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(54) Title: METHOD OF SEPARATING PARTICLES FROM A HYDROCARBON COMPOSITION

(57) **Abstract:** The invention provides a method of reducing solid particulate matter content of a crude tar feed, which crude tar feed includes a hydrocarbon fluid fraction, a water fraction, and a solid particulate matter fraction which is at least partially coated with the hydrocarbon fluid fraction, the method including at least the steps of introducing a solvent into the crude tar feed, and removing from the solid particulate matter at least a portion of the hydrocarbon fluid fraction that coats the solid particulate matter while decreasing the density of the crude tar feed to well below the density of water and of the solid particulate matter in the crude tar feed.

Method of Separating Particles from a Hydrocarbon Composition

Field of the Invention

This invention relates to a method of separating particles from a hydrocarbon composition prior to refining of said composition and, more specifically, to the separation of coal and ash particles from a crude tar feed derived from the gasification of coal.

Background to the Invention

During gasification of coal various hydrocarbon streams are produced which are processed further to obtain a range of chemical products. One such hydrocarbon stream is a so-called crude tar feed stream that is further refined to produce tar.

Said crude tar feed stream contains solid particles that are typically fine coal particles and/ or ash and which must be separated from the tar feed prior to refining.

The inventor is aware of decanting and filtration methods used in the industry to separate the unwanted solid particulate matter from the crude tar feed prior to refining.

These methods are very costly and filtration especially is difficult to carry out since the fluid flow properties of the crude tar feed may vary greatly often resulting in the formation of a water-tar emulsion as well as the viscosity and density of the crude tar feed varying around that of water, making process control difficult.

The inventor therefore believes, that a need exists for a cost-effective method of separating a substantial amount of solid particulate matter from a crude tar feed as described above.

In the specification that follows the term “crude tar feed” is to be interpreted as meaning a hydrocarbon feed stream produced during coal gasification and which is to be refined further to produce tar.

Summary of the Invention

According to the invention there is provided a method of reducing solid particulate matter content of a crude tar feed, which crude tar feed includes a hydrocarbon fluid fraction, a water fraction, and a solid particulate matter fraction which is at least partially coated with the hydrocarbon fluid fraction, the method including at least the steps of:-

introducing a solvent into the crude tar feed; and

removing from the solid particulate matter at least a portion of the hydrocarbon fluid fraction that coats the solid particulate matter while decreasing the density of the crude tar feed to well below the density of water and of the solid particulate matter in the crude tar feed.

A typical crude tar feed when analysed according to ASTM D1160 has the following boiling point analysis as shown in table 1.

Table 1: D1160 Tar Analysis

Volume %	**°C**
IBP	183.5
5	214.1
10	242.7
15	275.3
20	303.9
25	325.8
30	341.7
35	354.8
40	368.7
45	383.4
50	399.9
55	414.4
60	428.1
65	430.0
70	372.3
75	485.1
80	-
85	-
90	-
95 (FBP)	-
Recovered (volume %)	79.4

No measurements were taken above 500°C.

The method may further include the step of allowing the resulting mixture to settle into a water phase and a hydrocarbon phase or tar phase for a predetermined period of time and to allow at least a fraction of the solid particulate matter to migrate from the hydrocarbon phase into the water phase.

The migration mechanism for the solid particulate matter from the hydrocarbon phase into the water phase may be gravity settling.

The method may include the use of a wetting agent as a settling aid for settling fine particles from out of the hydrocarbon phase into the water phase.

The method may include the use of a de-emulsifying agent as a settling aid for settling fine particles from out of the hydrocarbon phase into the water phase.

The method may further include the step of separating the water phase and the solvent from the hydrocarbon phase by any suitable separation process.

The water and solvent phase may be separated from the hydrocarbon phase by centrifugation or distillation.

The hydrocarbon fluid fraction that coats the solid particulate matter in the crude tar feed may be a tar fraction including asphaltenes.

The solvent may be any solvent capable of washing off matter that coats the solid particulate matter so as to free the solid particulate matter for migration from the hydrocarbon phase into the water phase.

The solvent may be a solvent rich in benzene but may alternatively be a solvent rich in toluene, xylene, paraffins, pyridine, quinoline or the like.

A benzene rich solvent may typically include about 40 mass percent benzene and alkyl benzenes, about 27 mass percent xylenes and toluene, about 17 mass percent alkenes and dienes, about 10 mass percent alkanes and about 3 mass percent alcohols and carbonyls, the remainder of the solvent being made up by miscellaneous compounds.

The solvent may have about 39 mass% benzene, about 21.5 mass% toluene, and about 4 mass% xylene.

The solvent may have an analysis approaching that appearing in table 2 below.

Table 2: Solvent Analysis

Components	Mass %
1,2 Propadiene	0.0303
C3-Hydrocarbons	0.0041
Methanol	0.1415
1-Butene + Iso-Butene + 1,3-Butadiene	0.6427
Butane	0.3558
t-2-Butane	0.2484
c-2-Butene	0.2416
Ethanol	0.0011
1,2-Butadiene	0.0025
Acetonitrile + 3-Methyl-1-Butene	0.1527
Acetone	0.6080
Iso-Pentane	0.2875
1,2-Butadiene	0.0045
1-Pentene	0.5563
Ethanethiol	0.0000
2-Methyl-1-Butene	0.2591
Pentane	1.0591
Isoprene	0.1987
t-2-Pentene	0.4954
c-2-Pentene	0.2807
2-Methyl-2-Butene	0.5917
t-1,3-Pentadiene	0.2767
1,3-Cyclopenladiene + c-1.3-Pentadiene	0.5694
Propanenitrile	0.0766
2-Propanethiol	0.0000
Cyclopentene	0.6667
4-Methyl-1-Pentene	0.0708
3-Methyl-1-Pentene	0.0354
Cyclopentane	0.4747
1.1,2-Trimethyl-Cyclopropane	0.0000
2,3-Dimethyl -1-Butene	0.0000
2-Methyl-Pentane	0.4447
MEK	0.7107
3-Methyl + Pentane	0.1489
1-Hexene + 2-Methyl-1-Pentene	1,3731
2-Methyl-Furan	0.0232
1,4-Hexadiene + Propanethiol	0.0310
Unidentified hydrocarbons eluting before hexane	0.0016
Hexane +2-Ethyl-1-Butene	1.8169
t-3-Hexene	0.1309
c-3-Hexene	0.0404
t-2-Hexene	0.3540
2-Methyl-2-Pentene	0.2083
3-Methyl-Cyclopentene + c-3-Methyl-2-Pentene	0.3083
4-Methyl-Cyclopentene	0.1100

