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54 **Heavy oil conversion process.**

57 Process for the conversion of a heavy hydrocarbon oil comprising contacting a hydrocarbon oil which comprises at least 35 %wt of material boiling above 520 °C with a hydrogen containing gaseous stream and a catalyst at a temperature of 450-850 °C and a hydrogen partial pressure of 10-80 bar, whereby coke-bearing catalyst is withdrawn continuously from the reactor and replaced at least partially by regenerated catalyst.

EP 0 400 743 A1

HEAVY OIL CONVERSION PROCESS

The present invention relates to a process for the conversion of a heavy hydrocarbon oil by contacting the hydrocarbon oil with a hydrogen containing gaseous stream and a catalyst at elevated temperature and moderate pressure.

As a result of the growing demand for valuable light hydrocarbon products such as gasolines and middle distillates various processes have been proposed over the years to convert heavy hydrocarbon oils or residues into more valuable light products at increasing extents.

In nowadays oil refining heavy hydrocarbon oils or residues are usually processed in either carbon-rejection type processes such as thermal cracking and fluidized catalytic cracking or hydrogen-addition type processes such as hydrocracking.

Thermal cracking of residual material is usually performed at a relatively low or moderate pressure (usually 5 to 30 bar) and at a relatively high temperature (420-520 °C) without catalysts and in the absence of hydrogen. The thermal cracking reactions take place in a cracking furnace, which is usually followed by a soaker vessel, in which the cracking reactions continue further. Dependent on the applied cracking temperature, pressure and unit configuration (soaker/non-soaker) a relatively long residence time may be applied: 2-60 minutes. The middle distillates obtained from thermal cracking of high boiling residues are of good quality as far as the ignition properties are concerned. The high content of olefins and heteroatoms (especially sulphur and nitrogen), however, make a hydrofinishing treatment necessary for many applications. An intrinsic problem of thermal cracking, however, is the occurrence of condensation reactions which lead to the forming of poly-aromatics. The cracked residue from thermal cracking, therefore, is as such of a moderate quality (high viscosity and high carbon residue after evaporation and pyrolysis, expressed for instance by its Conradson Carbon Residue (CCR) content). The cracking severity in the thermal cracking unit is normally controlled in such a way, however, that a residue is obtained of sufficient quality to be blended to commercial fuels or bitumen.

Fluidized catalytic cracking is usually performed at a relatively low pressure (1.5 to 3 bar), and at relatively high temperatures (480-600 °C) in the presence of an acid catalyst (for instance zeolite containing catalysts). The reaction is carried out in the absence of hydrogen and the residence time of the feed is very short (0.1-10 seconds). During the reaction a rather large amount of carbonaceous materials, hereinafter to be referred to as coke, is deposited onto the catalyst (on average 3 to 8 %wt of the feed). Continuous regeneration of the catalyst by burning-off coke is therefore necessary. The products obtained in this process contain relatively large quantities of olefins, iso-paraffins and aromatics boiling in the gasoline range. Further, light cycle oils boiling in the kerosene range and some heavy cycle oils boiling in the gas oil range and above are obtained, both of a moderate to low quality for use as kerosene and gas oil.

Hydrocracking is usually performed at a relatively high hydrogen partial pressure (usually 100-140 bar) and a relatively low temperature (usually 300 to 400 °C). The catalyst used in this reaction has a dual function: acid catalyzed cracking of the hydrocarbon molecules and activation of hydrogen and hydrogenation. A long reaction time is used (usually 0.3 to 2 l/h liquid hourly space velocity). Due to the high hydrogen pressure only small amounts of coke are deposited on the catalyst which makes it possible to use the catalyst for 0.5 to 2 years in a fixed bed operation without regeneration. The product slates obtained in this process are dependent on the mode of operation. In one mode of operation, predominantly naphtha and lighter products are obtained. The naphtha fraction contains paraffins with a high iso/normal ratio, making it a valuable gasoline blending component. In a mode for heavier products, kerosene and gas oil are mainly obtained. In spite of the extensive hydrogenation, the quality of these products is rather moderate, due to the presence of remaining aromatics together with an undesired high iso/normal ratio of the paraffins among others.

At the present moment, however, there is a growing interest in processes which could combine the separate features of carbon-rejection and hydrogen-addition. Conceptually, these type of processes combine the benefits of carbon-rejection and hydrogen-addition, both contributing to the desired hydrogen/carbon-ratio of the valuable distillate products, in one process step. Such integrated processes could be very attractive because of controlled production of coke and simultaneous upgrading of the distillates obtained.

