

Description

The invention relates to a new process for the conversion of a heavy oil fraction, especially a heavy oil fraction containing a limited amount of asphaltenic constituents, into lighter components.

In the refining process of crude oil to final products, heavy fractions, e.g. fractions boiling between 370-520 °C, are usually processed in cracking processes such as fluidized catalytic cracking, hydrocracking and thermal cracking, in order to convert these high boiling fractions into more valuable lighter fractions.

At the present moment there is a growing demand for middle distillates, i.e. kerosene and gas oil, especially high quality middle distillates. Kerosene usually has a boiling point between about 150 and about 270 °C and is mainly used for jet fuel. A major quality parameter for kerosene and related to the burning properties thereof is the smoke point. Gas oil usually has a boiling point between about 250 and about 370 °C and is mainly used as fuel for compression-ignition engines. Important quality parameters comprise its ignition quality as expressed by the cetane number and its cold flow properties as expressed by the cloud point.

As indicated above three main cracking processes are used in oil refining.

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 acidic 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 large amount of carbonaceous materials (coke) is deposited onto the catalyst (3 to 8 %w 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. Thus, a major product obtained by fluidized catalytic cracking is a gasoline component of good quality. 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 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 the 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 products 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 directed to heavier products, kerosene and gas oil are mainly obtained. In spite of the extensive hydrogenation, the quality of these products is moderate only, due to the presence of remaining aromatics together with an undesired high iso/normal ratio of the paraffins amongst others.

Thermal cracking 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. A long reaction time is used (residence time normally 2-60 minutes). The middle distillates obtained from thermal cracking of high boiling distillates are of good quality as far as the ignition properties are concerned. The high content of olefins and heteroatoms (especially sulphur and nitrogen), however, requires a hydrofinishing treatment. A major problem in thermal cracking, however, is the occurrence of condensation reactions which lead to the forming of polyaromatics. The cracked residue from thermal cracking, therefore, is of a low quality (high viscosity and high carbon residue after evaporation and pyrolysis, expressed for instance by its Conradson Carbon Residue (CCR) content).

It is known from U.S. patent specification 4,017,380 to subject a residual oil to a hydrodesulphurization treatment and to use the thus deactivated hydrodesulphurization catalyst as a fixed or packed (non-fluid) bed of catalytically inert and non porous solids in a hydrovisbreaking process, which process has to be carried out in upward flow. It is stated categorically in said U.S. patent specification that the use of a hydrotreating catalyst in down flow operation under visbreaking conditions would only tend towards undesired aftercracking without increasing the yield of the desired middle distillate product.

A new cracking process has now been found which is especially suitable for the conversion of heavy oil fractions containing a low amount of asphaltenic constituents into middle distillates of good quality boiling in the range of 150-370 °C, i.e. kerosene and gas oil. The new process, hydrocatalytic thermal cracking, (HCTC), is performed at a relatively high temperature (400-550 °C). It is carried out under a moderate hydrogen pressure (10 to 60 bar) in the presence of a non-acidic, hydrogen activating catalyst.

Notwithstanding the relatively low hydrogen pressure the process of the present invention shows an

extremely low rate of coke formation. Undisturbed operation in a fixed bed reactor can be readily achieved for a period of at least 1000 hours. Depending on the specific conditions applied, even substantial longer operation times are possible. In this respect it is remarked that lowering the hydrogen pressure in a conventional hydrocracking process immediately would lead to deactivation of the catalyst by basic nitrogen and carbonaceous deposits, thus limiting the run length.

The present invention thus relates to a process for the conversion of a heavy oil fraction into lighter fractions, comprising passing a heavy oil fraction having a content of asphaltenic constituents of less than 3%w together with a hydrogen containing gas stream through a reaction zone containing a non-acidic, hydrogen activating catalyst at a temperature of 400-550 °C, preferably 410-530 °C, more preferably 440-510 °C, and a hydrogen partial pressure of 10-60 bar, preferably 20-40 bar.

The molecular weight reduction is essentially effected by thermal cracking of feedstock molecules. Thus, in contrast with catalytic cracking and hydrocracking, the novel process does not depend on the presence of acidic sites on the catalyst, which should remain active during the cracking cycle or life of the catalyst. Due to the presence of hydrogen even at relatively moderate pressure, only very small amounts of coke are deposited on the catalyst, thus making it possible to operate in a fixed bed mode (e.g. swing reactor) or a moving bed mode (e.g. bunker flow reactor).

The middle distillates obtained are of good quality due to the high amount of n-paraffins and the low amount of olefins, in spite of the presence of a certain amount of aromatic compounds. The hydrogen consumption of the process is relatively low, as the aromatic compounds are hardly hydrogenated. A further advantage is the fact that, dependent on the catalyst, 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.

The bottom material, i.e. material boiling above the boiling point of the middle distillate products, has excellent properties (viscosity, carbon residue and sulphur content) and can be used as a valuable fuel oil blending component. Further, said heavy material is unexpectedly an excellent feedstock for a fluidized catalytic cracking reaction. When compared with a usual feedstock for a fluidized catalytic cracking reactor, for example a straight run flashed distillate, the gasoline yield and quality are similar. When compared with the bottom material obtained from a distillate thermal cracking reactor as feedstock for a fluidized catalytic cracking process a much higher gasoline yield is obtained.

When compared with a usual thermal cracking process a comparable middle distillate product is obtained, provided that the thermal cracking product is subjected to an additional hydrofinishing treatment. The quality of the unconverted fraction of the product obtained by the new process, however, is much better than the quality of the unconverted fraction of thermal cracking. Due to the presence of activated hydrogen during the reaction the heavy fraction resulting from the present process has a low viscosity, a low content of polyaromatic compounds and a low sulphur content.

When compared with a usual catalytic cracking process the HCTC-process does not depend on the presence of acidic sites on the catalyst. The HCTC process can be suitably carried out in the substantial or even complete absence of acidic sites in the catalyst. Thus, feeds containing a substantial amount of basic nitrogen and/or sulphur containing compounds can be processed without difficulties. Due to the presence of activated hydrogen only very small amounts of coke are deposited on the catalyst, while in fluidized catalytic cracking large amounts of coke are deposited on the catalyst, making continuous regeneration of the catalyst necessary. The products obtained by the present process are predominantly middle distillates of good quality together with a heavy, unconverted fraction of relatively good quality. The major product obtained by fluid catalytic cracking is a gasoline blending component together with a smaller amount of light cycle oil of moderate to low quality as aromatic compounds form the larger part of this light fraction. During the process according to the present invention hardly any hydrogen transfer reactions, resulting in the formation of (poly)aromatic compounds and paraffins from naphthenes and olefins, occur.