c-2-Hexene	0.1881
2,3-Dimethyl-1,3-Butadiene	0.0297
t-3-Methyl-2-Pentene +2,4-Hexadiene	0.1886
1,3-Hexadiene	0.0132
2,2-Dimethyl-Pentane	0.0015
Methyl-Cyclopentane	0.7909
2.3-Dimethyl-2-Butene	0.0621
2-Methyl-1,3-Pentadiene	0.0626
5-methyl-1,3-Pentadiene	0.1640
4-Methyl-1,3-Pentadiene	0.0532
1-Methyl-1,3-Pentadiene	0.1277
3-Methyl-1,3-Pentadiene	0.0826
1-Methyl-Cyclopentene + Benzene	39.1160
Thiophene	0.2175
3,4-Dimethyl-2-Pentene	0.0060
5-Methyl-1-Hexene	0.0323
Cyclohexane	0.2221
C6-Diene	0.0000
1,3-Cyclohexadiene	0.2261
4-Methyl-1-Hexene	0.0774
2-Pentanone	0.2739
2-Methyl-Hexane	0.1586
2,3-Dimethyl-Pentane	0.1100
1,1-Dimethyl-Cyclopentane	0.0162
C6-Diene	0.0209
Cyclohexene	0.2119
3-Methyl-Hexane	0.2019
3-Heptene	0.0160
1-t-3-Dimethyl-Cyclopentane	0.1028
1-c-3-Dimethyl-Cyclopentane	0.0872
1,2-Dimethyl-Cyclopentane	0.0876
2-Methyl-1-Hexene	0.0282
1-Heptene	0.9523
3-Methyl-t-3-Hexene	0.0269
2,4-Dimethyl-1,3-Pentadiene	0.0063
1-3-Heptene + Dimethyl-Cyclopentene	0.3019
Unidentified hydrocarbons eluting between hexane and heptane	0.0358
Heptane	1.9769
2-Methyl-2-Hexene	0.0084
3-Methyl-c-3-Hexene	0.0146
t-2-Heptene	0.2454
C7-Diene	0.0097
Dimethyl-Cyclopentene	0.1814
c-2-Heptene	0.1913
3-Ethyl-Cyclopentene	0.0674
Methyl-Cyclohexane + 1-Ethyl-Cyclopentene	0.4411
Pyridine	0.0184
C7-Nephthene	0.0000
2-Hexanone	0.0107
C8-Cyclic-Olefin (131°C)	0.0149
Ethyl-Cyclopentene	0.2501
C7-Dienes	0.3983
Trimethyl-Cyclopentane	0.0363

C7-Diene	0.0527
Methyl-Cyclohexene	0.3507
Toluene	21.5059
2-Methyl-Thiophene	0.0333
3-Methyl-Thiophene	0.1847
1-Methyl-Cyclohexene	0.1461
C7-Diene	0.0758
2-Methyl-Heptane	0.2158
4-Methyl-Heptane	0.0925
3-Methyl-Heptane	0.1488
2-Methyl-1-Heptene	0.0545
1-Ethyl-3-Methyl-Cyclopentane	0.0398
1-Octene	0.6739
Unidentified hydrocarbons eluting between heptane and octane	0.4223
3-Octene	0.1002
Octane	1.1548
t-2-Octene	0.1329
c-2-Octene	0.0659
Prophyl-Cyclopentane	0.1801
Ethyl-Benzene	1.0267
M+P-Xylene	4.0595
Styrene	0.2210
O-Xylene	0.9339
1-Nonene	0.2220
Unidentified hydrocarbons eluting between octane and nonane	1.2996
Nonane	0.4562
Prophyl-Benzene	0.0738
Ethyl-Methyl-Benzene	0.3548
1,3,5-Trimethyl-Benzene	0.1148
1-Ethyl-2-Methyl-Benzene	0.0509
Benzofuran	0.0421
1,2,4-Trimethyl-Benzene	0.1711
1-Decene	0.0701
Unidentified hydrocarbons eluting between nonane and decane	0.6376
Decane	0.1280
1,2,3-Trimethyl-Benzene	0.0405
Indane	0.4655
Indene	0.1124
O-Cresol	0.0161
1-Undecene	0.2329
Unidentified hydrocarbons eluting between decane and undecane	0.4182
Undecane	0.2666
Naphthalene	0.0878
Unidentified hydrocarbons eluting after undecane	0.6708
Total	100.000

The solvent may be Rectisol™ Naphtha solvent available from Sasol™ in South Africa.

The mass ratio of crude tar feed to solvent on addition of the solvent may be between 1:5 and 3:2 and is typically about 2:5, or even 1:1.

The method may include adding water to the crude tar feed before, during or after the addition of the solvent, but typically after addition of the solvent.

The amount of water added is a function of the amount of solid particulate matter particles contained in the crude tar feed and is typically 0,4 volume percent or more of the crude tar feed.

The crude tar feed, solvent and water may be fed to a settling tank to allow separation of the hydrocarbon phase and water phase from the mixture.

The solvent and crude tar feed may be mixed prior to the addition of water to allow the solvent to access the matter coating the solid particulate matter particles in the crude tar feed.

The feed line to the settling tank may include a valve, mixing orifice or any other suitable mixing device to achieve high shear mixing in a fluid flowing into the settling tank. The fluid flowing into the settling tank may be a crude tar feed or a crude tar feed – water mixture and is typically a crude tar feed-water-solvent mixture.

The temperature and pressure in the settling tank may be such that the solvent remains a liquid, i.e. below the boiling point of the solvent.

The pressure in the settling tank may be between atmospheric and 14 bar and is typically about 1-3 bar.

The temperature in the settling tank may be between ambient and 150°C and is typically about 30-40°C.

The settling tank may be a conventional desalination tank known in the art or may be any other suitable settling tank. Typically, however, the settling tank is a conical bottom type tank.

The crude tar feed, water and solvent mixture may be allowed to separate in the settling tank for between 15 and 120 minutes, preferably between 30 and 90 minutes and typically for about 45 minutes.

Migration of the solid particulate matter from the hydrocarbon phase to the water phase may be improved by ionisation of the solid particulate matter.

