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(54) Title: A PROCESS FOR REDUCING THE TOTAL ACID NUMBER (TAN) OF A LIQUID HYDROCARBONACEOUS FEEDSTOCK

(57) Abstract: A process for reducing the total acid number (TAN) of a liquid hydrocarbonaceous feedstock, wherein the feedstock is contacted, in the presence of a hydrogen-containing gas and at a temperature in the range of from 200 to 400 °C and at elevated pressure, with a catalyst comprising an oxide of a metal of Column 3 or 4 of the Periodic Table of Elements or of a lanthanide, which catalyst is essentially free of Column 5 to 10 metals or compounds thereof, to obtain a liquid hydrocarbonaceous product with a reduced total acid number.

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A PROCESS FOR REDUCING THE TOTAL ACID NUMBER (TAN) OF A
LIQUID HYDROCARBONACEOUS FEEDSTOCK

Field of the invention

The present invention provides a process for reducing the total acid number (TAN) of a liquid hydrocarbonaceous feedstock, in particular crude oil.

5 Background of the invention

Crude oil and other liquid hydrocarbonaceous streams with a high amount of acids are difficult to refine. Especially in the distillation unit of a crude oil refinery, a high amount of acids leads to corrosion
10 problems. It is known that acids are removed by hydrotreating, i.e. the same process wherein other heteroatoms like sulphur and nitrogen are removed from liquid hydrocarbonaceous feedstocks. Hydrotreating, however, is a process that is carried out downstream of
15 the distillation unit in a refinery.

In order to avoid corrosion problems resulting from the acid content of the crude oil, different crude oil streams are typically blended to obtain a crude oil feedstock with an acceptable amount of acids.

20 The acid content of a crude oil or of other hydrocarbonaceous liquids is generally expressed as the total acid number (TAN) of such liquid. The TAN represents milligrams KOH per gram liquid needed to neutralise the acid according to a procedure described in
25 ASTM D664.

There is a need in the art for a process that is able to reduce the TAN of liquid hydrocarbonaceous streams such as crude oil that are used as feedstock in

refineries, with minimum conversion of sulphur- and nitrogen-containing compounds and unsaturated hydrocarbons. By such process, an acceptable refinery feedstock would be obtained with minimal hydrogen consumption.

Summary of the invention

It has been found that catalysts that are essentially free of the hydrogenating components that are typically used for hydroconversion reactions such as hydrodesulphurisation, hydrodenitrogenation, and hydrocracking, i.e. compounds of metals of any one of Columns 5 to 10 of the Periodic Table of Elements, can be used for the selective hydrogenation of acids in liquid hydrocarbonaceous streams, in particular crude oil.

Accordingly, the present invention provides a process for reducing the total acid number (TAN) of a liquid hydrocarbonaceous feedstock, wherein the feedstock is contacted, in the presence of a hydrogen-containing gas and at a temperature in the range of from 200 to 400 °C and at elevated pressure, with a catalyst comprising an oxide of a metal of Column 3 or 4 of the Periodic Table of Elements or of a lanthanide, which catalyst is essentially free of Column 5 to 10 metals or compounds thereof, to obtain a liquid hydrocarbonaceous product with a reduced total acid number.

An advantage of the process according to the invention is that the total acid number of the feedstock is reduced by hydrogenation whilst other hydrogenation reactions such as hydrodesulphurisation, hydrodenitrogenation and saturation of unsaturated hydrocarbons are minimised.

Detailed description of the invention

In the process according to the invention, a liquid hydrocarbonaceous feedstock is contacted, in the presence of a hydrogen-containing gas at a temperature in the range of from 200 to 400 °C and at elevated pressure, with a catalyst comprising an oxide of a Column 3 or 4 metal or of a lanthanide, which catalyst is essentially free of Column 5 to 10 metals or compounds thereof.

The feedstock may be any liquid hydrocarbonaceous stream comprising carboxylic, i.e. organic, acids. The process is particularly suitable for feedstocks comprising naphthenic acids. Preferably, the feedstock is a crude oil, a distillate stream such as naphtha or gasoil, a residue fraction of an atmospheric crude oil distillation or a hydrocarbonaceous distillate product not meeting TAN product specifications, such as for example heating oil. The process according to the invention is particularly suitable for the reduction of the total acid number of crude oil.