With regard to the usual hydrocracking process the process according to the present invention does not depend on the presence of acidic sites on the catalyst. Therefore, HCTC is relatively insensitive to feedstock impurities, especially (basic) nitrogen and carbon residue (CCR). As the process according to the present invention can be carried out during a substantial period at relatively low hydrogen pressure investment costs are considerably lower when compared with a conventional hydrocracking process. The hydrogen consumption in the HCTC-process is relatively low. With regard to the iso/normal ratio of the paraffins it may be remarked that due to the radical type of cracking in the HCTC-process the iso/normal ratio of the paraffins is low, which is favourably for the ignition quality of the gas oil. The classic hydrocracking process results in a high iso/normal ratio due to the carbonium ion reaction mechanism, thus unfavourably affecting the quality, of the middle distillates, especially the ignition quality of the gas oil.

A suitable feed for the HCTC-process according to the present invention is a heavy oil fraction having a

content of asphaltenic constituents of less than 3%w. Vacuum distillates, and/or deasphalted oils of any source and almost limitless as far as the sulphur and nitrogen content is concerned can be used. Suitably the content of asphaltenic constituents in the feed is less than 2%w, more preferably less than 1.5%w, and most preferably less than 1.0%w. Under the asphaltenic constituents mentioned hereinbefore "C₇-asphaltenes" are meant, i.e. the asphaltenic fraction removed from the heavy oil fraction by precipitation with heptane. The feed may contain a substantial amount of carbon residue (CCR), suitably below 15%w, preferably below 10%w, more preferably below 6%w. The amount of sulphur in the feed is suitably below 10%w, preferably below 6%w, more preferably below 4%w. The amount of nitrogen is suitably below 6%w, preferably below 4%w.

Very suitably a vacuum distillate or flashed distillate can be used as feed having a boiling range substantially between 350 and 580 °C, preferably between 370 and 520 °C. Another very suitable feed is a deasphaltized residual oil (DAO), for instance a propane, butane or pentane deasphalted long or short residue.

Also synthetic distillates and/or synthetic deasphalted oils, which are available in for instance complex refineries, are suitable feeds for the present process. A very suitable source for producing such synthetic feeds comprises the so-called hydroconversion process of residual oil fractions, for instance short residue. Such a hydroconversion process preferably comprises a hydrodemetallization step, followed by a hydrodesulphurization/hydrodenitrogenation step and/or a hydrocracking step. It is remarked that usually synthetic flashed distillates or synthetic deasphalted oils are processed in a catalytic cracking process. However, this results mainly in the production of gasoline but no kerosene or gas oil of acceptable quality is obtained. Conventional hydrocracking of such feeds is hardly possible due to the very refractory nature of the nitrogen compounds present and the need for low nitrogen-feeds in the hydrocracking process. Hydrogen conversion processes such as H-oil, LC-fining and Residfining can also be used for the production of the above-indicated synthetic feeds.

Another very suitable feed for the HCTC-process originates from a visbreaking process of for instance short residue. Upon thermally cracking a heavy residue followed by flashing or distillation of the product, a distillate can be obtained substantially boiling in the range between 350 and 520 °C which is an excellent feedstock for the process according to the present invention.

Mixtures of relatively heavy and relatively light feedstocks, e.g. a DAO and a flashed distillate, may be used advantageously in view of reduced coke formation.

The hydrocatalytic thermal cracking process is suitably carried out at a reaction temperature of 400-550 °C, preferably 410-530 °C, more preferably between 440-510 °C, most preferably at about 450 °C. It will be appreciated that a higher conversion will be obtained when the temperature is higher, as the rate of thermal cracking of hydrocarbons will be faster at higher temperatures. To obtain the same conversion rate a (slightly) higher temperature should be used for a feedstock which is more difficult to crack thermally, for instance a feedstock rich in cyclic compounds, than for a feedstock which cracks more easily.

The space velocity of the feed in the novel HCTC process is suitably chosen between 0.1 to 10 l/h, preferably between 0.5 to 6 l/h, more preferably between 1.0 to 5 l/h.

The hydrogen partial pressure under which the HCTC-process is carried out suitably lies between 10-80 bar, preferably 20-40 bar, more preferably about 25 bar. The total pressure in the reactor usually will be between 15 and 65 bar, and is preferably between 25 and 45 bar, more preferably about 30 bar. In this respect it is remarked that the hydrogen partial pressure at the reactor inlet usually will be 3-10 bar higher than at the outlet of the reactor.

The catalysts to be used in the process according to the present invention should contain a hydrogen activating function. Suitable catalysts comprise one or more group IVa, group VIb or group VIII metals. Suitably supports such as silica, alumina, aluminium phosphates, spinel compounds, titania and zirconia can be used. Conventional Group VIb and VIII metal combinations can be employed. It is remarked that the term "non-acidic" in this specification relates to the substantial absence of one or more active acidic sites in the catalyst which are able to accelerate the cracking reaction of hydrocarbons via carbonium ion chemistry. Under initial reaction conditions some acidic sites may be present. However, these acidic sites rapidly deactivate due to coke formation and basic nitrogen adsorption whilst the hydrogen activating function remains substantially unchanged.

When the catalyst comprises a group VIII noble metal the use of palladium or platinum is preferred. When the catalyst comprises a group IVa metal preferably tin is used. When the catalyst comprises a group VIb metal, preferably molybdenum, chromium or tungsten is used. When a group VIII non-noble metal is used, preferably iron, cobalt or nickel is used.

It has been found that very good results can be obtained using Mo-based catalysts, in particular with catalysts containing silica as carrier and having a surface area between 125 and 250 m²/g. The use of such

catalysts allows good hydrodesulphurization activity together with a low coke make.

Preferred catalysts are those catalysts which show a distinct but limited hydrodesulphurization activity. These catalysts show a very low coke formation together with relatively good product properties for the middle distillate fraction. Preferably the second order rate constant of the hydrodesulphurization reaction under the HCTC conditions lies between 0.1 and 1.0, more preferably between 0.2 and 0.5 $1/(h.\%S)$, defined under stationary conditions at 450 °C and using Kuwait flashed distillate.

