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(54) **Title**: PROCESS FOR TREATING A HEAVY HYDROCARBON FEEDSTOCK TO REDUCE ITS VISCOSITY

(57) **Abstract**: A process for reducing the viscosity a heavy hydrocarbon feedstock, comprising: supplying the heavy hydrocarbon feedstock and elemental sulphur to a reaction zone and reacting, in the liquid phase, at a temperature in the range of from 300 to 750°C, a part of the heavy hydrocarbon feedstock with the elemental sulphur to form a reaction mixture comprising heavy hydrocarbon stream, carbon disulphide and hydrogen sulphide, followed by cooling the reaction mixture to provide treated heavy hydrocarbon stream comprising carbon disulphide. The invention also concerns products obtainable by the above process, as well as its use in pipeline transportation.

PROCESS FOR TREATING A HEAVY HYDROCARBON FEEDSTOCK TO REDUCE ITS VISCOSITY

This invention provides a process for reducing the viscosity of a heavy hydrocarbon feedstock, a heavy hydrocarbon stream obtained by such a process and the use of the heavy hydrocarbon stream in pipeline transportation.

Heavy hydrocarbon feedstocks, like heavy crude oil and bitumen, particularly that produced from certain geological formations as oil sands, can be relatively viscous, that is, can have a viscosity that makes it difficult to transport through a pipeline. Heavy, thick viscous hydrocarbon feedstock is referred to in the petroleum industry as “low gravity” oil; high gravity oil being that which is relatively thin and relatively easy to pump.

Several methods and systems to decrease the viscosity of heavy hydrocarbon feedstocks are known from US 5025863, US 5104516 and FR2484603.

In US 6644334 a method is disclosed to reduce the viscosity of crude oil by injecting into crude oil, under high pressure, a gas, or a combination of gases. Particularly the method is concerned with injecting into crude oil carbon dioxide (CO_2) or more preferably, a combination of CO_2 and nitrogen. This method suffers the disadvantage that reducing the viscosity of crude oil by injecting into the crude oil a gas, or a combination of gases has to be carried out at high gas pressures.

Carbon disulphide is known to be a suitable solvent for enhanced oil recovery. In US 3847221 for example, the use of carbon disulfide for enhanced heavy hydrocarbon feedstock recovery from oil sands by miscible displacement is disclosed. The process involves introducing a slug of solvent mixture for heavy hydrocarbon feedstock recoverable from the oil sands into the reservoir which solvent has a density equal to or greater than water and comprises carbon disulfide and an aromatic hydrocarbon or aliphatic hydrocarbon. Following the solvent mixture, an aqueous fluid is introduced into the reservoir, to force the solvent through the reservoir. The heavy hydrocarbon feedstock and solvent are moving towards a point below the point of introducing of the solvent where the heavy hydrocarbon stream is produced.

A disadvantage of the prior art process described above is that fresh solvents are required for the process, which are introduced into the reservoir. This process works effectively to reduce the viscosity of heavy hydrocarbon feedstocks so it can be more effectively pumped but is expensive and in many applications impractical.

It has now been found that the viscosity of a heavy hydrocarbon feedstock can be reduced without addition of any fresh solvent or solvent mixture. The viscosity of the heavy hydrocarbon feedstock can be advantageously reduced by adding elemental sulphur to the heavy hydrocarbon and heating at a temperature in the range of from 300 to 750 °C. This will result in partly conversion of the heavy hydrocarbon feedstock with elemental sulphur into carbon disulphide and hydrogen sulphide. Cooling down the reaction mixture results in a product in which

carbon disulphide is dissolved in the heavy hydrocarbon feedstock.

Accordingly, the invention provides a process for reducing the viscosity a heavy hydrocarbon feedstock, comprising:

supplying the heavy hydrocarbon feedstock and elemental sulphur to a reaction zone and reacting, in the liquid phase, at a temperature in the range of from 300 to 750°C, a part of the heavy hydrocarbon feedstock with the elemental sulphur to form a reaction mixture comprising heavy hydrocarbon stream, carbon disulphide and hydrogen sulphide, followed by cooling the reaction mixture to provide treated heavy hydrocarbon stream comprising carbon disulphide.

An advantage of the process is that the viscosity of the heavy hydrocarbon feedstock is reduced without addition of fresh solvents or solvent mixtures. In this way the costs of the process of the present invention are sufficiently reduced. Furthermore, the viscosity of heavy hydrocarbon feedstock is reduced in-situ.