Object of the present invention is to provide a catalytic process wherein the production of liquid hydrocarbons together with substantial amounts of coke can be controlled and optimized. Moreover it would be highly advantageous when part or all of the coke produced could be converted into energy or hydrogen containing streams for further use in e.g. refineries.

A process has now been found which is especially suitable for the catalytic conversion of heavy

hydrocarbon oils into valuable middle distillates of good quality. The process combines the favourable aspects of carbon-rejection and hydrogen-addition in one process step. The process is carried out at a relatively high temperature and under a moderate hydrogen pressure in the presence of a catalyst. Formation of coke is suitably controlled, whilst a large amount of heavy material is converted into lighter products and moreover upgraded distillates are also obtained.

The present invention thus relates to a process for the conversion of a heavy hydrocarbon oil comprising contacting a hydrocarbon oil which comprises at least 35 %wt of material boiling above 520 °C with a hydrogen containing gaseous stream and a catalyst at a temperature of 450-850 °C and a hydrogen partial pressure of 10-80 bar, whereby coke-bearing catalyst is withdrawn continuously from the reactor and replaced at least partially by regenerated catalyst.

For the sake of completeness reference is made to related non-catalytic processes.

An example of such an process is the so-called Dynacracking Process, described for example in Hydrocarbon Processing, May 1981 pp. 86-92, which is in essence a thermal hydroconversion process carried out in a moving particles system. The feed is thermally hydrocracked in the upper part of the system in the presence of synthesis gas producing substantial amounts of coke which are deposited on inert carrier material. In the lower part of the system coke on the inert material is gasified to synthesis gas with steam and oxygen. The problems to be faced in designing and operating such reactor would seem to be quite formidable.

Another related process is the so-called Asphalt Residue Treating (ART) process which is, for instance, described in United States patent specification No. 4,243,514. The process can be described as a fluidized carbon-rejecting/demetallizing process which is carried out in the absence of hydrogen, and wherein the coke produced is deposited on an inert carrier which is subjected to a regeneration treatment.

A further process is the Fluid Thermal Cracking (FTC) process which is, for instance, described in United States patent specification No. 4,668,378. The process is carried out in a fluidized system in which residual feedstock is contacted with fine porous catalytically inactive particles, which particles are fluidized by steam or a hydrogen-containing gas at a rather low (hydrogen) partial pressure.

The molecular weight reduction in the present process is essentially determined by catalytically induced control of coke make and liquid hydrocarbon production. Due to the presence of hydrogen at a pressure which may vary between 10 and 80 bar the coke make expressed as Conradson Carbon Content of the feedstock varies respectively between 0.4 and 1.0 weight/weight. The activated hydrogen apparently participates in the radical reaction mechanisms and contributes to the saturation of the larger hydrocarbyl radicals resulting in less condensed aromatic structures and finally a lower coke make.

The middle distillates obtained in the present process are of good quality due to the high amount of n-paraffins and the low amount of olefins although they may contain a certain amount of aromatic compounds. The hydrogen consumption of the process is relatively low compared to pure hydrogen-addition processes, as the aromatic components are not substantially hydrogenated. A further advantage resides in the fact that the sulphur present in the feed can be converted for a substantial part into hydrogen sulphide, thus resulting in a product containing a relatively small amount of sulphur. A large part of the metals and nitrogen components present in the feed are deposited in the coke on the catalyst leaving a high quality distillate with a low metal(s) and nitrogen content, which makes it very suitable for product blending or as a feedstock for further upgrading in, for instance, catalytic cracking or hydrocracking units.

When compared with a usual thermal cracking process a higher middle distillate yield is produced with a comparable product quality, assuming that the thermal cracking product is subjected to an additional hydrofinishing treatment.

When compared with a usual catalytic cracking process for residual feedstocks it should be noted that the present process does not entirely depend on the presence of acidic sites on the catalyst. Thus the residual feeds, which normally contain substantial amounts of basic nitrogen and/or sulphur containing compounds can be processed without difficulties. Due to the presence of activated hydrogen less coke is deposited on the catalyst, than would be deposited on the catalyst in case the same feedstock would be processed in a fluidized catalytic cracking process, which implies that the present process can handle considerable heavier feeds than the heaviest feeds which can be processed in catalytic cracking of residual feedstocks.

