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(54) Process for hydroconversion of sulphur containing heavy hydrocarbons with synthesis gas.

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Description

The invention relates to a process for the hydroconversion of sulphur-containing heavy hydrocarbons with synthesis gas in the presence of steam in which synthesis gas and the hydrocarbons are reacted in a reactor at elevated temperature and pressure. Recycle gas from the hydroconversion reaction may be mixed with the synthesis gas.

GB 257 256 discloses the conversion of coal or mineral oils into valuable liquid products by the action of hydrogen and carbon monoxide. The possible presence of sulphur in the material to be treated and the recycle of unreacted synthesis gas is mentioned.

There is no suggestion that the presence of H_2S is desirable. The example shows the use of a gas mixture said to contain 10% of carbon monoxide and 90% of hydrogen. However in practice the gas mixture will contain small quantities of carbon dioxide. If no steps are taken to remove the carbon dioxide, the concentration of carbon dioxide will increase steadily with an adverse effect on the partial pressure of the hydrogen and carbon monoxide reactants. This will also be true for any hydrogen sulphide present in the recycle gas. A skilled person seeking to carry out the reaction of GB 257 256 will therefore insert a separation stage e.g. a scrubber, to remove these undesirable materials from any recycled gas.

GB 400 844 and GB 407 127 disclose the hydrogenation of oil and coal/oil paste with hydrogen alone or with CO, H_2S, steam.

Although these references mention hydrogen sulphide as part of the initial feed there is no suggestion that the use of hydrogen sulphide gives any special advantages. As hydrogen sulphide is well-known to be an axtremely toxic gas, no one will deliberately add it to a chemical reaction in the absence of a clear indication that substantially improved results will be obtained.

DE 713 792 discloses the hydrogenation of wood tars. The presence of 1-15% by weight (based on material to be hydrogenated) of H_2S is said to improve the effectiveness of iron, cobalt and nickel catalysts. There is however no mention of the use of synthesis gas.

DE 2 751 863 describes a two stage hydrotreatment for heavy hydrocarbons. The first stage is preferably carried out in the presence of a quantity of H_2S sufficient to ensure that the volume of this gas is more than 10% at the reactor outlet. There is however no mention of the of synthesis gas in place of pure hydrogen.

However we have found in our process that any benefits obtained by using mixtures of hydrogen and hydrogen sulphide in heavy oil hydrocracking are only minor, and would not compensate for the additional hazards of using large quantities of toxic hydrogen sulphide.

Hettinger et al, Ind. Eng. Chem., 47, pp 719-750 discuss hydroforming reactions to produce gasoline. The presence of sulphur is mentioned.

However Hettinger et al are concerned with the hydroforming of relatively low boiling hydrocarbons to give gasoline, and sulphur is stated to have an adverse effect on this reaction.

The type of process with which the present invention is concerned is disclosed in GB 2 072 697 which is typical of recent publications of this type of process. It discloses a heavy oil cracking process using synthesis gas (H_2, CO). The gas recovered from the cold separator contains H_2, CO, CO_2 and some impurities e.g. H_2S and light hydrocarbon gases. After water and oil scrubbing it is returned to the cracking reactor. However, as we have already explained, if the unreacted gas is recycled it is necessary to remove certain materials such as carbon dioxide which would otherwise increase in concentration in the recycle gas. GB 2 072 697 describes passing the recycled gas through a scrubbing system. This scrubbing process will remove materials such as carbon dioxide and hydrogen sulphide. The hydrogen sulphide concentration in the recycled gas will therefore be low. Moreover hydrogen sulphide is stated to be an impurity and not a desirable constituent of the reaction mixture.

We have now found that by using a specific reactant mixture containing hydrogen sulphide, higher yields of lighter products can be obtained.

According to the present invention a process for the hydroconversion of sulphur containing heavy hydrocarbons in which (1) a gas containing carbon monoxide and steam, and (2) the hydrocarbons are converted in a reactor at elevated temperature and pressure is characterised in that the gas fed to the reactor comprises at least 3% by volume of hydrogen sulphide, based on water free gas.

The gas containing CO and steam used as a feed in the process of the present invention may be derived only from fresh synthesis gas with added steam or may also contain recycled unreacted gas.

Where recycle gas is mixed with fresh synthesis gas the H_2S content is calculated on the total volume of mixture.