The invention further provides a product obtainable by said process. The product formed by said process generally has a viscosity in the range of from 50 to 10000 mPa/s, preferably of from 100 to 1000 mPa/s. In this way the flowability of the heavy hydrocarbon stream has been improved.

The present invention also concerns the use of the product obtained in said process in pipeline transportation.

An advantage of the use of the product obtainable by said process in pipeline transportation is that a product can be made meeting the Canadian pipeline specification for viscosity of 250 cSt (250 mPa/s).

In the process according to the invention, a heavy hydrocarbon feedstock is reacted with elemental sulphur phase at a temperature in the range of from 300 to 750 °C.

Elemental sulphur may be introduced in the form of a vapour phase or a liquid phase. Preferably, elemental sulphur is a liquid elemental sulphur phase. The liquid sulphur phase may consist of sulphur in the form of S_2, S_8 or S_∞ or mixtures thereof. Generally, sulphur has a melting point between 96 and 116 °C. The liquid sulphur phase and heavy hydrocarbon feedstock are added to a reaction zone, in which they are reacted with each other in the liquid phase. The reaction zone may typically be a reactor vessel or tube. The heavy hydrocarbon feedstock may be supplied to the reaction zone containing liquid elemental sulphur phase.

The heavy hydrocarbon feedstock may be oil sand derived bitumen or an atmospheric residuum obtained by distillation, especially by vacuum distillation of heavy crude oil or by vacuum distillation of oil sand derived bitumen, especially residual bitumen with a solubility of at least 99.5% in carbon disulphide.

The heavy hydrocarbon feedstock comprises a hydrocarbonaceous compound having carbon and hydrogen atoms and, optionally, a smaller amount of heteroatoms such as oxygen, sulphur or nitrogen. The hydrocarbonaceous compound is liquid at the reaction conditions applied. The heavy hydrocarbon feedstock may have a starting boiling point between 350 and 850 °C.

In the process according to the invention, the hydrocarbonaceous compound and elemental sulphur react with each other. The overall reaction equation is:

$$C_x H_y + (2x+\tfrac{1}{2}y)S \longrightarrow xCS_2 + \tfrac{1}{2}yH_2S$$

The heavy hydrocarbon feedstock may comprise more than one hydrocarbonaceous compound.

In the process according to the invention, both the heavy hydrocarbon feedstock and the elemental sulphur will typically continually be supplied to the reaction zone. Suitably, the heavy hydrocarbon feedstock is supplied to the reaction zone by pre-mixing it with the liquid sulphur phase. The amount of elemental sulphur added to the reaction zone is in the range of from 1 to 25 wt.% based on the heavy hydrocarbon stream.

The contact time of the heavy hydrocarbon feedstock with the liquid sulphur is preferably in the range of from 1 to 3600 seconds, preferably in the range of from 5 to 600 seconds.

In the process according to the invention the liquid elemental sulphur phase is kept at a temperature in the range of from 250 to 750 °C. At temperatures below 250 °C, the high viscosity of the liquid sulphur phase would impede proper processing. Preferably, the temperature is in the range of from 350 to 700 °C, more preferably of from 400 to 650 °C.

The reactants are reacted with each other at a pressure that is sufficient to maintain a liquid elemental sulphur phase. Therefore, the pressure may strongly depend on the reaction temperature. Preferably, the pressure in the reaction zone is in the range of from 3 to 200 bar (absolute), more preferably of from 4 to 100 bar (absolute), even more preferably of from 5 to 30 bar (absolute).

In the process according to the invention, a reaction mixture comprising heavy hydrocarbon stream, carbon

disulphide and hydrogen sulphide is formed. This reaction mixture is transported to a second reactor vessel or tube wherein the reaction mixture is cooled down to obtain a liquid stream comprising carbon disulphide.

The amount of carbon disulfide formed is preferably between 1 and 25 wt% based on the weight of heavy hydrocarbons. Typically, the liquid stream comprising carbon disulphide obtained by the process according to the invention will also comprise hydrogen sulphide.

A typical hydrogen sulphide concentration is in the range of 0.05 to 50 wt%, especially 0.2 to 10 wt.% hydrogen sulphide based on the amount of heavy hydrocarbon.

After the reaction is completed, the mixture is cooled down, resulting in a reduced viscosity of the heavy hydrocarbon. The product comprising partly converted heavy hydrocarbons, carbon disulphide and hydrogen sulphide has a reduced viscosity in the range of from 50 to 10000 mPa/s, more preferably in the range of from 100 to 1000 mPa/s.

It is known that the reaction between heavy hydrocarbons and sulphur can be performed in the presence of a catalyst, for instance as described in EP06116866.2. Preferably, the hydrocarbonaceous compound is reacted with the sulphur in the absence of a catalyst.