Methods such as electrostatic precipitation may be used to improve settling of the solid particulate matter into the water phase.

After a sufficient degree of separation has been achieved, the water phase that now contains the solid particulate matter that has migrated out of the hydrocarbon phase may be pumped out of the settling tank.

The remaining hydrocarbon phase may then be subjected to trim filtration to obtain the desired solid particulate matter content which is typically about 0,02 percent by mass when measured by the ashing method or loss on ignition method.

Thereafter the hydrocarbon phase may be fed to an evaporator for distillation where the solvent is distilled from the tar fraction after which the solvent may be recycled.

A method analogous to the method as described above may be used in other applications where solid particulate matter needs to be separated from a viscous liquid coating said matter, for example, the method may be used to separating catalyst particles from a fluid catalytic cracking slurry or for separating solid particulate matter from an oily mixture.

Detailed Description of the Invention

The invention will now be described by way of the following non-limiting examples with reference to the accompanying drawing.

In the drawings:-

Figures 1, and 4 show schematic flow diagrams of a method of separating particulate matter from a crude tar feed that includes water and particulate matter in accordance with the present invention; and

Figures 2 and 3 show graphical representations of Tables 3 and 4 below.

In the Figures 1 and 4, reference numeral 10 generally indicates a process wherein a method of separating particulate matter from a crude tar feed which includes water and particulate matter in accordance with the present invention is utilised.

The method of separating particulate matter (not shown) from a crude tar feed 12 which includes water and particulate matter includes adding a solvent stream 14 to the crude tar feed 12 for removing matter that coats the solid particulate matter particles with a fluid constituent of the crude tar feed 12 by dissolving at least a portion of it and for decreasing the density of the crude tar feed 12 to well below the density of water and of the solid particulate matter in the crude tar feed 12.

The crude tar feed 12 typically contains about 10 percent by mass water. The size distribution of particulate matter in the crude tar feed 12 is typically such that 50 percent thereof is larger than 50 micron and 10 percent thereof is less than 10 micron.

The matter that coats the particles or particulate matter in the crude tar feed 12 is typically a tar fraction including asphaltenes.

The solvent may be any solvent capable of washing off matter which coats the solid particulate matter so as to free the solid particulate matter for migration from the hydrocarbon phase into the water phase.

The solvent 14 is a solvent rich in benzene and typically includes about 40 mass percent benzene and alkyl benzenes, about 27 mass percent xylenes and toluene, about 17 mass percent alkenes and dienes, about 10 mass percent alkanes and about 3 mass percent alcohols and carbonyls, the remainder of the solvent being made up by miscellaneous compounds.

The mass ratio of crude tar feed 12 to solvent 14 on addition of the solvent 14 is typically about 1:1. The solvent 14 and crude tar feed 12 are allowed to mix thoroughly to allow the solvent 14 to access the matter coating the solid particulate matter particles in the crude tar feed 12.

A water stream 16 is also added to the crude tar feed 12. The amount of water 16 added is typically a function of the amount of solid particulate particles in the crude tar feed.

A wetting agent or demulsifier (chemical) is added to the water stream 16 to assist the solid particulate settling in the settling tank.

An additional water stream 22 is provided to provide additional water if necessary.

In Figure 1, the crude tar feed, solvent and water mixture 18 is fed to a settling tank 20 to allow separation of a hydrocarbon phase 24 and a water phase 26 from the mixture 18.

The feed line to the settling tank 20 includes a mixing device 28 to create high shear mixing in the mixture 18.

The mixture 18 is allowed to settle for about 45 minutes to allow the solid particulate matter to migrate from the hydrocarbon phase 24 into the water phase 26.

The settling tank 20 is a conventional desalination tank known in the art or conical bottom type for ease of solids removal..

The temperature and pressure in the settling tank 20 is such that the solvent 14 remains a liquid, i.e. below the boiling point of the solvent 14.

The pressure in the settling tank 20 is typically about 1-3 bar and the temperature in the settling tank 20 is typically about 30-40°C.

After a sufficient degree of separation has been achieved, the water phase 26 that now contains the solid particulate matter that has migrated out of the hydrocarbon phase 24 is pumped out of the settling tank 20.Stream 26 is then subjected to filtration to remove the solids from the water. Residue water is returned to the process.

As an alternative to Figure 1,(see Figure 4) instead of the crude tar feed, solvent and water mixture 18 is fed to a settling tank 20 to allow separation of a hydrocarbon phase 24 and a water phase 26 from the mixture 18, the mixture is fed to a centrifuge 50 which serves both as a contactor for the components of mixture 18 as well as to separate the solids from the water phase (26 in Figure 1) into which the particles have migrated and the hydrocarbon phase 24 is treated similarly to that in Figure 1 as is described below.

In Figures 1 and 4, the hydrocarbon phase 24 is fed to an evaporator 30 for distillation where the solvent 14 is distilled from the tar fraction 34 after which the solvent 14 is recycled.

The hydrocarbon phase 24 is subjected to trim filtration in filtration unit 32 prior to distillation.

The tar fraction 34 thus obtained typically contains about 0,02 mass percent solid particulate matter.

After distillation the tar fraction 34 is fed to a filtration unit (not shown).

Experiments to ascertain the optimum crude tar feed solvent mass ratio, the optimum settling time in the settling tank and the optimum crude tar to additional water mass ratio were conducted – see Examples 1 to 3.

An explanation of the experiments conducted as well as their results are set out below.

The solvent used during all examples typically had the following composition in mass percent:

40	Benzene & Alkyl Benzenes
27	Xylenes & Toluene
17	Alkenes & Dienes
10	Alkanes
3	Alcohols & Carbonyls
3	Miscellaneous

EXAMPLE 1

Determination of the optimum crude tar feed to solvent ratio

A sample of crude tar feed was obtained from a tar feed tank and was homogenized by stirring continuously before use. The ash content of crude tar sampled was 2,115 mass percent.

The following mixtures of crude tar feed tar and solvent were prepared at room temperature (27 °C) using a 100-cm^3 volumetric flask:

a. 20 g of tar plus 80 g of solvent;
b. 40 g of tar plus 60 g of solvent;

c. 50 g of tar plus 50 g of solvent;
d. 60 g of tar plus 40 g of solvent;
e. 80 g of tar plus 20 g of solvent; and
f. crude tar only

Mixtures a to f were shaken for 2 minutes and allowed afterwards to stand for 1 hour, thus allowing the solids to settle to the bottom of the flask.