The hydrogen/feed ratio of the process according to the present invention may be varied over a wide range. A suitable hydrogen/feed ratio lies between 50 NI/kg and 5000 NI/kg, especially between 100 NI/kg and 2000 NI/kg. It is preferred to use a hydrogen/feed ratio between 100 and 500 NI/kg, more preferably between 200 NI/kg and 400 NI/kg. Using these preferred low hydrogen/feed ratios the coke laydown on the catalyst is surprisingly very low. Furthermore, a high cracking conversion is obtained. When compared with a conventional hydrocracking process the hydrogen/feed ratio is significantly lower for the process of the present invention, which is beneficial for process economics. The usual hydrogen/feed ratio in hydrocracking operations lies between 700 and 1500 NI/kg. Generally in hydroprocessing high hydrogen/feed ratios are necessary to suppress coke-formation and to improve the conversion rate. Surprisingly, in the HCTC process a low gas rate is not only possible but also beneficial with respect to both coke formation and conversion.

In a preferred embodiment the above described preferred hydrogen/feed ratio of 200 to 400 NI/kg is used in combination with a catalyst comprising a group VIII noble metal, preferably palladium and/or platinum. The use of the above-indicated hydrogen/feed ratio in combination with the indicated catalyst resulted in a very low coke rate, while the amount of sulphur on the catalyst was also surprisingly low.

In another preferred embodiment of the invention the hydrogen containing stream comprises a mixture of hydrogen and hydrogen sulphide. Carrying out the HCTC-reaction with a mixture of hydrogen and hydrogen sulphide leads to an increase of both conversion level and the selectivity to middle distillates. The amount of hydrogen sulphide in the mixture present in the reactor is suitably up to 50% (v/v) of the amount of hydrogen. Preferably an amount of hydrogen sulphide is used between 1 and 30%, more preferably between 5 and 25%, and most preferably about 10%.

The HCTC reaction according to the present invention is suitably carried out in a fixed bed mode, e.g. a trickle bed downflow reactor. In view of periodical catalyst regeneration, preferably two or more fixed bed are used, operated in a swing-operation. The HCTC reaction is conveniently carried out in an upflow fixed bed reactor, especially when relatively light feedstocks are used. Application of an upflow reactor in that case will result in a reduced rate of coke deposition on the catalyst, thereby increasing the possible run length between two catalyst regenerations. The reduction of the amount of coke on the catalyst in the upflow mode can be 50% or more when compared with the downflow mode. Other preferred modes of operation the process according to the present invention are moving bed operations, e.g. a bunker flow reactor, and an ebullated bed operation.

The products produced in the HCTC process can either be used as such or can be subjected to further treatment. It is possible, for instance, to subject part or all of the product(s) obtained to a desulphurization treatment, in particular a hydrodesulphurization treatment, to adjust the sulphur amount of the product to the desired amount. A further possibility comprises subjecting part or all of the (hydrodesulphurized) product to a hydrofinishing treatment, optionally before or after distillation of the (hydrodesulphurized) product. It is also possible to recycle at least part of the unconverted material present in the product to the HCTC reactor.

Catalyst regeneration is suitably carried out by burning off the carbonaceous material deposited on the catalyst using an oxygen and/or steam containing gas. In case of a fixed bed (e.g. a swing bed) the catalyst regeneration may be carried out in the cracking reactor itself. In case of for instance a bunker flow reactor, the regeneration is typically carried out in a separate regenerator.

The invention is illustrated by the following Examples, although the invention is not limited to these Examples.

Example 1

Catalyst screening experiments

A Kuwait flashed distillate was subjected to the hydrocatalytic thermal cracking process according to the present invention. The feed properties are described in Table I.

The reaction was carried out in an isothermally operated microflow trickle bed downflow reactor. The catalysts were prepared by conventional pore volume impregnation techniques, unless stated otherwise.

Commercial available carriers (silica or alumina) were used (catalysts 1 to 12 and 19-21). Commercially available catalysts, either as such or slightly modified, were used in experiments 13 to 18. The carrier properties are described in Table II. Inorganic precursors were used to prepare catalysts 1-12 and 19-21 (e.g. metal nitrates, ammonium molybdate). Chloride precursors were omitted. Tin was deposited as an organometallic compound (e.g. tin(II)2-ethylhexanoate). NiMo/SiO₂ was prepared via a deposition-precipitation technique as described in e.g. British patent specification 2,189,163. Before use, the catalysts were calcined at 350-450 °C (except for NiMo/SiO₂ catalysts), followed by crushing to smaller particles (Standard sieve designation 180-550 micrometer (30-80 mesh)). An overview of the catalyst formulations is given in Table III.

Prior to exposing the catalysts to reaction conditions a sulphiding procedure is applied. Especially in the case of molybdenum-containing catalysts this is a preferred embodiment as otherwise during the first hours of the experiment sometimes excessive coke formation occurred.

Two sulphiding procedures have been applied. The first one consisted of heating the catalyst together with a sulphur-containing feedstock and hydrogen at a rate of 75 °C/h to 375 °C and keeping the temperature constant overnight. Subsequently, the temperature was increased to 400 °C, kept constant for 6 h, increased to 425 °C and again kept constant overnight followed by heating to 450 °C. Another sulphiding and start-up procedure was applied making use of H₂S. Exposing the catalyst to a mixture of H₂/H₂S (7/1 v/v) at 10 bar, the temperature was increased at a rate of 75 °C/h to 375 °C. Next, the feedstock was introduced and the temperature was increased at a rate of 75 °C/h. It was checked that both procedures lead to identical catalyst performance in terms of e.g. coking. With noble metal catalysts it turned out that also reduction with hydrogen prior to testing gave satisfactory results.

The reactions were carried out at 450 °C and a total pressure of 30 bar. The space velocity (LHSV) was about 1.0 l/h. The H₂/feed ratio was between 850 and 1100 Ni/kg. The reaction time varied between 170 and 220 hours.

Analyses and data handling

The liquid product was analyzed for the boiling point distribution using TBP-GLC. Moreover, GLC analysis of the off-gas was carried out. On basis of these analyses conversions and selectivities were calculated. The conversion has been defined as the net removal (%) of material boiling above 370 °C. The product slate was split up into gas (C1-C4), naphtha (C5-150 °C), middle distillates (150-370 °C) and coke. The selectivities (%) have been calculated as the amount of the product in question, divided by the total amount of products (material boiling below 370 °C and coke). Hydrogen consumptions were calculated on basis of CME (Combustion Mass Spectrometric Element) analyses of both the feedstock and the liquid product and of the gas analyses. The hydrodesulphurization (HDS) activity (second order rate constant) was determined from the sulphur content of liquid product. The results of the experiments are summarized in Table IV.