The hydrogen-containing gas is preferably hydrogen or synthesis gas. The use of synthesis gas as hydrogen-containing gas is particularly advantageous in a situation wherein no hydrogen gas is available, for example at remote places such as off-shore oil platforms.

The temperature and pressure at which the feedstock is contacted with the catalyst is such that hydrogenation of carboxylic acids takes place, i.e. at least 200 °C. The temperature is below the temperature at which thermal decomposition of carboxylic acids occurs, i.e. below 400 °C. Preferably, the temperature is in the range of from 250 to 390 °C, more preferably of from 300 to 380 °C.

The process is performed at elevated pressure, i.e. above atmospheric pressure. Preferably, the pressure is in the range of from 2 to 200 bar g, more preferably of from 10 to 150 bar g, even more preferably of from 25 to 120 bar g.

The catalyst comprises an oxide of a metal of Column 3 or 4 of the Periodic Table of Elements (latest IUPAC notation) or of a lanthanide. The oxide may also be a mixed oxide of two or more of such metals. The catalyst may also comprise a mixture of two or more of such oxides. The catalyst is essentially free of metals of Columns 5 to 10 of the Periodic Table of Elements (latest IUPAC notation) or of compounds thereof. Reference herein to a catalyst essentially free of certain compounds is to a catalyst that is free of such compounds except for minimal amounts, typically in the ppm range or lower, that may be present as unintentional contaminants or as left-overs from a mineral ore refining process for obtaining the oxide of the Column 3 or 4 metal or lanthanide.

Preferably, the catalyst comprises an oxide of a Column 4 metal or of a lanthanide. Preferred Group 4 metal oxides are titanium oxide and zirconium oxide, a preferred oxide of a lanthanide is ceria. More preferably, the catalyst consists of titanium oxide and/or zirconium oxide, even more preferably of zirconium oxide.

The catalyst may be prepared by any preparation method known in the art. Preferably, the catalyst is prepared such that its specific surface area is at least $10 \text{ m}^2/\text{g}$, more preferably at least $30 \text{ m}^2/\text{g}$.

The feedstock for the process according to the invention preferably has a total acid number of at least

0.2 mg KOH/g feedstock, preferably at least 0.5 mg KOH/g feedstock, more preferably at least 1.0 mg KOH/g feedstock. Reference herein to the total acid number is to the amount of KOH (in mg) per gram feedstock as determined by ASTM D664.

The liquid hydrocarbonaceous product has preferably a TAN of at most 0.2 mg KOH/g feedstock, more preferably at most 0.1 mg KOH/g feedstock, even more preferably at most 0.05 mg KOH/g feedstock.

The TAN is preferably reduced to such extent that the liquid hydrocarbonaceous product with a reduced total acid number has at most 50% of the TAN of the feedstock, more preferably at most 30%.

Example

Hydrogenation process

In a microflow reactor, crude oil was contacted with a solid inert material (0.1 mm silicon carbide particles) or with one of the catalysts described below (catalyst particles diluted with silicon carbide particles:

1/1 v/v) in the presence of a hydrogen-containing gas or nitrogen for at least 100 hours. Two different crude oils were used. For experiments 1 to 8 and 13 to 16, a West-African crude oil was used (crude 1); for experiments 9 to 12, a crude oil from the Middle-East was used (crude 2). The specifications of both crude oils are shown in table 1. The exact conditions for each experiment are given in table 2.

The total acid number (TAN) of the liquid effluent of each of the experiments was determined according to ASTM D664. The hydrogen sulphide concentration in the vapour phase effluent was determined by gas chromatography. TAN of the liquid effluent and the

hydrogen sulphide concentration in the vapour phase effluent are also shown in table 2.

Experiments 3, 4, 6, 7, 9, 10, 12 and 14 to 16 are experiments according to the invention. Experiments 1, 2, 5, 8, 11, and 13 are comparison experiments.

Table 1 Crude oil specification

Property	Crude 1	Crude 2
Sulphur content (% wt)	0.41	4.1
Ni content (mg/kg)	32	36
V content (mg/kg)	4	138
TAN (mg KOH/g oil)	2.7	1.3
Density (g/ml)	0.93	0.91
Sediment (mg/kg)	10	1250
Water content (% wt)	0.08	0.27
C ₅ + asphalthenes (mg/kg)	0.26	9.7

Catalysts

The following catalysts were used in the hydrogenation experiments.