An amount of sample was carefully decanted from each flask into respective crucibles, making sure that the solids at the bottom of the flask remained intact. Thereafter the sample in each respective crucible was ignited and allowed to burn in order to remove the carbonaceous material.

The residual material obtained in each crucible from was ashed at 600 °C.

The final ash obtained in was expressed as a percentage of the net tar fraction present in each of the tar-solvent mixtures. Results of ash content vs. tar-solvent ratio are tabulated in table 3, and Figure 2 graphically shows this relationship.

Table 3: Tar –Solvent mass ratio v solids content of tar fraction

Tar-Solvent Ratio (m/m)	Solids Content of Tar Fraction (measured as ash content)
80:20	0,184
60:40	0,097
50:50	0,059
40:60	0,057
20:80	0,052

EXAMPLE 2

Determination of the optimum settling time in the settling tank using a tar-solvent mixture containing 60 mass percent solvent and 40 mass percent crude tar feed

A sample of crude tar feed was obtained form a tar feed tank and was homogenized by stirring continuously before use.

The following mixtures of tar and solvent were prepared at room temperature (27 °C), using a 100-cm^3 volumetric flask:

a. 4 separate flasks, labelled as 1M, 2M, 3M and 4M, each containing 40 g of tar plus 60 g of solvent; and
b. 4 separate flasks, labelled only as 1, 2, 3 and 4, each containing crude tar only.

The respective mixtures were shaken for 2 minutes and allowed afterwards to stand, thus allowing the solids to settle to the bottom of the respective flasks.

After 15 minutes, an amount of sample was carefully decanted from the respective flasks, labelled as M1 and 1, into respective crucibles correspondingly labelled as M1 and 1, making sure that the gross amount of solids at the bottom of each flask remained intact.

This procedure was repeated after 30, 45 and 60 minutes for the respective mixtures labelled as M2 and 2, M3 and 3, M4 and 4.

The sample in each respective crucible was ignited and allowed to burn in order to remove the carbonaceous material.

The residual material obtained in each crucible was ashed at 600 °C.

The final ash obtained was expressed as a percentage of the net tar fraction present in each of the tar-solvent mixtures. Results of ash content vs. settling time are tabulated in Table 4 and Figure 3 graphically shows this relationship.

Table 4: Settling time v solids content of a 40/60 (m/m) tar-solvent mixture with neat crude tar feed as reference

Settling Time (min)			
15	30	45	60

Solids content of tar fraction not treated with solvent in mass percent (measured as ash content)	1,974	1,621	1,476	1,377
Solids content of tar fraction treated with solvent in mass percent (measured as ash content)	0,224	0,111	0,063	0,054

EXAMPLE 3

Characterisation of the solid material present in the crude tar feed and the effect of the addition of water to the tar-solvent mixture

A mixture of 60 g solvent and 40 g of crude tar was prepared in a glass bottle. The bottle was stoppered and the content was shaken-up for 2 minutes. An amount of tap water (50 cm^3) was added to the contents in the bottle and allowed to separate for 30 minutes.

The solid material settled into the water phase, and the organic liquid phase was then carefully decanted.

The water phase with the solid material was filtered through a Whatman 41 filter paper.

The solid material was washed with benzene until the residual oil/tar attached to it has been removed, indicated by a clear benzene wash-solution.

The benzene-washed solid material was dried in an oven at 105 °C.

The dried solid material was then ashed at 900 °C and the remaining ash fused with $LiBO_2$ at 900 °C.

The flux was dissolved in hydrochloric acid (1:1), diluted to a known volume and the metal content determined using ICP-AES.

The carbon, hydrogen, nitrogen and sulphur content of the benzene-washed solid material were determined, using the Carlo Erba Elemental Analyser.

Results obtained appear in Table 5 below.

Table 5: Typical Composition of the solid material settled out from the crude tar feed

Solid material recovered form crude tar	
COMPONENT	RESULT, mass %
Al	3,49
Si	4,76
Ca	2,27
Mg	0,52
Fe	0,51
K	0,16
Na	0,19
Other metals	0,58
Loss on ignition @ 900 °C	72,77
Ash content	27,23
C	64,58
H	2,01
N	1,47
S	0,70

Ash of solid material	
COMPONENT	RESULT, mass %
Al asAl_2O_3	24,20
Si as SiO_2	37,39
Ca as CaO	11,65
Mg as MgO	3,14
Fe as Fe_2O_3	2,68
K as K_2O	0,73
Na as Na_2O	0,96
Other	balance

Discussion of Results of Examples 1 to 3

For the purpose of this investigation any reference to solids content of the tar fraction implicates the ash content of the tar fraction as determined per the procedure described in Example 1.

The solids content (measured as ash content) of the crude tar feed as sampled was 2,115 mass percent. The solids remaining in suspension reduced to 1,974 mass percent for a settling time of 15 minutes and to 1,377 mass percent after a settling time of 60 minutes.

Table 3 and Figure 2 show that for a settling time of 1 hour, little variation in the solids content of the tar fractions (measured as ash content) is obtained for the tar-solvent mixtures, containing 50 mass percent or less tar.

Adequate separation of the solid material from the tar should be obtained for any tar-solvent mixture containing less than or equal to 50 mass percent tar.

A tar-solvent mixture containing 50 percent tar relates to a solids content of 0,059 mass %, a tar-solvent mixture containing 40 percent tar relates to a solids content of 0,057 mass % and a tar-solvent mixture containing 20 percent tar relates to a solids content of 0,052 mass%

Table 4 and Figure 3 show that for a chosen optimum ratio of 40% tar and 60% solvent settling of the solid material is obtained within 15 minutes, after shaking the mixture for 2 minutes.

An amount of 0,224 mass% of solids (measured as ash content) was measured after a settling period of 15 minutes, which reduced further to 0,054 mass percent after 1 hour.

With the addition of water to the tar-solvent mixtures containing respectively 60% and 80% solvent, it was observed that the water phase clearly separates from the organic phase and that the solid material settles into the water phase.

The solid material removed from the tar and washed with benzene to remove traces of oil and tar still attached to it, analysed to be coal.

The results obtained showing carbon (65 mass %), hydrogen (2 mass%), nitrogen (1,5 mass %), sulphur (0,7 mass %), Al (3,5 mass%), Ca (2 mass %), Mg (0,5 mass %) and Si (5 mass %) confirmed this observation.