The product properties of the middle distillates obtained are described in Tables IVa and IVb. The product properties of the bottom fractions are described in Table IVc.

TABLE I

PROPERTIES OF KUWAIT FLASHED DISTILLATE FEEDSTOCK

5	Specific gravity,	d 70/4	0.8858
	Sulphur	%w	2.95
10	Nitrogen (total)	%w	0.0680
	Nitrogen (basic)	%w	0.0250
	Carbon	%w	84.76
15	Hydrogen	%w	12.11
	Ramsbottom carbon test	%w	0.55
	Viscosity at 100 °C	$10^{-6} \text{ m}^2/\text{s}$	7.312
20	Aromatics (UV)	mmol/100 g	
	Mono		55.6
	Di		27.3
25	Tri		23.9
	Tetra		10.5
	Tetra+		12.5
30	TBP/GLC		
	IBP	C	353
	10 %w recovered at	C	395
35	20 %w recovered at	C	412
	30 %w recovered at	C	426
	40 %w recovered at	C	439
40	50 %w recovered at	C	450
	60 %w recovered at	C	462
	70 %w recovered at	C	476
45	80 %w recovered at	C	491
	90 %w recovered at	C	515
	96 %w recovered at	C	523
50	FBP	C	--

TABLE II

PROPERTIES OF CATALYST CARRIERS		
Carrier	Al ₂ O ₃	SiO ₂
Shape	0.8 mm extrudates	1.5 mm spheres
Pore volume, ml/g (H ₂ O)	0.76	0.85
Pore volume, ml/g (N ₂)	n.d.	0.98
Surface area, m ² /g (N ₂)	247	263
Pore diameter, nm (N ₂)	n.d.	19
Pore diameter, nm (Hg)	8.0	14.1
n.d. = not determined		

TABLE III

SURVEY OF EXPERIMENTAL CATALYSTS USED FOR HCTC OF KUWAIT FLASHED DISTILLATE				
Catalyst number	Composition %w on carrier	PV ml/g	SA m ² /g	Bulk density (g/ml)*
1	0.3Pt/0.4Sn/2Cs/Al ₂ O ₃	-	-	0.53
2	0.2Mo/2.5Sn/Al ₂ O ₃	-	-	0.65
3	2Mo/2.5Sn/Al ₂ O ₃	-	-	0.66
4	1.2Ni/2.5Sn/Al ₂ O ₃	-	-	0.61
5	1.2Co/2.5Sn/Al ₂ O ₃	-	-	0.62
6	0.26Mo/3.2Sn/SiO ₂	-	-	0.50
7	3.9Co/11.8Mo/2.4Sn/Al ₂ O ₃	-	-	0.75
8	0.3Pt/Al ₂ O ₃	-	-	0.60
9	0.3Pt/2.5Sn/Al ₂ O ₃	-	-	0.62
10	4.7Ni/16.2Mo/SiO ₂	-	-	0.66
11	0.4Ni/2.0V/SiO ₂	-	-	0.40
12	4.0Mo/SiO ₂	-	-	0.50
13	2.7Ni/13.2Mo/3P/Al ₂ O ₃	0.5	149	0.73
14	3.2Ni/9.1Mo/Al ₂ O ₃	0.56	164	0.74
15	3.2Ni/9.1Mo/2Cs/Al ₂ O ₃	-	-	0.78
16	3.2Co/9.6Mo/Al ₂ O ₃	0.59	221	0.71
17	3.2Co/9.1Mo/Al ₂ O ₃	0.56	165	0.80
18	3.2Co/9.1Mo/2Cs/Al ₂ O ₃	-	-	0.78
19	0.3Pt/0.3Pd/Al ₂ O ₃	-	-	0.66
20	2.5Sn/Al ₂ O ₃	-	-	0.66
21	10Mo/2.5Sn/Al ₂ O ₃	-	-	0.74
PV = pore volume determined with water				
SA = surface area determined with nitrogen (BET method)				
* Bulk density of crushed catalyst				

TABLE IV

Experiment number	1	2	3	4	5	6	7	8	9	10
Catalyst number	3	8	9	1	2	6	11	12	4	5
Conversion	49.9	47.7	50.0	51.6	46.6	46.0	45.4	44.8	42.4	45.9
Selectivity C1-C4 %	6.6	4.9	4.9	7.0	6.9	7.1	9.2	6.0	6.7	6.7
Selectivity C5-150 %	12.6	15.6	14.3	14.0	13.2	12.9	15.2	14.1	9.4	13.8
Selectivity 150-250 %	23.7	24.0	24.8	23.6	24.0	24.5	22.0	24.0	83.7	79.4
Selectivity 250-370 %	57.0	55.3	55.8	55.3	55.8	55.2	53.6	55.8		
Selectivity Coke %	0.16	0.18	0.17	0.10	0.16	0.17	0.10	0.10	0.10	0.11
Total H2 cons. %wof	0.54	0.46	0.28	0.49	0.37	0.18	0.25	0.46	0.29	0.29
K2 HDS 1/(h.%ws)	0.40	0.35	0.31	0.44	0.27	0.11	0.11	0.18	0.23	0.20

TABLE IV (cont'd)

Experiment number	11	12	13	14	15	16	17	18
Catalyst number	16	14	15	18	17	13	7	10
Conversion	%	52.8	51.1	55.3	52.3	55.0	50.8	43.2
Selectivity C1-C4	%	7.5	6.9	6.7	6.9	7.3	7.4	5.4
Selectivity C5-150	%	9.3	12.1	11.1	13.8	13.9	11.0	11.1
Selectivity 150-250	%	24.5		24.6	22.4	23.7	23.6	83.3
Selectivity 250-370	%	58.2	80.6	57.3	56.6	54.6	57.5	
Selectivity Coke	%	0.34	0.30	0.28	0.29	0.36	0.36	0.24
Total H2 cons.	%wof	0.67	0.69	0.36	0.64	0.53	0.59	0.52
X2 HDS	1/(h.%wS)	5.82	6.36	--	4.12	5.35	--	7.00

TABLE IVa

PRODUCT QUALITY ASPECTS OF KEROSENE FRACTIONS (150-250 °C)

Catalyst number	16	12	19*	11*
Yield on feed, %w	10.6	10.9	16.9	13.2
Specific gravity, d 20/4	0.8130	0.8044	0.8077	0.8030
Mid boiling point, C	208	205	207	204
Freezing point, C	-57	n.d.	n.d.	n.d.
Smoke point, mm	15.5	18.5	22.0	19.0
Sulphur, %w	0.025	0.620	0.602	0.697
Carbon, %w	86.77	86.01	85.80	85.91
Hydrogen, %w	13.21	13.55	13.69	13.59
Ozone number, mmol/g	0.38	n.d.	1.6	n.d.