Titania catalyst 1

10 A titania catalyst further referred to as titania 1 was prepared as follows. An amount of 3192 grams of titania powder (P25, ex. Degussa; loss on ignition: 4.4 wt% at 540 °C) was mixed with 100 grams oxalic acid dihydrate in a mix-muller kneader (Simpson). After
15 4 minutes of mix-mulling, 981 grams of de-ionised water and 100 grams of polyethylene glycol were added and mix-mulling was continued for another 12 minutes. Then, 100 grams of methyl cellulose were added and mix-mulling was continued for another 20 minutes. The thus-formed

mixture was shaped by extrusion through a 1.7 mm diameter trilobe-shaped die-plate. The trilobes were dried for 2 hours at 120 °C and calcined for 2 hours at 500 °C.

The resulting titania trilobes have a surface area of 52 m²/g as measured by nitrogen adsorption (BET method) and a pore volume of 0.31 ml/g as measured by mercury intrusion.

Titania catalyst 2

Titania particles commercially available as X096 (ex. CRI Catalyst Company) were used as titania catalyst (further referred to as titania 2). These titania particles have a surface area of 120 m²/g as measured by nitrogen adsorption (BET method) and a pore volume of 0.32 ml/g as measured by mercury intrusion.

Zirconia catalyst

A zirconia catalyst was prepared as follows. An amount of 264 grams of zirconia powder (RC100, ex. Daiichi; loss on ignition: 5.3 wt% at 540 °C) was mixed with 90 grams of a solution of 5 wt% polyvinyl alcohol in de-ionised water in a kneader (Werner&Pfeider Sigma kneader type LUK 0.75). After 7 minutes of kneading, 2.5 grams of a cationic poly acryl amide (Superfloc, ex. Cytec) were added and after 20 minutes of kneading 8 grams of de-ionised water were added. The mixture was kneaded for another 22 minutes. The thus-formed mixture was shaped by extrusion into 1.7 mm diameter trilobes. The extrudates were dried for 2 hours at 120 °C and calcined for 2 hours at 550 °C.

The resulting zirconia trilobes have a surface area of 54 m²/g as measured by nitrogen adsorption (BET method) and a pore volume of 0.35 ml/g as measured by mercury intrusion.

NiMo on alumina

A conventional hydrodesulphurisation catalyst comprising Ni and Mo on alumina, which is commercially available as CRITERION RM-5030 (ex. Criterion Catalyst Company) , was used.

5

Table 2 Process conditions; TAN in liquid effluent and H₂S in vapour effluent.

Experiment No.	crude oil	catalyst	gas	p (bar g)	T (°C)	WHVa	gas rate ^b	TANC	H ₂ S in vapour (ppmv)
1	1	none (SiC)	H ₂	10	300	-	720	2.3	n.d.d
2	1	none (SiC)	H ₂	100	300	-	760	2.3	n.d.d
3	1	titania 1	H ₂	10	300	1.2	260	0.7	n.d.d
4	1	titania 1	H ₂	100	300	1.1	270	0.3	n.d.d
5	1	titania 1	N ₂	100	300	1.1	370	2.5	n.d.d
6	1	titania 2	H ₂	10	350	3	290	<0.05	n.d.d
7	1	titania 2	syngas ^f	10	350	3	280	0.3	n.d.d
8	1	NiMo/ alumina	H ₂	10	350	3.7	280	0.05	n.d.e
9	2	titania 2	H ₂	10	350	2	250	0.1	n.d.d
10	2	titania 2	syngas ^f	10	350	2	300	0.2	n.d.d
11	2	NiMo/ alumina	H ₂	40	350	1.7	250	< 0.05	8800
12	2	titania 2	H ₂	40	350	2	250	< 0.05	148

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Table 2 (cont'd) Process conditions; TAN in liquid effluent and H₂S in vapour effluent.