On analysing the ash obtained after a loss on ignition at 900 °C was performed on the solid material, a typical coal-ash analysis was obtained:

Al as Al_2O_3 = 24 mass% Si as SiO_2 = 37 mass%
Ca as CaO = 12 mass% Mg as MgO = 3 mass%
Fe as Fe_2O_3 = 3 mass%

Thus, the solvent used does act as a suitable dissolvent for the tar and it was found that a homogeneous mixture of crude tar and solvent is obtained where the solvent component of the mixture equals or exceeds 50 mass percent.

The viscosity and density of these mixtures allow for the settling of the denser solid material into the water phase.

From the various ratios of crude tar to solvent investigated, an optimum ratio of 60 mass % solvent to 40 mass% of crude tar is suggested. This will allow for an optimum tar-solvent mixture for further processing. See Table 3 and Figure 2 for detailed results.

An additional filtration of the tar-solvent mixture will reduce the ash content to within the desired limit of less than or equal to 0,02 mass%.

Evaluating the suggested optimum 40:60 ratio of crude tar to solvent, partial settling of the solid material occurred within 15 minutes of the mixture being prepared.

Table 4 and Figure 3 show the relationship between the settling time and solids content of this tar-solvent mixture.

The addition of water to the organic phase consisting of the tar-solvent mixture, enhances the settling of the solid material from the organic phase into the water phase.

The solid material removed from the crude tar consists mainly of fine coal particles. On ashing this material at 900 °C, a typical coal ash composition is analysed as shown in Table 5.

Example 4

A procedure to remove solids, mainly coal ash, from tar was carried out.

The procedure comprised using a solvent, as per table 2 above, to solvate tar from the solids and to allow the settling of the solids into a water phase.

The addition of a wetting agent or some de-emulsifying agents was also investigated as to aid the settling of the very fine particles from the hydrocarbon mixture into the water phase.

Results obtained show that use of the wetting- or de-emulsifying agents dosed at a level of 50 µl / dm^3 of hydrocarbon phase will aid the removal of solids from the tar fraction to a level of < 0.02 mass%, see Table 6.

Rectisol™ Naphta of table 2 was mixed with crude tar feed in a 1:1 mass ratio.

Different wetting-and demulsifying agents were dosed at respective levels of 10-, 30 and 50 µl per liter of the hydrocarbon phase.

The following agents were investigated:

- Dispersall a™ wetting agent
- EC2134A™ - a demulsifier
- EC2043A™ - a demulsifier
- SAX816™ - a combination of a wetting & demulsifying agent(s)

All the above wetting and de-emulsifying products were obtained from Nalco-Chemserve™.

An amount of water (20% of the volume of the total hydrocarbon phase) was added to the hydrocarbon phase and allowed to mix by vigorous shaking of the total mixture.

The solids were then allowed to migrate by settling into the water phase using a retention time of 60 minutes.

The hydrocarbon phase was analysed for solids content by igniting a known portion of the hydrocarbon phase, thus allowing it to burn in order to remove excess of carbonaceous material. The residue obtained in this manner was further ashed at 600 °C for 2 hours. The amount of final residue obtained was measured and expressed as mass% solids to be present in the hydrocarbon phase.

As a result of initially preparing a 1:1 (m/m) mixture of tar and Rectisol Naphta the result obtained had to be multiplied by 2 to obtain the actual solids content of the tar fraction alone (without the presence of Rectisol™ Naphta).

A blank run was included without addition of any wetting or demulsifier agent.

The results are shown in tables 6 and 7 below.

Table 6: Solids Content Of Hydrocarbon Phase Treated With Different Wetting- And Demulsifying Agents

Note: ***Value in brackets represents an average from duplicate results***

	ASH CONTENT OF HYDROCARBON PHASE AFTER TREATMENT, mass%				
DOSAGE LEVEL μl / dm³	**Blank [no agent]**	**DISPERSALL [wetting agent]**	**EC2134A Demulsifier**	**EC2043A Demulsifier**	**SAX 816 Demulsifier & Wetting Agent**
0	0.1323 0.1287 *[0.1305]*	---	---	---	---
10	---	0.1263 0.1112 *[0.1188]*	0.0231 0.0305 *[0.0268]*	0.0175 0.0230 *[0.0202]*	0.0198 0.0178 *[0.0188]*
30	---	0.0233 0.0177 *[0.0205]*	0.0211 0.0258 *[0.0234]*	0.0170 0.0153 *[0.0162]*	0.0184 0.0202 *[0.0193]*
50	---	0.0024 0.0031 *[0.0027]*	0.0018 0.0021 *[0.0020]*	0.0024 0.0043 *[0.0031]*	0.0047 0.0078 *[0.0062]*

Table 7: Solids Content of Tar Fraction Alone After Treatment Calculated From Table 1

Note: ***Value in Table below is obtained by multiplying average value in Table 6 by 2***

	ASH CONTENT OF TAR FRACTION ALONE, AFTER TREATMENT, mass%				
DOSAGE LEVEL μl / dm³	**Blank [no agent]**	**DISPERSALL [wetting agent]**	**EC2134A Demulsifier**	**EC2043A Demulsifier**	**SAX 816 Demulsifier & Wetting Agent**
0	***0.2610***	---	---	---	---
10	---	***0.2376***	***0.0536***	***0.0404***	***0.0376***
30	---	***0.0410***	***0.0468***	***0.0324***	***0.0386***
50	---	***0.0054***	***0.0040***	***0.0062***	***0.0124***

It is to be appreciated, that the invention is not limited to any specific embodiment or configuration as hereinbefore generally described or illustrated.

Claims

1. A method of reducing solid particulate matter content of a crude tar feed, which crude tar feed includes a hydrocarbon fluid fraction, a water fraction, and a solid particulate matter fraction which is at least partially coated with the hydrocarbon fluid fraction, the method including at least the steps of:-

introducing a solvent into the crude tar feed; and

removing from the solid particulate matter at least a portion of the hydrocarbon fluid fraction that coats the solid particulate matter while decreasing the density of the crude tar feed to well below the density of water and of the solid particulate matter in the crude tar feed.

2. A method as claimed in claim 1, including the step of allowing the resulting mixture to settle into a water phase and a hydrocarbon phase for a predetermined period of time and to allow at least a fraction of the solid particulate matter to migrate from the hydrocarbon phase into the water phase.