The process of the present invention is preferably carried out continuously. In a preferred embodiment the hydrocarbons and the gas are heated in a preheating step before they are fed to the reactor.

According to an advantageous embodiment of the process of the invention, especially with sulphur-poor feeds, the gas fed to the reactor comprises at least 5% by volume of H_2S.

By synthesis gas we mean a gas mixture principally of CO and H_2 obtained for example by gasification of fossil fuels such as lignite, crude oil, natural gas, coal, wood, heavy oil residues and the like by steam cracking of normally gaseous or liquid light hydrocarbon fractions. A typical synthesis gas for use in the process of the invention contains CO and H_2 in various ratios to each other as well as distinguishable quantities of steam and small quantities of CO_2, COS and lower hydrocarbons. The latter originate in particular from the recycle gas. Synthesis gas freed from hydrogen i.e. consisting mainly of CO can be used. Preferably H_2 is present.

The process of the present invention may be applied to uncatalysed reactions e.g. hydrovisbreaking. However it is particularly useful to apply the process to reactions carried out in the presence of a catalyst. Thus the process may be applied to catalyst hydrocracking.

Catalysts which can be used in the process of the invention are known for eaxample from the above mentioned GB 1 072 697 as well as from DE OS 3 212 389. Examples of suitable catalysts are carbonaceous solids e.g. coal, coke or charcoal, which may be coated with up to 20% wt of a metal catalyst such as iron group metal (iron, nickel, cobalt), molybdenum, zinc, tin, tungsten, chromium.

The catalysts can be used in finely divided suspension form («slurry phase»), as an ebulliated bed or as a solid bed. The catalysts quantities employed in the «slurry phase» method are for example 0.2-5% by weight, calculated on the hydrocarbon feed.

The steam required for the reaction can be added together with the fresh feed gas, or fresh gas and recycle gas, or can be added separately. The quantity of steam used will depend on the quantity of hydrogen fed to the reactor as it is believed that the water produces hydrogen by the shift reaction. An excessively high proportion of steam will reduce the partial pressure of the CO. The optimum quantity can be found by simple tests. The quantity of steam may be defined by the amount of liquid water used to produce the steam. The optimum amount of liquid water will in general be within the range 10 to 1000 ml liquid water per kg of liquid hydrocarbon fed, for example 20-200 ml of water per kg of liquid hydrocarbon fed.

The reaction temperature is typically 300-500°C and the reaction pressure 1.5-30 MPa.

Among heavy hydrocarbons which can be used are for example atmospheric or vacuum residues from crude oil distillation as well as heavy hydrocarbons from tar sands and oil shales.

The hydrocarbon is introduced to the reactor with a LHSV rate of 0.2-10 l/l/h in continuous processes.

The ratio of gaseous feed to hydrocarbon is preferably in the range 500-5000 l/kg (litres gas at normal temperature and pressure (0°C, 0.1 MPa pressure) per kg of hydrocarbon). As indicated above this gaseous feed can consist of fresh synthesis gas only (and steam) or synthesis gas and recycle gas (and steam).

As already explained any recycled unreacted gas will be treated so as to remove impurities, and this will result in removal of most of any hydrogen sulphide present. In order to obtain the desired level of hydrogen sulphide in the feed to the reactor, hydrogen sulphide must be added. The hydrogen sulphide may be hydrogen sulphide produced in the reactor from sulphur-containing compounds and which is recovered from the gas treatment step. Such recovered hydrogen sulphide may be added back to the recycle gas immediately after the gas treatment step, or may be added to the fresh gas feed, or to the mixture of fresh and recycle gas.

It may be desirable to use hydrogen sulphide which is not produced in the process, particularly on starting the plant or when using a feed with a relatively low sulphur content. Thus hydrogen sulphide can also be introduced from other sources e.g. from a Claus process.

Increasing hydrogen sulphide content in the reaction system can lower the partial pressure of hydrogen and carbon monoxide to such an extent that the degree of conversion of the heavy hydrocarbon declines; the practical upper limit for the hydrogen sulphide content in the system can however be determined easily by the person of ordinary skill for each individual case.

In general the H_2S content of the feed gas (fresh synthesis gas or a mixture of synthesis gas and recycle gas) preferably does not exceed 20% volume.

The process of the invention will be discussed by reference to the drawing which shows a simplified flow scheme for a continuous apparatus for carrying out of the process of the invention.