n.d. = not determined

* H₂/feed ratio 250 Nl/kg

TABLE IVb

PRODUCT QUALITY ASPECTS OF GAS OIL FRACTIONS (250-370 °C)

Catalyst number	16	12	19	11
Yield on feed, %w	28.6	25.2	31.1	26.1
Specific gravity, d 20/4	0.8842	0.8897	0.8893	0.8874
Mid boiling point, C	333	324	324	321
Cloud point, C	0	-3	1	-6
Aniline point, C	59.5	n.d.	n.d.	n.d.
Sulphur, %w	0.241	2.51	2.26	2.79
Carbon, %w	87.75	85.76	85.80	85.50
Hydrogen, %w	12.05	12.07	12.06	12.15
Ozone number, mmol/g	0.39	n.d.	0.91	n.d.
Cetane number	43	47	47	47

n.d. = not determined

TABLE IVc

PRODUCT QUALITY ASPECTS OF BOTTOM FRACTIONS (>370 °C)

Catalyst number	16	12	19	11
Yield on feed, %w	51.1	54.1	35.6	49.3
Specific gravity, d 70/4	0.8572	0.8843	0.9116	0.9174
Viscosity (60 °C), cSt	67.70	15.45	19.98	23.26
Mid boiling point, °C	420	424	423	432
Sulphur, %w	0.299	2.19	2.67	3.41
Carbon, %w	87.38	85.78	86.71	85.92
Hydrogen, %w	12.42	11.84	11.12	11.22
RCT, %w	0.15	0.19	1.24	0.87

Example IIEffect of pressure

Using the same general reaction conditions as described in Example I the effect of the total pressure was investigated. The results are summarized in Table V.

TABLE V

Experiment number	1	2	3	4	5	6	7
Catalyst number	11	11	16	16	16	16	16
Pressure	bar	15	30	60	30	20	10
H ₂ /Feed	Nl/kg	228	230	850	230	230	230
Runhours	h	96	208	167	20	20	20
Conversion	%	57.2	57.4	52.8	65.1	70.8	68.2
Selectivity C1-C4	%	4.7	4.4	7.5	5.6	5.5	5.5
Selectivity C5-150	%	16.6	18.0	9.3	13.8	16.6	15.8
Selectivity 150-250	%	26.1	27.6	24.5	80.4	77.9	78.7
Selectivity 250-370	%	52.2	49.9	58.2	0.15	n.d.	n.d.
Selectivity Coke	%	0.43	0.02	0.34	0.15	n.d.	n.d.
Total H ₂ cons.	%wof	0.09	0.28	0.67	0.80	---	---
K ₂ HDS	1/(h.%wS)	0.06	0.10	5.82	---	---	---

n.d. = not determined

Example III

Comparison of catalysts with different HDS-activities

Using the same general reaction conditions as described in Example I, the relationship between the

hydrodesulphurization activity and the coke selectivity of some catalysts was studied. The results are summarized in Table VI.

TABLE VI

Experiment number	1	2	3	4	5	6
Catalyst number	20	2	3	21	19	16
H ₂ /Feed	915	910	895	900	250	250
Runhours	h 179	197	174	179	200	200
Conversion	% 41.4	46.6	49.9	51.8	60.0	65.0
Selectivity C1-C4	% 6.8	6.9	6.6	7.5	5.0	5.0
Selectivity C5-150	% 13.7	13.2	12.6	12.0	16.0	15.0
Selectivity 150-250	% 22.6	24.0	23.7	23.8	24.0	27.0
Selectivity 250-370	% 56.2	55.8	57.0	56.4	55.0	52.0
Selectivity Coke	% 0.46	0.16	0.16	0.26	0.18	0.32
Total H ₂ cons.	%wof 0.06	0.37	0.54	0.55	--	--
K ₂ HDS	l/(h.%w/s) 0.17	0.27	0.40	0.91	0.4	4.7
Smoke point (150-250) °C	--	--	--	--	22.0	15.0
Cetane number (250-370) °C	--	--	--	--	47.0	43.0

Example IV

Effect of temperature

Using the same general conditions as described in Example I, the effect of the temperature was investigated. Catalyst No. 16 was used in experiments 1, 2 and 3, catalyst No. 12 was used in experiment 4. The results are summarized in Table VII.

TABLE VII

Experiment number	1	2	3	4
Temperature deg.C	390	425	450	500
Runhours h	213	165	171	166
H ₂ /feed Nl/kg	900	900	900	1800
Conversion %	19.1	43.1	52.8	51.8
Selectivity C1-C4 %	2.6	5.0	7.5	13.8
Selectivity C5-150 %	6.4	10.9	9.3	18.6
Selectivity 150-250 %	19.0	22.4	24.5	22.5
Selectivity 250-370 %	71.7	61.4	58.2	44.8
Selectivity Coke %	0.15	0.18	0.34	0.52
Total H ₂ cons. %wof	0.64	0.55	0.67	n.d.

Example V

Effect of run length

Using the same general reaction conditions as described in Example I, the effect of the run length at a low H₂/feed ratio was investigated. Catalyst 11 was used for all experiments. The results are summarized in Table VIII.

TABLE VIII

Experiment number	1	2	3	4
H ₂ /Feed	Nl/kg	280	270	230
Runhours	h	23	47	208
Conversion	%	64.0	66.2	57.4
Selectivity C1-C4	%	3.8	4.5	4.4
Selectivity C5-150	%	19.8	20.8	18.0
Selectivity 150-250	%	27.0	26.8	27.6
Selectivity 250-370	%	49.3	47.9	49.9
Selectivity Coke	%	0.09	0.04	0.02
Total H ₂ cons.	%wof	0.23	0.17	0.28
K ₂ HDS	1/(h.%wS)	0.16	0.13	0.10

Example VI

35. Effect of catalyst composition on sulphur deposition

Using the same general reaction conditions as described in Example I, the effect of the catalyst composition on sulphur deposition was investigated. The results are summarized in Table IX.