3. A method as claimed in claim 1 or claim 2, including the use of a wetting agent as a settling aid for settling fine particles from out of the hydrocarbon phase into the water phase.

4. A method as claimed in any one of the preceding claims, including the use of a de-emulsifying agent as a settling aid for settling fine particles from out of the hydrocarbon phase into the water phase.

5. A method as claimed in any one of the preceding claims, including the step of separating the water phase from the hydrocarbon phase by a separation process.

6. A method as claimed in claim 5, wherein the water phase is separated from the hydrocarbon phase by centrifugation.

7. A method as claimed in any one of the preceding claims, wherein the hydrocarbon fluid fraction that coats the solid particulate matter in the crude tar feed is a tar fraction including asphaltenes.

8. A method as claimed in any one of the preceding claims, wherein the solvent is a solvent rich in benzene.

9. A method as claimed in any one of the preceding claims, wherein the solvent is rich in one or more of toluene, xylene, paraffins, pyridine, and quinoline.

10. A method as claimed in claim 8 or claim 9, wherein the solvent includes about 40 mass percent benzene and alkyl benzenes, about 27 mass percent xylenes and toluene, about 17 mass percent alkenes and dienes, about 10 mass percent alkanes, and about 3 mass percent alcohols and carbonyls.

11. A method as claimed in any one of the preceding claims, wherein the mass ratio of crude tar feed to solvent on addition of the solvent is between 1:5 and 3:2.

12. A method as claimed in any one of the preceding claims, wherein the mass ratio of crude tar feed to solvent on addition of the solvent is 2:5.

13. A method as claimed in any one of the preceding claims, wherein the mass ratio of crude tar feed to solvent on addition of the solvent is 1:1.

14. A method as claimed in any one of the preceding claims, including the step of adding water to the crude tar feed before, during or after the addition of the solvent, typically after addition of the solvent.

15. A method as claimed in claim 14, wherein the amount of water added is a function of the amount of solid particulate matter particles contained in the crude tar feed.

16. A method as claimed in claim 14, wherein the amount of water added is at least 0,4 volume percent of the crude tar feed.

17. A method as claimed in any one of claims 14 to 16, wherein the crude tar feed, solvent, and water are fed to a settling tank to allow separation of the hydrocarbon phase and water phase from the mixture.

18. A method as claimed in claim 17, wherein the solvent and crude tar feed are mixed prior to the addition of water to allow the solvent to access the matter coating the solid particulate matter particles in the crude tar feed.

19. A method as claimed in claim 17 or claim 18, wherein a feed line to the settling tank includes high shear mixing means to achieve high shear mixing in a fluid flowing into the settling tank.

20. A method as claimed in any one of the preceding claims, in which temperature and pressure is maintained below the boiling point of the solvent thereby to keep the solvent liquid.

21. A method as claimed in claim 20, wherein the pressure is between atmospheric and 14 bar.

22. A method as claimed in claim 20, wherein the pressure is 1 to 3 bar.

23. A method as claimed in claim 20, wherein the temperature is between ambient and 150°C.

24. A method as claimed in claim 20, wherein the temperature is 30 to 40°C.

25. A method as claimed in any one of claims 17 to 24, wherein the settling tank is a conical bottom tank.

26. A method as claimed in any one of claims 17 to 25, wherein the crude tar feed, water, and solvent mixture is allowed to separate in the settling tank for between 15 and 120 minutes.

27. A method as claimed in any one of claims 17 to 25, wherein the crude tar feed, water, and solvent mixture is allowed to separate in the settling tank for between 30 and 90 minutes.

28. A method as claimed in any one of claims 17 to 25, wherein the crude tar feed, water, and solvent mixture is allowed to separate in the settling tank for about 45 minutes.

29. A method as claimed in any one of the preceding claims, wherein migration of the solid particulate matter from the hydrocarbon phase to the water phase is improved by ionisation of the solid particulate matter.

30. A methos as claimed in any one of the precedin claims, wherein electrostatic precipitation is used to improve settling of the solid particulate matter into the water phase.

31. A method as claimed in any one of the preceding claims, wherein the hydrocarbon phase is fed to an evaporator for distillation where the solvent is distilled from the tar fraction after which the solvent is recycled.

32. A method analogous to the method as claimed in any one of the preceding claims, wherein catalyst particle concentration in a fluid catalytic cracking slurry is reduced by applying said method.

33. A method of reducing solid particulate matter content of a crude tar feed as claimed in claim 1, substantially as herein described and illustrated.

34. A method of reducing catalyst particle concentration in a fluid catalytic cracking slurry as claimed in claim 33, substantially as herein described and illustrated.

35. A new method of reducing solid particulate matter content of a crude tar feed or a new method whereby catalyst particle concentration in a fluid catalytic cracking slurry is reduced.