When compared with a usual hydrocracking process the present process is relatively insensitive to feedstock impurities, especially nitrogen and Conradson Carbon Residue, which are detrimental in hydrocracking processes.

When compared with the Dynacracking, ART and FTC processes as described hereinbefore the present process has the important advantage that a considerable desulphurization and hydrogenation takes place in the presence of a hydrogen activating catalyst at relatively elevated hydrogen partial pressures. This results

both in a higher middle distillate yield of a higher quality and a lower and controllable coke production on feed.

Feedstocks which can suitably be applied in the present process comprise heavy hydrocarbon oils which contain at least 35 %wt of material boiling above 520 °C, and usually more than 15 %wt of material boiling above 620 °C. Atmospheric or vacuum distillates, catalytically cracked cycle oils and slurry oils, deasphalted oils, atmospheric and vacuum residues, thermally cracked residues, asphalts originating from various kinds of deasphalting processes, synthetic residues and hydrocarbon oils originating from tar sands and shale oils of any source can suitably be converted as such or in mixtures in the process according to the present invention, provided that the feedstocks comprise at least 35 %wt of material boiling above 520 °C. Preference is given to the use of feedstocks which comprise at least 50 %wt of material boiling above 520 °C, in particular feedstocks comprising at least 90 %wt of material boiling above 520 °C. Feedstocks comprising more than 3 %wt of asphaltenic constituents, in particular more than 10 %wt, can suitably be processed. Under the asphaltenic constituents mentioned hereinbefore "C₇-asphaltenes" are meant, i.e. the asphaltenic fraction removed from the oil fraction by precipitation with heptane.

Feedstocks containing substantial amounts of sulphur and nitrogen can suitably be applied in the process according to the present invention. Good results have been obtained using feedstocks containing no less than 4000 ppmw nitrogen and 5 %wt of sulphur.

The process according to the present invention is suitably carried out at a reaction temperature of 450-850 °C and a hydrogen partial pressure of 10-80 bar.

It will be appreciated that a higher conversion will be obtained when the temperature is higher, as the rate of cracking of hydrocarbons will be faster at higher temperatures. To obtain the same conversion rate a (slightly) higher temperature or a more acidic catalyst should be used for a feedstock which is more difficult to crack, for instance, a feedstock rich in cyclic compounds.

The process according to the present invention can suitably be carried out in various types of moving bed reactors: a wet fluidized bed reactor, a slurry-type reactor and a riser-type of reactor. Each type of moving bed reactor has its specific preferred reaction conditions.

In case the process according to the present invention is carried out in a wet fluidized bed reactor, i.e. in which part or all of the liquid feed is sprayed on the catalyst particles, normally in the expanded fluidized bed, a suitable reaction temperature is 450-650 °C, preferably 470-600 °C. The hydrogen partial pressure is then suitably chosen between 10-80 bar, preferably between 12-50 bar, more preferably between 15-40 bar. The catalyst/oil ratio can suitably be chosen between 1-20 weight/weight, preferably between 2-12 weight/weight, more preferably between 2-8 weight/weight. Suitably the catalyst residence time in the wet fluidized bed reactor is chosen between 0.2-2.5 minutes, preferably between 0.4-2.0 minutes.

A hydrogen containing gaseous stream is supplied to the wet fluidized bed reactor to provide the hydrogen required for the desired reactions and to maintain a good fluidization, this is suitably achieved at a superficial gas velocity between 0.01-3.50 m/s.

If the present process is carried out in a slurry-type reactor the feed may be pretreated in a mixing zone to produce a slurry of feed and hot catalyst particles which can suitably be introduced into the hydroconversion zone at a temperature of 450-600 °C, preferably 470-550 °C. The hydrogen partial is then suitably chosen between 10-80 bar, preferably between 12-50 bar, most preferably between 15-40 bar. The catalyst/oil ratio in the slurry-type reactor is suitably chosen between 0.01-2.0 weight/weight. The catalyst residence time in the slurry-type reactor is suitably chosen between 0.3-2.0 hours. Suitably the slurry of feed and catalyst is introduced into the reactor at a space velocity of 0.1-10.0 l/l/hr, preferably between 0.25-5.0 l/l/hr. The hydrogen containing gaseous stream can suitably be supplied to the slurry-type reactor at a superficial gas velocity of between 0.05-4.0 m/s to supply the hydrogen required for the desired process reactions and to provide a sufficient high superficial gas velocity to ensure catalyst particulate fluidization. It will be clear from the process conditions as defined hereinabove that a "slurry reactor" in this description also includes a three phase fluid bed reactor.