The apparatus comprises a hydrocracking reactor 1, which can consist of one or more similar reactors arranged in series, one or more hot separators 2 giving a first coarse separation of the hydrocracking product, one or more reactors 3 in which a post hydrogenation of unsaturated hydrocarbons takes place e.g. in a solid bed with Co/Mo or Ni/Mo-catalysts takes place, as well as a section 4 for gas and product separation in the form of for example a plurality of product separators working with or without pressure, and further apparatus for gas separation such as wash towers, membrane and/or low temperature separation stages.

The reactor 1 is provided with a mixture of heavy hydrocarbons and catalyst through line 5. In line 5 there are one or more pumps and preheater stages 7. Synthesis gas is led through line 8, and H_2S is led through line 9. Steam is led through line 10 or 11 and recycled gas through line 12. Unconverted or insufficiently converted hydrocarbon material separated in hot separator 2 is removed by line 13 or is partly recycled to the conversion reaction through line 14. At the separating stage 4 H_2S and synthesis gas are taken off separately through lines 15 and optionally returned to the process. Lines 16 serves for removal of CO_2, C_1-C_3 hydrocarbons as well as higher hydrocarbons.

The invention will now be illustrated by the following batch experiments, in which comparative tests, not according to the invention, are identified by letters, and examples of the invention are identified by numbers.

The heavy liquid hydrocarbon feedstock used in these experiments was an atmospheric residue (derived from a Boscan crude) with the following characteristics:

Density	1.029 g/ml
C	83.2% wt
H	10.2% wt
S	5.7% wt
N	0.7% wt
Ni	150 ppm
V	1900 ppm
Viscosity 2424 cSt/100°C	
	(2424.10^{-3} Pa.s/100°C)
Conradson Carbon	14% wt
Asphaltenes	16% wt
Distillation ASTM D 1160%	
	recovered at 530°C, 35%.

An autoclave was used with a volume of 5 l. 1 kg of liquid hydracarbon was charged to this reactor together with the catalyst (5% wt based on hydrocarbon feed) and water (70 ml). The catalyst was 3.8% iron (as iron sulphide) on charcoal and it was added as a suspension in waxy distillate derived from Boscan crude (30% wt catalyst, 70% waxy distillate).

After the hydrocarbon, catalyst, and water have been added the autoclave is pressurised to 80 bar (8 MPa) with hydrogenating gas, heated quickly to 440°C, maintained at this temperature for one hour, and then cooled down.

Experiments were carried out with various hydrogenating gases.

Experiment	*Hydrogenating Gas*
Comparative Test A	H_2
Comparative Test B	CO/H_2
Example 1	$CO/H_2/H_2S$
Comparative Test C	H_2/H_2S
Comparative Test D	CO/H_2S

The results obtained are given in the Table.

Comparative Test D shows that the use of mixtures of CO and H_2S give very high coke yields. Such results would not encourage anyone to believe that hydrogen sulphide was in any way satisfactory as a hydrogenating gas.

A comparison of Comparative Test A and Comparative Test C shows that there has been a relatively small increase in hydrogen consumption. The total amount of material boiling in the range C_1-530°C is slightly lower when H_2S is used while the amount of the less desirable high boiling material (boiling at temperatures above 530°C) is higher when H_2S is added.

These results would not encourage the skilled person to believe that there was a significant advantage in using hydrogen sulphide which would compensate for the toxicity problems arising from the use of a hydrogen sulphide feed.

If we now compare Test B with Example 1 however we find that there is a substantial increase in the total amount of material boiling in the range C_1-530°C. Coke formation is lower. Furthermore, although hydrogen sulphide has been added in the feed, the percentage content of sulphur in the liquid product and coke is slightly less. It is of course desirable for the sulphur content of liquid hydrocarbons for fuels to be as low as possible.

The asphaltene content is also lower in the product obtained according to the invention, and the hydrogen content in the fraction boiling above 170°C is higher.