Preferably, the process according to the invention comprises splitting the heavy hydrocarbon feedstocks into two feedstocks (first and second feedstock), from which the first feedstock is reacted with elemental sulphur in the reaction zone, and the treated first stream is combined with the second feedstock in a second vessel or tube. Preferably, the first feedstock is 1 to 50 wt%, especially 5 to 40 wt% based on the weight of the heavy

hydrocarbon feedstock. In this way, only 1 to 50 wt% of the heavy hydrocarbon feedstock has to be heated to a temperature in the range of from 300 to 750 °C, in order to obtain a product according to the present invention with the same reduced viscosity as described above.

The product comprising carbon disulphide formed in the process according to the invention, is particularly suitable to be transported via pipelines as it generally will meet requirements such as the Canadian specifications for pipeline transport.

The product comprising carbon disulphide may be transported at a temperature usually range of from 5 to 80 °C. Heating of the pipeline is not necessary. Therefore, the transport temperatures can be reduced by a temperature decrease of from 30 to 80 °C, preferably of from 40 to 60 °C. In this way the transportation of heavy hydrocarbon feedstocks is economically viable.

Suitably, the hydrogen sulphide may be removed from the reaction mixture by a gas/liquid separation. Optionally, after the gas/liquid separation the reaction mixture can be further purified from hydrogen sulphide by stripping of the liquid stream by a gas stream, for instance nitrogen, carbon dioxide or methane.

Suitably, the hydrogen sulphide may be removed from the reaction mixture after pipeline transportation. Optionally, the separated hydrogen sulphide can be converted to elemental sulphur, e.g. in a Claus process, and recycled to the reaction zone. The amount of hydrogen sulphide removed from the reaction mixture is in the range of 0.05 to 40 wt.%, especially 0.2 to 10 wt% hydrogen sulphide based on the amount of heavy hydrocarbon.

Carbon disulphide may be separated from the heavy hydrocarbon stream after pipeline transportation. The separation of carbon disulphide may be done by any suitable method, such as distillation. The separated carbon disulphide is preferably recycled and mixed with heavy hydrocarbons in a mixing vessel or tube.

Due the formation of carbon disulphide the viscosity of the heavy hydrocarbon stream may be reduced in a range of from 10 to 99.9%, especially 80 to 99%, expressed as mPa/s.

The process according to the invention will be further illustrated by means of the following non-limiting examples.

Examples

Peace River Bitumen (PR-B) and Peace River Long Residue (PR-LR) are heavy oils with high viscosities. Carbon disulphide was used to reduce the viscosity of both oils. Several mixtures of oil and carbon disulphide were tested to measure the influence the carbon disulphide /oil ratio on the viscosity.

Example 1

In a glass bottle an amount of carbon disulphide was added to 31.1 gram of PR-LR (44.9 mmol) to prepare PR-LR samples based on 1.2, 5, 10, 15 and 40 wt% carbon disulphide. After the addition was complete, the mixture was shaken for one hour in order to allow the carbon disulphide to dissolve and to obtain a homogeneous liquid. On a HAAKE Viscotester Typle 7R plus (Thermo Electron, GmbH) the viscosity of the samples were measured in a temperature controlled bath at several temperatures. Table 1 show the viscosity date of PR-LR. The calculated %wt carbon disulphide in the oil were based on the total amount of oil and carbon disulphide.

The results from Table 1 show that the viscosity of PR-LR is reduced upon the addition of carbon disulphide. Increasing the amount of carbon disulphide reduces the viscosity further. Furthermore, when similar weight ratios of PR-LR are used at different temperatures the viscosity decreases with increasing temperatures. This observation indicates that the dissolvement of carbon disulphide in oil and the viscosity is sensitive to the temperature.

Example 2

In a glass bottle an amount of carbon disulphide was added to 31.1 gram of PR-B (46.8 mmol) to prepare PR-LR samples based on 0, 1.2, 6.2, 10.5 and 20.1 wt% carbon disulphide. The same procedure was performed as for Example 1. Table 2 shows the results for PR-B. The calculated %wt carbon disulphide in the oil were based on the total amount of oil and carbon disulphide.

The results in Table 2 show that similar results were obtained with the use of carbon disulphide in PR-R compared to the results obtained with PR-B.