If the present process is carried out in a riser reactor, in which the liquid feed is sprayed onto the incoming hot catalyst particles, the reaction temperature is suitably between 450-850 °C, preferably between 500-750 °C. The hydrogen partial pressure is suitably chosen between 10-80 bar, preferably between 12-50 bar, most preferably between 15-40 bar. The catalyst/oil ratio is suitably chosen between 1-20 weight/weight, preferably between 2-12 weight/weight, most preferably between 2-8 weight/weight. Suitably the catalyst residence time in the riser reactor is below 2 minutes, preferably between 0.1-10.0 seconds. The hydrogen containing gaseous stream is suitably supplied to the riser reactor at a superficial gas velocity of 0.6-3.5 m/s to provide the hydrogen required for the desired process reactions and to maintain a good fluidization and aeration.

The catalysts to be used in the process according to the present invention should contain a hydrogen

activating function. The catalysts may also contain a moderate acidic function. Suitable catalysts comprise one or more components of a Group IVa, VIb or VIII metal. Good results have been obtained using Ni, V, Mo, Co and/or mixtures thereof. The metal component(s) can be incorporated into various support materials. Suitable support materials comprise silica, alumina, alumina-silica, aluminophosphates, zeolitic compounds, spinel compounds, titania, zirconia and/or mixtures thereof.

It is remarked that the term "acidic" in this specification relates to the presence of one or more active acidic groups, which are able to accelerate the cracking reaction of hydrocarbons presumably by carbonium ion chemistry.

The hydrogen containing gaseous stream used in the process according to the present invention suitably comprises molecular hydrogen. Hydrogen containing refinery streams can be applied. They may also contain lower hydrocarbons, steam and/or mixtures thereof. If desired, synthesis gas can also be used as hydrogen source.

Catalyst regeneration can suitably be carried out by burning off or gasifying the coke deposited on the catalyst using an oxygen and/or steam containing gas. The synthesis gas obtained in the gasification of the coke can suitably be used as a refinery fuel gas or as a hydrogen source for hydroprocesses in the refinery, or as a feedstock for hydrocarbon synthesis processes. If desired, the regeneration process can be suitably carried out by supplying the heat required for gasification via hot particles which preferably have a larger diameter and a higher density than the catalyst particles to be regenerated. The use of relatively large particles (e.g. 3-20 times the diameter of the catalyst particles) allows easy separation by fluidization and/or centrifugation in a cyclone. The hot particles which provide the external heat for the regeneration procedure are suitably brought to the desired temperature by heating in a combustive atmosphere (e.g. in an air/fuel gas system).

Preferably, at least 90% of the coke-bearing catalyst being withdrawn is replaced by regenerated catalyst.

The present invention will now be illustrated by means of the following Example.

EXAMPLE

An Arabian heavy vacuum residue was used as feedstock to demonstrate the conversion process according to the present invention. The feed properties are described in Table 1. Experiments were carried out using a Ni/V/SiO₂ catalyst, a Mo/SiO₂ catalyst, and a SiO₂ carrier as such. The catalysts were prepared by conventional pore volume impregnation techniques. A commercially available carrier was used. Before use, the catalysts were calcined at 500 °C.

Prior to the initial exposure of the catalyst to reaction conditions a sulphidation procedure can suitably be applied.

Suitable sulphidation procedures comprise heating the catalyst together with a sulphur-containing feedstock and hydrogen at appropriate conditions or the use of H₂S and hydrogen.

The reactions were carried out at 459-525 °C and a hydrogen partial pressure of 5-50 bar.

The feedstock and the liquid product were analyzed for the boiling point distribution using a TBP-GLC method up to 620 °C. Moreover GLC analysis of the off-gas was carried out. On the basis of these analyses conversions and product yields were calculated. The 520 °C⁺ conversion has been defined as the amount of 520 °C⁺ material present in the feedstock minus the amount of 520 °C⁺ material present in the total liquid product, divided by the amount of 520 °C⁺ material present in the feedstock. The product slate was split up into gas (C₁-C₄), the total liquid product (C₅⁺) and the coke deposited on the catalyst. The respective fractions have been calculated as the amount of product in question, divided by the total amount of products.