TABLE

Experiment	A	B	1	C	D
Test conditions			80		
Catalyst/H_2O	5%	5% + H_2O	5% + H_2O	5%	5%
Temperature °C	440	440	440	440	440
Pressure (cold/hot)	80/164 bar	82/225 bar	80/197 bar	80/163 bar	80/198 bar
Residence time h	1	1	1	1	
Gas	H_2	CO/H_2	$CO/H_2/H_2S$	H_2/H_2S	CO/H_2S
Composition	100	40/60	34.8/53.2/12	88/12	79/21
H_2-Consumption (Nm3/t)	90	155	184	111	
Mass Balance					
Feed	100	100	100	100	100
H_2	0.8	1.4	1.6	1	*
C_1-C_4	5.4	10	12.4	7.3	*
C_5-170°C	27.6	23.8	26.5	26.4	*
170-350°C	27.6	30.1	26.9	23.5	*
350-530°C	12.2	10.2	14.1	12.7	*
C_1-530°C	72.8	74.1	79.9	69.9	*
greater than 530°C	12.2	11.1	8.9	16.1	*
Coke	13.3	13.7	10.2	12.2	ca. 20
NH_3	0.1	0.1	0.1	0.1	*
H_2S	2.4	2.4	2.7	2.7	*
Summary	100.8	101.4	101.7	101	

1 bar = 0,1 M.Pa

* inaccurate mass balance due to high gas and coke formation

TABLE (Continued)

Experiment	A	B	1	C	D
Asphaltene: wt%	2.7	3	2.6	3.8	
Liquid product + coke					
C	86.1	85.6	85.8	86.2	
H	10.1	10.5	10.5	10.3	
N	0.6	0.6	0.6	0.6	
S	3.2	3.3	3.1	2.9	
Oil phase greater than 170°C					
C	84.9	84.6	85.3	85.2	82.9
H	9.1	10.3	10.7	9.6	9.2
N	0.5	0.4	0.4	0.6	0.7
S	4.1	4	3.7	4.6	4.6

Claims

1. A process for the hydroconversion of sulphur containing heavy hydrocarbons in which (1) a gas containing carbon monoxide, and steam and (2) the hydrocarbons, are converted in a reactor at elevated temperature and pressure characterised in that the gas fed to the reactor comprises at least 3% by volume of hydrogen sulphide, based on water free gas.

2. A process according to claim 1 wherein the process is carried out continuously.

3. A process according to claim 2 wherein the gas and hydrocarbon are subjected to a pre-heating step before being fed to the reactor.

4. A process according to any one of the preceding claims wherein the gas fed to the preheater contains at least 3% volume of H_2S.

5. A process according to any one of the preceding claims wherein the gas comprises at least 5% volume H_2S.

6. A process according to any one of the preceding claims wherein the gas comprises hydrogen.

7. A process according to any one of the preceding claims wherein the gas comprises H_2S not produced in the process.

8. A process according to any one of the preceding claims wherein the gas comprises H_2S separated from the product gas.

9. A process according to any one of the preceding claims wherein the hydroconversion process takes place in the presence of a catalyst.

10. A process according to any one of the preceding claims wherein the catalyst comprises solid carbonaceous material and an iron-group metal.

11. A process according to any one of the preceding claims wherein the process takes place in the presence of a dispersion of a catalyst.

Patentansprüche

1. Verfahren zur Wasserstoffumwandlung von schweren, Sulfur enthaltenden Kohlenwasserstoffen, bei dem (1) ein Carbonmonoxid und Wasserdampf enthaltendes Gas und (2) die Kohlenwasserstoffe in einem Reaktor bei erhöhter Temperatur und erhöhtem Druck umgewandelt werden, dadurch gekennzeichnet, dass das dem Reaktor zugeführte Gas wenigstens 3 Vol.-% Hydrogensulfid, bezogen auf das wasserfreie Gas, umfasst.

2. Verfahren nach Anspruch 1, worin das Verfahren kontinuierlich durchgeführt wird.

3. Verfahren nach Anspruch 2, worin das Gas und der Kohlenwasserstoff vor dem Einleiten in den Reaktor einem Schritt des Vorheizens unterworfen werden.

4. Verfahren nach irgendeinem der vorhergehenden Ansprüche, worin das der Vorheizeinrichtung zugeführte Gas wenigstens 3 Vol.% H_2S enthält.

5. Verfahren nach irgendeinem der vorhergehenden Ansprüche, worin das Gas wenigstens 5 Vol.-% H_2S enthält.

6. Verfahren nach irgendeinem der vorhergehenden Ansprüche, worin das Gas Wasserstoff umfasst.

7. Verfahren nach irgendeinem der vorhergehenden Ansprüche, worin das Gas H_2S enthält, das nicht in dem Verfahren erzeugt worden ist.