Table 1

PR-LR with 1.2 %wt CS_2		PR-LR with 5 %wt CS_2		PR-LR with 10 %wt CS_2		PR-LR with 15 %wt CS_2		PR-LR with 20.8 %wt CS_2		PR-LR with 40 %wt CS_2	
T (°C)	Viscosity (mPa·s)	T (°C)	Viscosity (mPa·s)	T (°C)	Viscosity (mPa·s)	T (°C)	Viscosity (mPa·s)	T (°C)	Viscosity (mPa·s)	T (°C)	Viscosity (mPa·s)
22.3	3178100	22.0	249500	22.3	123500	22.0	7800	26.0	970	20.4	80
39.2	214000	26.0	166000	30.0	51000	28.0	5400	31.1	890		
47.1	76600	33.0	64000	32.9	34600	34.0	3500	40.2	570		
								45.2	410		

Table 2

PR-B without CS_2		PR-B with 1.2 %wt CS_2		PR-B with 6.2 %wt CS_2		PR-B with 10.5 %wt CS_2		PR-B with 20.1 %wt CS_2	
T (°C)	Viscosity (mPa·s)	T (°C)	Viscosity (mPa·s)	T (°C)	Viscosity (mPa·s)	T (°C)	Viscosity (mPa·s)	T (°C)	Viscosity (mPa·s)
22.4	63060	24.0	35030	17.3	5800	20.8	950	17.8	220
35.0	18960	30.2	25130	22.1	5160	32.0	720	27.0	200
50.0	5330	40.0	15100	29.0	3340	40.0	530	37.0	150
59.7	3100	51.4	7440	39.1	1910	45.0	480	45.1	120
		60.0	4270	50.0	1230				
				60.3	890				

C L A I M S

1. A process for reducing the viscosity a heavy hydrocarbon feedstock, comprising:

supplying the heavy hydrocarbon feedstock and elemental sulphur to a reaction zone and reacting, in the liquid phase, at a temperature in the range of from 300 to 750°C, a part of the heavy hydrocarbon feedstock with the elemental sulphur to form a reaction mixture comprising heavy hydrocarbon stream, carbon disulphide and hydrogen sulphide, followed by cooling the reaction mixture to provide treated heavy hydrocarbon stream comprising carbon disulphide.

2. A process according to claim 1, wherein the amount of elemental sulphur added to the reaction zone is in a range of from 1 to 25 wt% based on the heavy hydrocarbon stream.

3. A process according to claim 1 or 2, wherein the amount of carbon disulfide formed is between 2 and 25 wt% based on the weight of heavy hydrocarbon feedstock, preferably between 5 and 20 wt%.

4. A process according to any of claims 1 to 3, wherein the heavy hydrocarbon feedstock is a heavy crude oil, preferably a residual heavy oil.

5. A process according to any of claims 1 to 4, wherein the heavy hydrocarbon feedstock is bitumen.

6. A process according to any of claims 1 to 5, wherein formed hydrogen sulphide is removed from the reaction mixture by a gas/liquid separation, optionally followed by stripping of the liquid stream with a gas stream.

7. A process according to any of claims 1 to 6, wherein the elemental sulphur is a liquid elemental sulphur phase.

8. A process according to any of claims 1 to 7, wherein the heavy hydrocarbon feedstock is split into two feedstocks, the first feedstock is reacted with elemental sulphur, and the treated stream is combined with the second feedstock.

9. A process according to any of claims 1 to 8, wherein the pressure in the reaction zone is in the range of from 3 to 200 bara (absolute), more preferably of from 5 to 30 bara (absolute).

10. A product obtainable by a process as claimed in any of claims 1 to 9, preferably wherein the viscosity of the product is in the range of from 50 to 10000 mPa/s, more preferably in the range of from 100 to 1000 mPa/s.

11. Use of the product as claimed in claim 10, in pipeline transportation.

12. Use of the product as claimed in claim 11, at a temperature range of from 5 to 80°C.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/067046

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B31/26 E21B43/16
ADD.

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)
C10G C01B E21B

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006/254769 A1 (WANG DEAN C [US] ET AL WANG DEAN CHIEN [US] ET AL) 16 November 2006 (2006-11-16) paragraphs [0042], [0044], [0069] - [0071]; claim 1	1-9
Y	WO 2007/131976 A (SHELL INT RESEARCH [NL]; MESTERS CAROLUS MATTHIAS ANNA [NL]; SCHOONEBE) 22 November 2007 (2007-11-22) page 2, line 6 - line 19 page 4, line 29 - line 31 page 7, line 24 - line 35	1-9
Y	WO 2007/131977 A (SHELL INT RESEARCH [NL]; MESTERS CAROLUS MATTHIAS ANNA [NL]; SCHOONEBE) 22 November 2007 (2007-11-22) claim 1	1-9

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/067046

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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