The following experiments were carried out:

Experiment 1

At a reaction temperature of 459 °C and a hydrogen partial pressure of 15.0 bar the Arabian heavy vacuum residue was contacted with a catalyst containing 0.5 %wt Ni and 1.9 %wt V on SiO₂.

Experiment 2

An experiment was carried out in substantially the same manner as described in experiment 1, except that the reaction temperature was 474 °C and the hydrogen partial pressure was 49.6 bar.

5 Experiment 3

At a reaction temperature of 525 °C and a hydrogen partial pressure of 10.7 bar the Arabian heavy vacuum residue was contacted with a catalyst containing 0.5 %wt Ni and 2.1 %wt V on SiO₂.

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Experiment 4

An experiment was carried out in substantially the same manner as described in experiment 3, except that the hydrogen partial pressure was 50.0 bar.

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Experiment 5

20 At a reaction temperature of 525 °C and a hydrogen partial pressure of 5.0 bar the Arabian heavy vacuum residue was contacted with a catalyst containing 4.1 %wt Mo on SiO₂.

Experiment 6

25 An experiment was carried out in substantially the same manner as described in experiment 5, except that the reaction temperature was 470 °C and the hydrogen partial pressure was 50.0 bar.

Experiment 7

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At a reaction temperature of 525 °C and a hydrogen partial pressure of 15.0 bar the Arabian heavy vacuum residue was contacted with pure SiO₂ carrier.

35 Experiment 8

An experiment was carried out in substantially the same manner as described in experiment 7, except that the hydrogen partial pressure was 49.7 bar.

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Experiment 9

An experiment was carried out in substantially the same manner as described in experiment 7, except that the hydrogen partial pressure was 5.0 bar.

45 The results of the experiments when carried out in a wet fluidized bed mode are summarized in Tables 2 and 3.

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EP 0 400 743 A1

Table 1

Properties of Arabian heavy vacuum residue		
Specific gravity	d 25/25	1.033
Sulphur	%wt	5.44
Nitrogen (total)	%wt	0.395
Carbon	%wt	84.45
Hydrogen	%wt	10.15
Vanadium	ppmw	152.8
Nickel	ppmw	49.0
C ₅ -asphaltenes	%wt	23.80
C ₇ -asphaltenes	%wt	11.80
Ramsbottom carbon test	%wt	22.4
Viscosity at 100 °C	cSt	3953.0
Pourpoint	°C	76
TBP/GLC:		
IBP	°C	364
2 %wt recovered at	°C	492
4 %wt recovered at	°C	516
6 %wt recovered at	°C	530
8 %wt recovered at	°C	540
10 %wt recovered at	°C	548
12 %wt recovered at	°C	556
14 %wt recovered at	°C	563
16 %wt recovered at	°C	570
18 %wt recovered at	°C	577
20 %wt recovered at	°C	584
22 %wt recovered at	°C	591
24 %wt recovered at	°C	599
26 %wt recovered at	°C	606
28 %wt recovered at	°C	614
30 %wt recovered at	°C	620
FBP	°C	---

Table 2

Experiment number		1	2	3	4	5
520 °C ⁺ conversion	%wt	94.8	95.7	95.6	94.5	95.1
Product yields:						
total gas make:	%wt	8.1	6.8	8.3	9.9	11.0
H ₂ S	%wt	1.6	1.5	1.3	1.0	1.3
C ₁ -C ₄	%wt	6.5	5.3	7.0	8.9	9.7
Total Liquid Product:	%wt	69.6	80.6	61.7	69.7	62.3
C ₅ -250 °C	%wt	16.7	27.2	17.8	22.8	18.0
250 °C-370 °C	%wt	20.6	26.7	18.4	21.7	18.8
370 °C-520 °C	%wt	27.2	22.2	21.0	19.0	21.1
520 °C ⁺	%wt	5.1	4.5	4.5	6.2	4.4
Coke	%wt	22.3	12.6	30.0	20.4	26.7

Table 3

Experiment number		6	7	8	9
520 °C ⁺ conversion	%wt	98.8	95.4	94.2	93.4
Product yields:					
total gas make:	%wt	9.4	11.1	8.7	13.2
H ₂ S	%wt	2.7	0.9	0.9	0.3
C ₁ -C ₄	%wt	6.7	10.2	7.8	12.9
Total Liquid Product:	%wt	77.8	63.2	68.9	59.5
C ₅ -250 °C	%wt	26.2	19.4	22.0	15.7
250 °C-370 °C	%wt	28.6	20.4	20.1	19.7
370 °C-520 °C	%wt	21.8	19.8	20.8	18.8
520 °C ⁺	%wt	1.2	3.6	6.0	5.3
Coke	%wt	12.8	25.7	22.4	27.3

From the experiments described hereinabove experiments 5 and 7-9 are comparative experiments outside the scope of the present invention.

