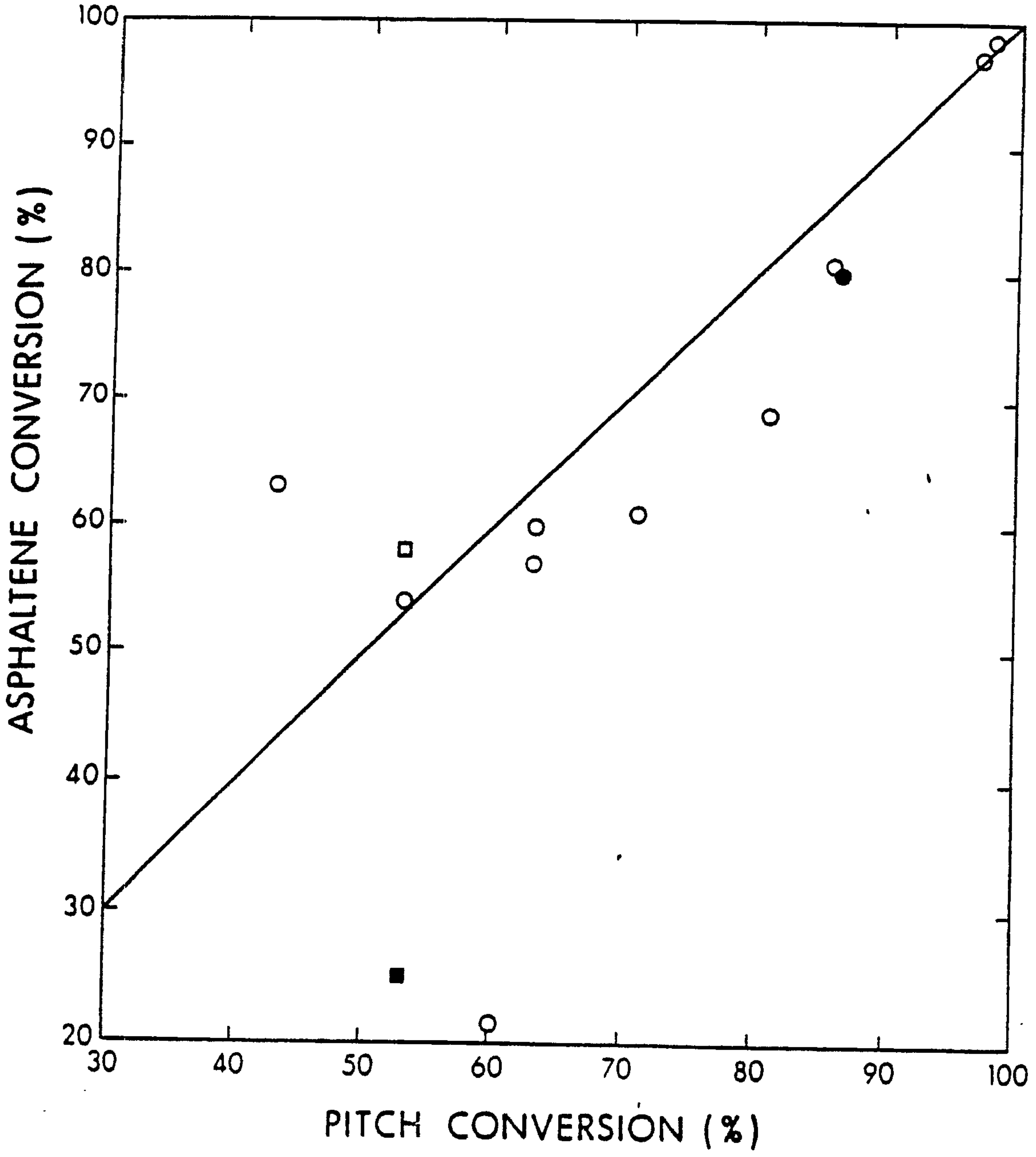

Fig. 4.