8. Verfahren nach irgendeinem der vorhergehenden Ansprüche, worin das Gas H_2S enthält, das von dem Produkt-Gas abgetrennt worden ist.

9. Verfahren nach irgendeinem der vorhergehenden Anprüche, worin das Verfahren der Wasserstoffumwandlung in Gegenwart eines Katalysators stattfindet.

10. Verfahren nach irgendeinem der vorhergehenden Ansprüche, worin der Katalysator ein festes, kohlenstoffhaltiges Material und ein Metall der Eisen-Gruppe umfasst.

11. Verfahren nach irgendeinem der vorhergehenden Ansprüche, worin das Verfahren in Gegenwart einer Dispersion eines Katalysators stattfindet.

Revendications

1. Procédé pour l'hydroconversion d'hydrocarbures lourds contenant du soufre, dans lequel on convertit, dans un réacteur à température et pression

élevées, (1) un gaz contenant du monoxyde de carbone et de la vapeur d'eau et (2) les hydrocarbures, procédé caractérisé en ce que le gaz alimentant le réacteur comprend au moins 3% en volume de sulfure d'hydrogène, sur la base du gaz sans eau.

2. Procédé selon la revendication 1, dans lequel on conduit le procédé en continu.

3. Procédé selon la revendication 2, dans lequel on soumet le gaz et l'hydrocarbure à une étape de préchauffage avant de les introduire dans le réacteur.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'alimentation gazeuse du préchauffeur contient au moins 3% en volume de H_2S.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel le gaz comprend au moins 5% en volume de H_2S.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel le gaz comprend de l'hydrogène.

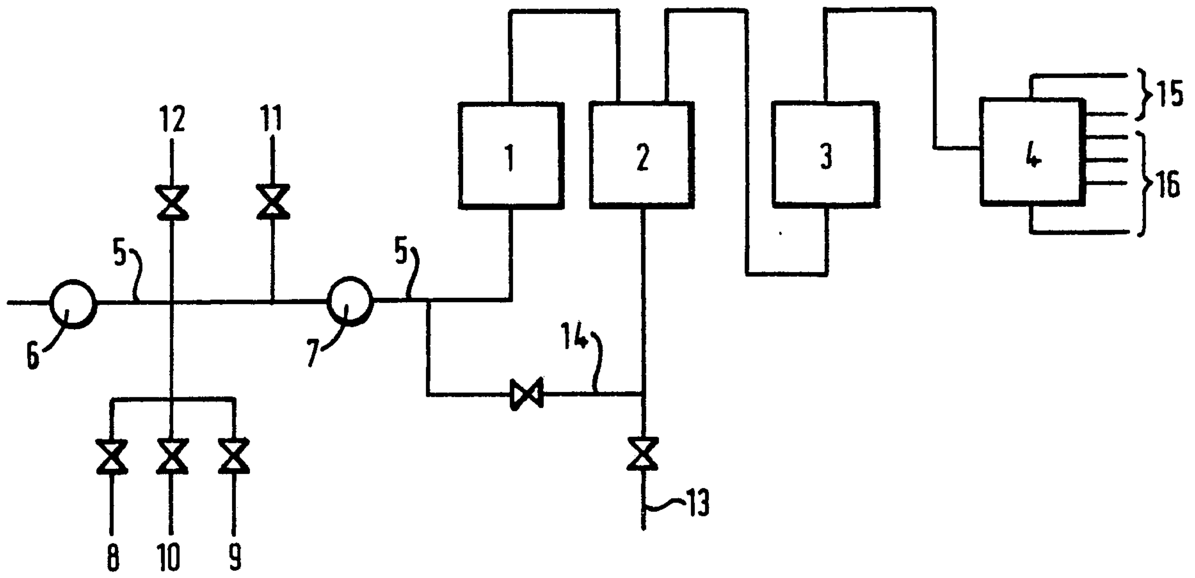
7. Procédé selon l'une quelconque des revendications précédentes, dans lequel le gaz comprend du H_2S non produit dans le procédé.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel le gaz comprend du H_2S séparé du gaz produit.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le procédé d'hydroconversion a lieu en présence d'un catalyseur.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel le catalyseur comprend de la matière carbonée solide et un métal du groupe du fer.

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le procédé a lieu en présence d'une dispersion d'un catalyseur.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