It will be clear from the results presented in Table 2 that in the presence of a metal function on the carrier, in particular Ni and V, the amount of liquid products obtained is markedly increased with increasing hydrogen partial pressure. Moreover, it was found that with increasing hydrogen partial pressure the amount of coke produced can suitably be controlled. In the absence of a metal function on the carrier (experiments 7-9) as well as in the presence of a metal function but at a hydrogen partial pressure below 10 bar (experiment 5), both the amount of coke produced and the amount of gas produced are rather high at the expense of liquid product.

Attractive levels of desulphurization have been found when using the catalysts in accordance with the present invention, in particular when use is made of Mo containing catalysts.

Similar results as discussed hereinabove can be obtained using alumina-based catalysts.

Claims

1. Process for the conversion of a heavy hydrocarbon oil comprising contacting a hydrocarbon oil which comprises at least 35 %wt of material boiling above 520 °C with a hydrogen containing gaseous stream and a catalyst at a temperature of 450-850 °C and a hydrogen partial pressure of 10-80 bar, whereby coke-bearing catalyst is withdrawn continuously from the reactor and replaced at least partially by regenerated catalyst.
2. Process according to claim 1, wherein the heavy hydrocarbon oil has a content of asphaltenic constituents of at least 3 %wt, preferably of at least 10 %wt.
3. Process according to claim 1 or 2, wherein the heavy hydrocarbon oil comprises at least 50 %wt of material boiling above 520 °C, preferably at least 90 %wt of material boiling above 520 °C.
4. Process according to any one of claims 1-3, wherein the reaction is carried out in a wet fluidized bed reactor at a temperature of 450-650 °C, and wherein the catalyst has a residence time of between 0.2-2.5 minutes.
5. Process according to any one of claims 1-3, wherein the reaction is carried out in a slurry-type reactor at a temperature of 450-600 °C, and wherein the catalyst has a residence time of between 0.3-2.0 hours.
6. Process according to any one of claims 1-3, wherein the reaction is carried out in a riser reactor at a temperature of 450-850 °C, and wherein the catalyst has a residence time below 2 minutes.
7. Process according to any one of claims 1-6, wherein the hydrogen partial pressure is between 12-50 bar, preferably between 15-40 bar.
8. Process according to any one of claims 1-7, wherein the catalyst comprises one or more components of a Group IVa, VIb or VIII metal, in particular Ni, in, Mo, Co and/or mixture thereof.
9. Process according to any one of claims 1-8, wherein the catalyst comprises silica, alumina, alumina-silica, zeolitic compounds, spinel compounds, aluminophosphates, titania, zirconia and/or mixtures thereof.
10. Process according to claim 8 or 9, wherein the metal components are in their sulphidic form.
11. Process according to any one of claims 1-10, wherein the hydrogen containing gaseous stream

comprises molecular hydrogen, synthesis gas, or a refinery stream comprising lower hydrocarbons, steam and/or mixtures thereof.

12. Process according to any one of claims 1-11, wherein the catalyst is regenerated by burning-off or gasifying the coke deposited on the catalyst.

5 13. Process according to any one of claims 1-12, wherein at least 90% of the coke-bearing catalyst is replaced by regenerated catalyst.

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European Patent
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EUROPEAN SEARCH REPORT

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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)
X	GB-A- 831 247 (ESSO) * Claims 1,6; example; page 4, lines 6-11 *	1,8,9, 10,11, 12,13	C 10 G 47/00
X	US-A-4 316 794 (SCHOENNAGEL) * Claims 1,4,6,7,9,13; column 3, lines 26-58 *	1,4,6,7 ,9,11, 12,13	
A	US-A-3 183 180 (SCHUMAN et al.) * Claims 1,2,5; column 4, lines 7-51; column 5, lines 38-52 *	1,5,8,9 ,11	
A	US-A-4 298 458 (BANTA et al.)		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 10 G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 05-09-1990	Examiner DE HERDT O.C.E.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			