TABLE IX

Experiment number	1	2	3	4	5
Catalyst number	1	1	11	11	19
Gas rate, Nl/kg	240	910	230	1020	250
Run time, h	190	196	208	138	209
Conversion of >370 °C	63	52	57	45	64
Coke on spent catalyst, %w					
Carbon + hydrogen	5.9	14.5	3.9	12.1	14.3
Sulphur	<0.6	0.3	7.4	2.0	0.6

Example VII

Effect of feedstock

Using the same general reaction conditions as described in Example I, three different feedstocks were compared. The feedstock properties are described in Table X. The Kuwait flashed distillate is described in more detail in Table I. The Kuwait deasphalted oil is a butane-deasphalted short residue. The Maya synthetic flashed distillate has been produced by hydrodemetallization and hydroconversion of Maya short residue, followed by flashing. The results of the experiments are summarized in Table XI.

TABLE X

Feedstock	Kuwait flashed distillate	Kuwait deasphalted oil	Maya synthetic flashed distillate
bp > 370 °C, %w	98	100	88
Sulphur, %w	2.95	4.15	0.42
Nitrogen, %w	0.07	0.21	0.35
ROD, %w	0.55	6.12	1.8
H/C (atomic)	1.71	1.63	1.59

TABLE XI

Feedstock	Kuwait FD	Kuwait DAO	Maya SFD
Catalyst number	16	14	16
Net conversion of bp > 370 °C material, %	52.8	47.9	29.0/43.9*
Selectivity to products, %w			
C ₁ -C ₄	7.5	9.4	6.5
C ₅ -150 °C	9.3	13.2	8.3
150-370 °C	82.7	77.0	84.9
coke	0.34	0.34	0.37
Total liquid product:			
sulphur content, %w	<0.2	0.8	<0.2
nitrogen content, %w	0.05	0.18	0.30
H ₂ consumption, %w on feed	0.7	1.2	n.d.
* at LHSV = 0.5 l.l ⁻¹ .h ⁻¹			
n.d. = not determined			

Example VIII

Effect of H₂S in hydrogen feed

Using the same general reaction conditions as described in Example I, the effect of H_2S in the hydrogen feed was investigated. Catalyst No. 3 was used. The results are summarized in Table XII.

TABLE XII

Experiment	1	2
Fresh gas composition		
% vol H_2	100	90
% vol H_2S	0	10
Net conversion of $370^\circ C^+$	46.5	51.3
Selectivities, %wof		
C_1-C_4 (gas)	6.0	4.9
$C_5-150^\circ C$ (naphtha)	13.5	12.6
$150-370^\circ C$ (mid. dist.)	80.5	82.5

Example IX

Use of HCTC-unconverted material in fluidized catalytic cracking

An HCTC experiment was carried out at $450^\circ C$, 30 bar pressure, an H_2 /feed ratio of 900 NI/kg, and a LHSV of 1.0 l/h using catalyst No. 16 and using Kuwait flashed distillate as feed. The unconverted material, i.e. the fraction boiling above $370^\circ C$ was used as feed for a fluidized catalytic cracking (FCC) reaction. The FCC-unit was operated at constant coke yield and stripper efficiency. A second experiment was carried out using Kuwait flashed distillate. The feed-properties and the FCC yields are summarized in Table XIII.

TABLE XIII

5	Feedstock:	Unconverted material	Kuwait Flashed
		of HCTC experiment	Distillate
	Properties:		
10	Specific gravity, d70/4	0.8572	0.8858
	Sulphur, %w	0.30	2.95
	RCT, %w	0.15	0.55
15	Viscosity, $10^{-6} \text{ m}^2/\text{s}$	67.70 (60 °C)	7.312 (100 °C)
	Mid boiling point, °C	420	420
	FCC-yields (% weight on feed):		
20	C ₂	2.0	3.3
	C ₃	5.5	5.6
	C ₄	9.7	10.0
25	C ₅ -220 °C	48.8	47.4
	LCO	19.4	18.6
	HCO	8.7	9.1
30	Coke	6.0	6.0

Example X

Use of thermally cracked flashed distillate as feed for HCTC

Thermally cracked flashed distillate originating from Arabian heavy feedstock was used as feed for an HCTC experiment carried out at a temperature of 450 °C, a pressure of 30 bar, a LHSV of 1.0 l/h, a H₂/feed ratio of 250 NI/kg and a run length of 161 hrs, using catalyst No. 12. Feedstock properties: specific gravity (d 70/4): 0.9139, sulphur (%w): 2.22, nitrogen (%w) 0.31, RCT: 0.4 (%w). The net conversion was 42.7%. The results are summarized in Table XIV.

TABLE XIV

Selectivities, %	
C ₁ -C ₄	3.9
C ₅ -150 °C	11.5
150-250 °C	21.6
250-370 °C	62.9
Coke	0.05
Total H ₂ cons. %wof	0.22
K ₂ HDS 1/(h.%wS)	0.24

Example XI

Use of feed containing enhanced amount of asphaltenes

A Kuwait long residue was used as feed for an HCTC experiment carried out at a temperature of 450 °C, a pressure of 50 bar, a LHSV of 1.0 l/h, a H₂/feed ratio of 1000 NI/kg and a run length of 50 hours, using catalyst No. 12. Feedstock properties: specific gravity (d 70/4): 0.9139, sulphur (%w): 3.69, nitrogen (%w): 0.15, metals (ppm): 42, RCT (%w): 5.1, C₇-asphaltenes (%w): 2.4. The net conversion was 45%. Selectivities (%): C₁-C₄: 8.0, C₅-150 °C: 11.1, 150 °C-370 °C: 80.1, coke: 0.7.