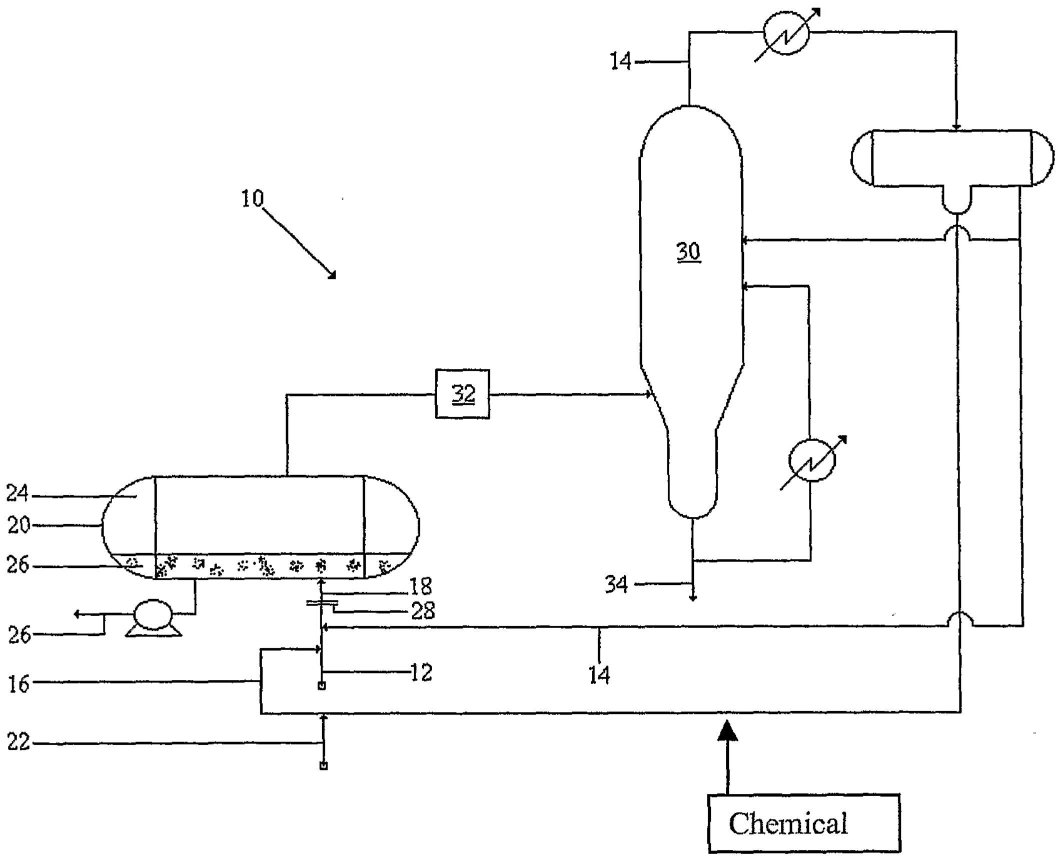

Figure 1

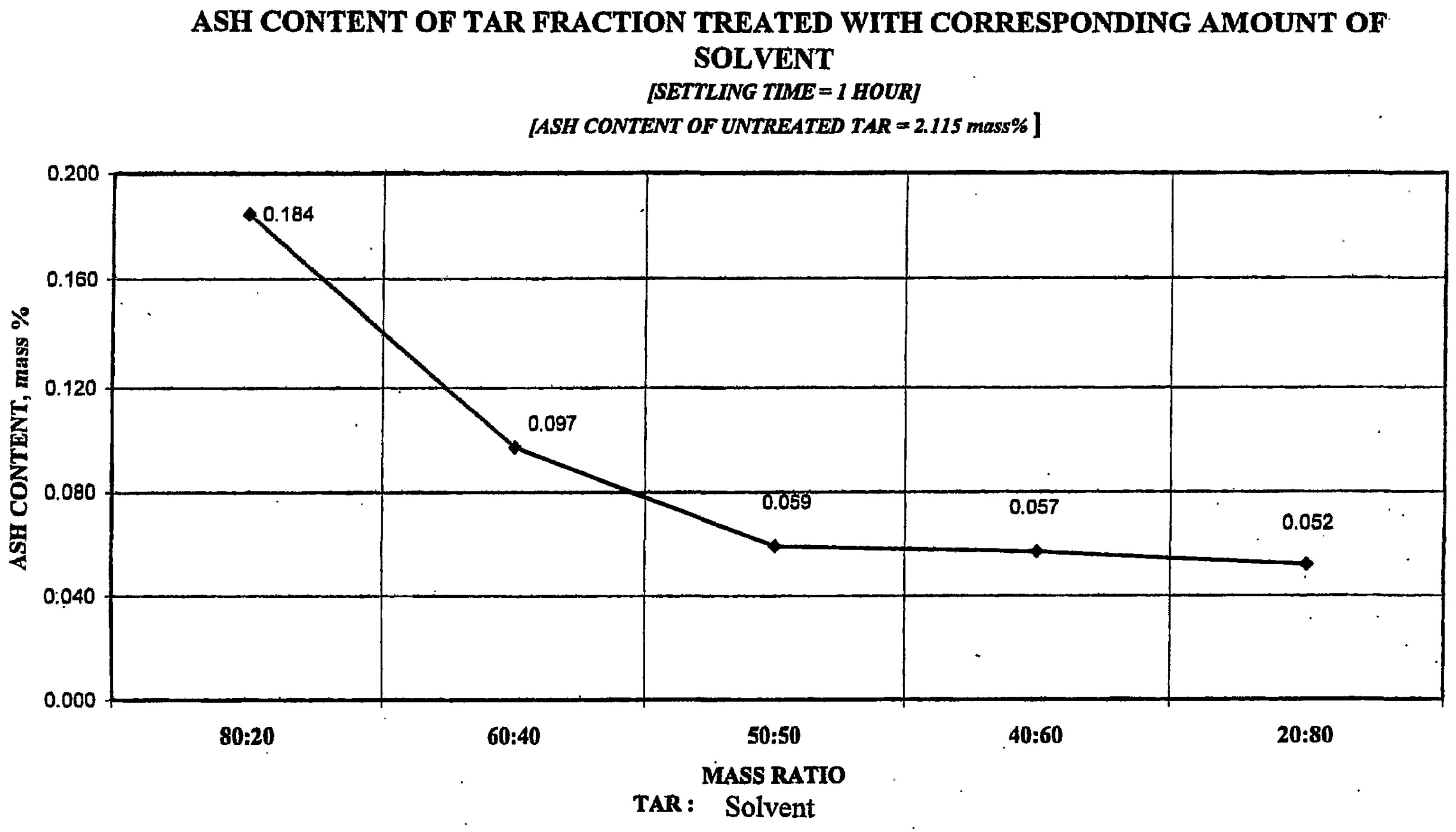
ASH CONTENT OF TAR FRACTION TREATED WITH CORRESPONDING AMOUNT OF SOLVENT
[SETTLING TIME = 1 HOUR]
[ASH CONTENT OF UNTREATED TAR = 2.115 mass%]
ASH CONTENT, mass %
0.200
0.160
0.120
0.080
0.040
0.000
0.184
0.097
0.059
0.057
0.052
80:20
60:40
50:50
40:60
20:80
MASS RATIO
TAR : Solvent