Experiment No.	crude oil	catalyst	gas	p (bar g)	T (°C)	WHV ^a	gas rate ^b	TANC	H ₂ S in vapour (ppmv)
13	1	NiMo/ alumina	H ₂	10	350	1.7	300	0.13	542
14	1	titania 2	H ₂	40	350	3	250	0.05	35
15	1	zirconia	H ₂	10	335	1.2	330	0.07	< 10
16	1	titania 1	H ₂	10	335	1.3	356	0.24	< 10

^a WHV : weight hourly velocity, i.e. kg oil/kg catalyst/hour. In experiments 1 and 2, no catalyst was present and no comparable WHV could be defined (the weight hourly velocity of the oil was 1.1 kg/kg SiC/h in experiments 1 and 2).

^b gas rate in normal litres gas per kg oil.

^c TAN in mg KOH/g oil.

^d not determined; liquid effluent did not have a smell of hydrogen sulphide.

^e not determined; liquid effluent had a smell of hydrogen sulphide.

^f syngas composition: 33.2 vol% hydrogen; 20.7 vol% CO; balance nitrogen.

C L A I M S

1. A process for reducing the total acid number (TAN) of a liquid hydrocarbonaceous feedstock, wherein the feedstock is contacted, in the presence of a hydrogen-containing gas and at a temperature in the range of from
5 200 to 400 °C and at elevated pressure, with a catalyst comprising an oxide of a metal of Column 3 or 4 of the Periodic Table of Elements or of a lanthanide, which catalyst is essentially free of Column 5 to 10 metals or compounds thereof, to obtain a liquid hydrocarbonaceous
10 product with a reduced total acid number.
2. A process according to claim 1, wherein the oxide is an oxide of a Column 4 metal or of a lanthanide, preferably is titanium oxide or zirconium oxide, more preferably zirconium oxide.
- 15 3. A process according to claim 2, wherein the catalyst essentially consists of titanium oxide and/or zirconium oxide .
4. A process according to any one of the preceding claims, wherein the pressure is in the range of from 2 to
20 200 bar g, preferably of from 10 to 150 bar g, more preferably 25 to 120 bar g .
5. A process according to any one of the preceding claims, wherein the temperature is in the range of from 250 to 390 °C, preferably of from 300 to 380 °C .
- 25 6. A process according to any one of the preceding claims, wherein the hydrogen-containing gas is synthesis gas or hydrogen.
7. A process according to any one of the preceding claims, wherein the feedstock has a TAN of at least

0.2 mg KOH/g feedstock, preferably at least 0.5 mg KOH/g feedstock, preferably at least 1.0 mg KOH/g feedstock.

8. A process according to any one of the preceding claims, wherein the liquid hydrocarbonaceous product has
5 a TAN of at most 0.2 mg KOH/g feedstock, preferably at most 0.1 mg KOH/g feedstock, more preferably at most 0.05 mg KOH/g feedstock.

9. A process according to any one of the preceding claims, wherein the liquid hydrocarbonaceous product with
10 a reduced total acid number has a TAN of at most 50% of the TAN of the crude oil product, preferably at most 30%.

10. A process according to any one of the preceding claims, wherein the liquid hydrocarbonaceous feedstock is crude oil.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/061302

A. CLASSIFICATION OF SUBJECT MATTER INV. C10G45/00 B01J21/06 B01G23/10		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) CIOG BOIO		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal , WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 3 846 288 A (CHUN S ET AL) 5 November 1974 (1974-11-05) claims 1,2 -----	1-10
X	GB 496 779 A (BATAAFSCHE PETROLEUM) 6 December 1938 (1938-12-06) claim 1 -----	1-10
X	WO 02/062925 A2 (BP CORP NORTH AMERICA INC [US]) 15 August 2002 (2002-08-15) claims 1,4 -----	1-10
A	US 6 547 957 B1 (SUDHAKAR CHAKKA [US] ET AL) 15 April 2003 (2003-04-15) claims 1,3 -----	1-10
<input type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3846288	A	05-11-1974	NONE
GB 496779	A	06-12-1938	NONE
WO 02062925	A2	15-08-2002	EP 1385922 A2 04-02-2004 JP 2004536159 T 02-12-2004 US 2002148754 A1 17-10-2002
US 6547957	BI	15-04-2003	AU 1419502 A 29-04-2002 BR 0114691 A 13-01-2004 CA 2425922 A1 25-04-2002 CN 1501970 A 02-06-2004 GB 2384783 A 06-08-2003 WO 0233029 A1 25-04-2002