Claims

1. Process for the conversion of a heavy oil fraction into lighter fractions, comprising passing a heavy oil fraction, having a content of asphaltenic constituents of less than 3%w together with a hydrogen containing gas stream through a reaction zone containing a non-acidic, hydrogen activating catalyst at a temperature of 400-550 °C, preferably 410-530 °C, more preferably 440-510 °C, and a hydrogen partial pressure of 10-60 bar, preferably 20-40 bar.
2. Process as described in claim 1 wherein the heavy oil fraction has a content of asphaltenic constituents of less than 2%w, preferably less than 1%w.
3. Process as described in claim 1 or 2 wherein the heavy oil fraction is a (synthetic) distillate having a boiling range substantially between 350 and 580 °C or a (synthetic) deasphalted oil.
4. Process as described in claim 1 or 2 wherein the heavy oil fraction is a distillate substantially boiling between 350 and 520 °C obtained by thermally cracking a heavy residue.
5. Process as described in claims 1-4 wherein the catalyst comprises one or more group VIII noble metals, preferably palladium or platinum.
6. Process as described in claims 1-5 wherein the catalyst comprises one or more group IVa metals, especially tin, one or more group Vlb metals, especially molybdenum, chromium or tungsten, and/or one or more group VIII metals, especially iron, cobalt or nickel, the metals preferably in their sulphide form.
7. Process as described in claim 6 wherein the catalyst comprises one or more group Vlb metals, especially molybdenum, chromium or tungsten, together with one or more metals chosen from iron, cobalt or nickel, the metals preferably in their sulphide form.
8. Process as described in claims 5-7 wherein the catalyst shows a distinct but limited hydrodesulphurization activity.
9. Process as described in claims 5-8 wherein the catalyst comprises a carrier on which the metals are deposited, preferably a carrier with a pore volume of at least 0.2 ml/g, especially at least 0.5 ml/g.
10. Process as described in claims 1-9 wherein the space velocity of the feed is 0.1 to 5 l/h, preferably 0.5 to 3 l/h and the hydrogen rate is 100-2000 NI/kg, preferably 100-500 NI/kg, more preferably 200-400 NI/kg.
11. Process as described in claims 1-10 wherein the hydrogen containing stream comprises a mixture of hydrogen and hydrogen sulphide, the amount of hydrogen sulphide being up to 50% (v/v) of the amount of hydrogen, preferably between 1 and 30%, more preferably between 5 and 25%.
12. Process as described in claims 1-11 wherein the reaction is carried out in a fixed bed operation, preferably in an upflow mode.
13. Process as described in claims 1-12 wherein at least a part of the unconverted material present in the product of the reaction is recycled.
14. Process as described in claims 1-13 wherein the unconverted material of the reaction is used as feed



Use of feed containing enhanced amount of asphaltenes

A Kuwait long residue was used as feed for an HCTC experiment carried out at a temperature of 450 °C, a pressure of 50 bar, a LHSV of 1.0 l/h, a H₂ feed ratio of 1000 NI/kg and a run length of 50 hours, using catalyst No. 12. Feedstock properties: specific gravity (d 70/4): 0.9139, sulphur (%w): 3.69, nitrogen (%w): 0.15, metals (ppm): 42, RCT (%w): 5.1, C₇-asphaltenes (%w): 2.4. The net conversion was 45%. Selectivities (%): C₁-C₄: 8.0, C₅-150 °C: 11.1, 150 °C-370 °C: 80.1, coke: 0.7.

Claims

1. Process for the conversion of a heavy oil fraction into lighter fractions, comprising passing a heavy oil fraction, having a content of asphaltenic constituents of less than 3%w together with a hydrogen containing gas stream through a reaction zone containing a non-acidic, hydrogen activating catalyst at a temperature of 400-550 °C, preferably 410-530 °C, more preferably 440-510 °C, and a hydrogen partial pressure of 10-60 bar, preferably 20-40 bar.
2. Process as described in claim 1 wherein the heavy oil fraction has a content of asphaltenic constituents of less than 2%w, preferably less than 1%w.
3. Process as described in claim 1 or 2 wherein the heavy oil fraction is a (synthetic) distillate having a boiling range substantially between 350 and 580 °C or a (synthetic) deasphalted oil.
4. Process as described in claim 1 or 2 wherein the heavy oil fraction is a distillate substantially boiling between 350 and 520 °C obtained by thermally cracking a heavy residue.
5. Process as described in claims 1-4 wherein the catalyst comprises one or more group VIII noble metals, preferably palladium or platinum.
6. Process as described in claims 1-5 wherein the catalyst comprises one or more group IVa metals, especially tin, one or more group Vlb metals, especially molybdenum, chromium or tungsten, and/or one or more group VIII metals, especially iron, cobalt or nickel, the metals preferably in their sulphide form.
7. Process as described in claim 6 wherein the catalyst comprises one or more group Vlb metals, especially molybdenum, chromium or tungsten, together with one or more metals chosen from iron, cobalt or nickel, the metals preferably in their sulphide form.
8. Process as described in claims 5-7 wherein the catalyst shows a distinct but limited hydrodesulphurization activity.
9. Process as described in claims 5-8 wherein the catalyst comprises a carrier on which the metals are deposited, preferably a carrier with a pore volume of at least 0.2 ml/g, especially at least 0.5 ml/g.
10. Process as described in claims 1-9 wherein the space velocity of the feed is 0.1 to 5 l/h, preferably 0.5 to 3 l/h and the hydrogen rate is 100-2000 NI/kg, preferably 100-500 NI/kg, more preferably 200-400 NI/kg.
11. Process as described in claims 1-10 wherein the hydrogen containing stream comprises a mixture of hydrogen and hydrogen sulphide, the amount of hydrogen sulphide being up to 50% (v/v) of the amount of hydrogen, preferably between 1 and 30%, more preferably between 5 and 25%.
12. Process as described in claims 1-11 wherein the reaction is carried out in a fixed bed operation, preferably in an upflow mode.
13. Process as described in claims 1-12 wherein at least a part of the unconverted material present in the product of the reaction is recycled.
14. Process as described in claims 1-13 wherein the unconverted material of the reaction is used as feed



for a fluidized catalytic cracking reaction.

Revendications

- 5 1. Procédé pour la conversion d'une fraction d'huile lourde en fractions plus légères, comprenant le passage d'une fraction d'huile lourde, ayant une teneur en constituants asphalténiques de moins de 3 % en poids, en même temps que d'un courant d'un gaz contenant de l'hydrogène, à travers une zone de réaction contenant un catalyseur non-acide activant l'hydrogène, à une température de 400-550 °C, de préférence de 410-530 °C, en particulier de 440-510 °C, et à une pression partielle d'hydrogène de 10-60 bars, de préférence de 20-40 bars.
- 10 2. Procédé selon la revendication 1, dans lequel la fraction d'huile lourde a une teneur en constituants asphalténiques de moins de 2 % en poids, de préférence de moins de 1 % en poids.
- 15 3. Procédé selon la revendication 1 ou 2, dans lequel la fraction d'huile lourde est un distillat (synthétique) ayant un intervalle d'ébullition compris substantiellement entre 350 et 580 °C ou une huile désasphaltée (synthétique).
- 20 4. Procédé selon la revendication 1 ou 2, dans lequel la fraction d'huile lourde est un distillat bouillant substantiellement entre 350 et 520 °C obtenu par craquage thermique d'un résidu lourd.
5. Procédé selon les revendications 1-4, dans lequel le catalyseur comprend un ou plusieurs métaux nobles du groupe VIII, de préférence du palladium ou du platine.
- 25 6. Procédé selon les revendications 1-5, dans lequel le catalyseur comprend un ou plusieurs métaux du groupe IVA, spécialement de l'étain, un ou plusieurs métaux du groupe VIb, spécialement du molybdène, du chrome ou du tungstène, et un ou plusieurs métaux du groupe VIII, spécialement du fer, du cobalt ou du nickel, les métaux étant de préférence dans leur forme sulfurée.
- 30 7. Procédé selon la revendication 6, dans lequel le catalyseur comprend un ou plusieurs métaux du groupe VIb, spécialement du molybdène, du chrome ou du tungstène, en même temps qu'un ou plusieurs métaux choisis parmi le fer, le cobalt ou le nickel, les métaux étant de préférence dans leur forme sulfurée.
- 35 8. Procédé selon les revendications 5-7, dans lequel le catalyseur présente une activité d'hydrodésulfuration nette, mais limitée.
9. Procédé selon les revendications 5-8, dans lequel le catalyseur comprend un support sur lequel les métaux sont déposés, de préférence un catalyseur ayant un volume de pores d'au moins 0,2 ml/g, spécialement d'au moins 0,5 ml/g.
- 40 10. Procédé selon les revendications 1-9, dans lequel la vitesse spatiale de la charge est de 0,1 à 5 l/l/h, de préférence de 0,5 à 3 l/l/h et le débit d'hydrogène est de 100-2000 NI/kg, de préférence de 100-500 NI/kg, de préférence de 200-400 NI/kg.
- 45 11. Procédé selon les revendications 1-10, dans lequel le courant contenant de l'hydrogène comprend un mélange d'hydrogène et de sulfure d'hydrogène, la quantité de sulfure d'hydrogène étant au maximum de 50 % (v/v) de la quantité d'hydrogène, de préférence comprise entre 1 et 30 %, en particulier entre 5 et 25 %.
- 50 12. Procédé selon les revendications 1-11, dans lequel la réaction est conduite dans une opération à lit fixe, de préférence avec écoulement de bas en haut.
13. Procédé selon les revendications 1-12, dans lequel au moins une partie de la matière non transformée présente dans le produit de la réaction est recyclée.
- 55 14. Procédé selon les revendications 1-13, dans lequel la matière non transformée de la réaction est utilisée comme charge pour une réaction de craquage catalytique à lit fluidisé.



Patentansprüche

1. Verfahren zur Umwandlung einer Schwerölfraction in leichtere Fraktionen, umfassend das Führen einer Schwerölfraction mit einem Gehalt an Asphaltenbestandteilen von unter 3 Gew.-% zusammen mit einem Wasserstoff enthaltenden Gasstrom durch eine Reaktionszone, die einen nicht-sauren, Wasserstoff aktivierenden Katalysator enthält, bei einer Temperatur von 400 bis 550 °C, vorzugsweise 410 - 530 °C, stärker bevorzugt 440 - 510 °C und bei einem Wasserstoffpartialdruck von 10 bis 60 bar, vorzugsweise 20 bis 40 bar.
2. Verfahren nach Anspruch 1, worin die Schwerölfraction einem Gehalt an Asphaltenbestandteilen von unter 2 Gew.-%, vorzugsweise unter 1 Gew.-% aufweist.
3. Verfahren nach Anspruch 1 oder 2, worin die Schwerölfraction ein (synthetisches) Destillat mit einem Siedebereich von im wesentlichen zwischen 350 und 580 °C oder ein (synthetisches) entasphaltiertes Öl ist.
4. Verfahren nach Anspruch 1 oder 2, worin die Schwerölfraction ein durch thermisches Cracken eines schweren Rückstandes erhaltenes, im wesentlichen zwischen 350 und 520 °C siedendes Destillat ist.
5. Verfahren nach den Ansprüchen 1 bis 4, worin der Katalysator ein oder mehrere Gruppe VIII-Edelmetalle, vorzugsweise Palladium oder Platin, umfaßt.
6. Verfahren nach den Ansprüchen 1 bis 5, worin der Katalysator ein oder mehrere Gruppe IVa-Metalle, insbesondere Zinn, ein oder mehrere Gruppe VIb-Metalle, insbesondere Molybdän, Chrom oder Wolfram, und/oder ein oder mehrere Gruppe VII-Metalle, insbesondere Eisen, Kobalt oder Nickel umfaßt, wobei die Metalle vorzugsweise in ihrer Sulfidform vorliegen.
7. Verfahren nach Anspruch 6, worin der Katalysator ein oder mehrere Gruppe VIb-Metalle, insbesondere Molybdän, Chrom oder Wolfram, zusammen mit einem oder mehreren Metallen, ausgewählt unter Eisen, Kobalt oder Nickel, umfaßt, wobei die Metalle vorzugsweise in ihrer Sulfidform vorliegen.
8. Verfahren nach den Ansprüchen 5 bis 7, worin der Katalysator eine ausgeprägte, aber begrenzte Hydrodesulfurierungsaktivität zeigt.
9. Verfahren nach den Ansprüchen 5 bis 8, worin der Katalysator einen Träger umfaßt, auf dem die Metalle abgelagert sind, vorzugsweise einen Träger mit einem Porenvolumen von wenigstens 0,2 ml/g, insbesondere wenigstens 0,5 ml/g.
10. Verfahren nach den Ansprüchen 1 bis 9, worin die Raumgeschwindigkeit des Einsatzmaterials 0,1 bis 5 l/h, vorzugsweise 0,5 bis 3 l/h beträgt, und die Wasserstoffrate 100 - 2.000 NI/kg, vorzugsweise 100 - 500 NI/kg, stärker bevorzugt 200 - 400 NI/kg ausmacht.
11. Verfahren nach den Ansprüchen 1 bis 10, worin der Wasserstoff enthaltende Strom ein Gemisch aus Wasserstoff und Schwefelwasserstoff umfaßt, wobei die Schwefelwasserstoffmenge bis zu 50 % (Volumen/Volumen) der Wasserstoffmenge beträgt, vorzugsweise zwischen 1 und 30 %, stärker bevorzugt zwischen 5 und 25 %.
12. Verfahren nach den Ansprüchen 1 bis 11, worin die Reaktion in einem Festbettbetrieb ausgeführt wird, vorzugsweise in einem Aufstrommodus.
13. Verfahren nach den Ansprüchen 1 bis 12, worin wenigstens ein Teil des im Reaktionsprodukt vorliegenden nicht umgewandelten Materials rezykliert wird.
14. Verfahren nach den Ansprüchen 1 bis 13, worin das nicht umgewandelte Material der Reaktion als Einsatzmaterial für eine fluidisierte katalytische Crackreaktion verwendet wird.