Figure 2

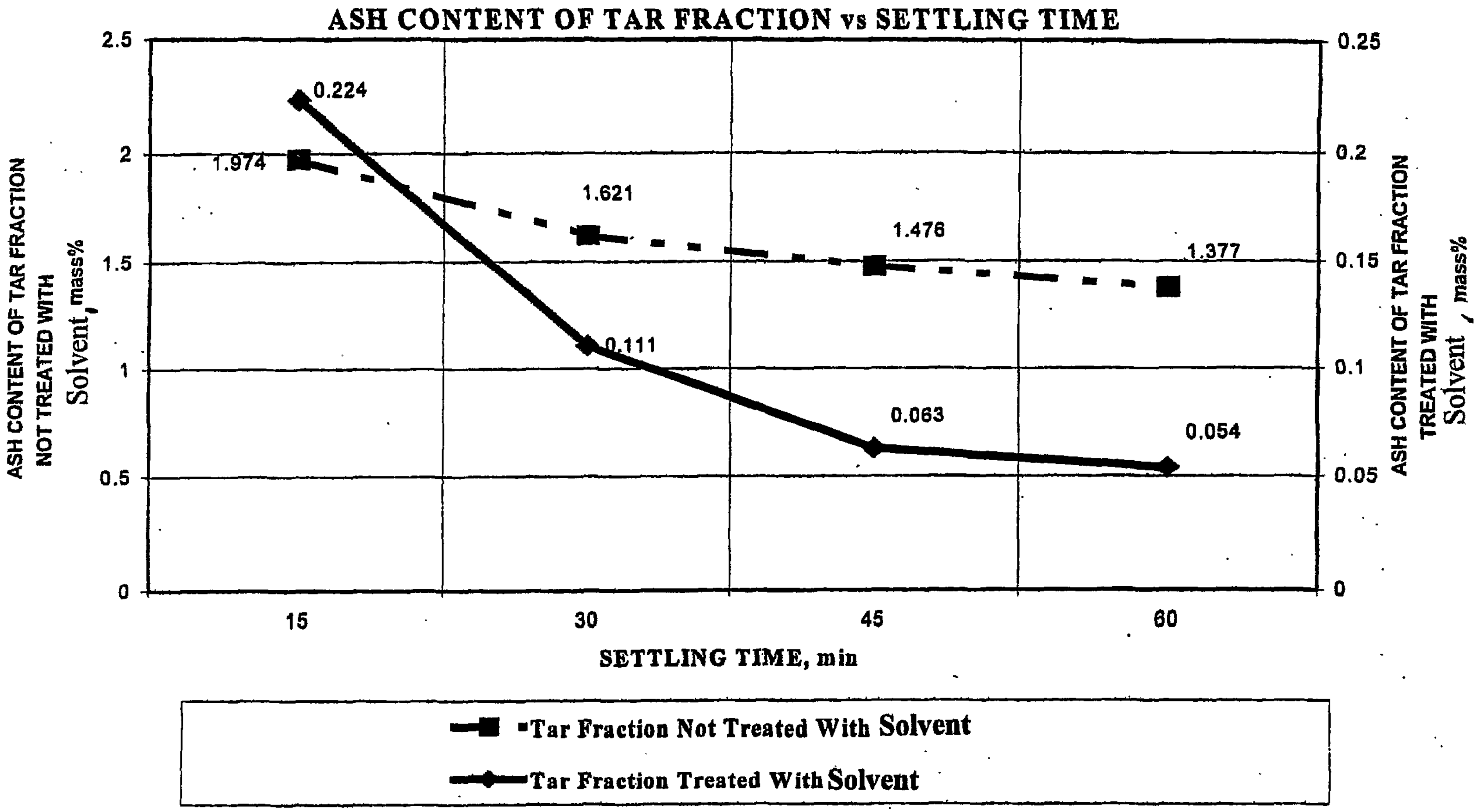
ASH CONTENT OF TAR FRACTION vs SETTLING TIME
ASH CONTENT OF TAR FRACTION NOT TREATED WITH Solvent, mass%
ASH CONTENT OF TAR FRACTION TREATED WITH Solvent , mass%
2.5
2
1.5
1
0.5
0
0.25
0.2
0.15
0.1
0.05
0
15
30
45
60
SETTLING TIME, min
0.224
1.974
1.621
0.111
1.476
0.063
1.377
0.054
Tar Fraction Not Treated With Solvent
Tar Fraction Treated With Solvent

Figure 3

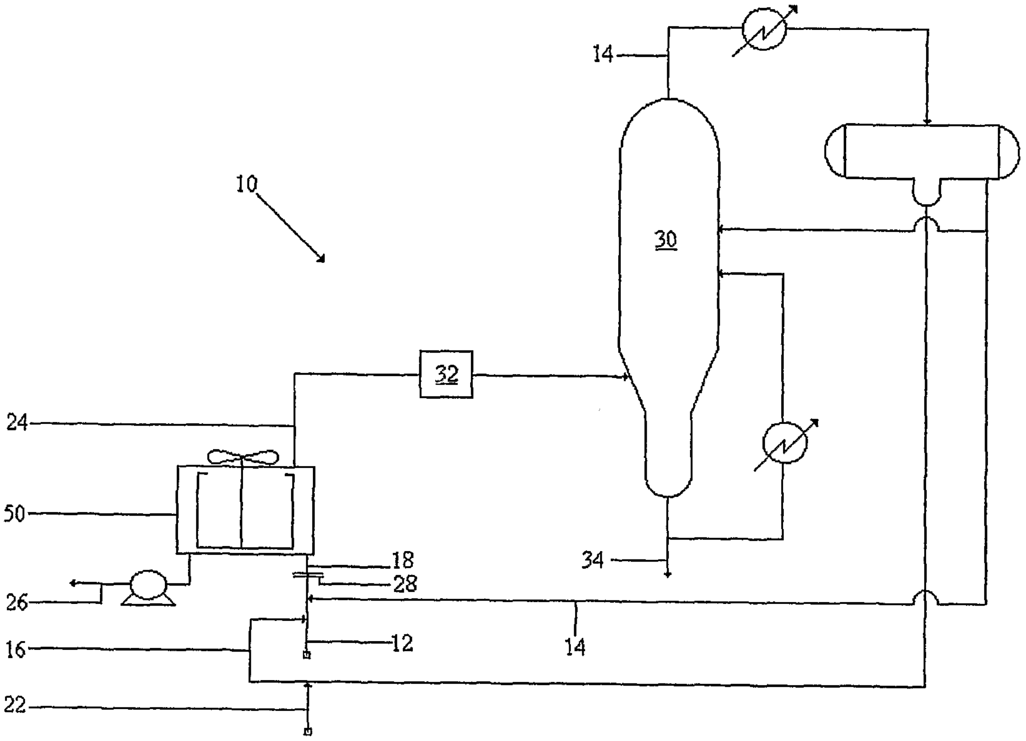

Figure 4

INTERNATIONAL SEARCH REPORT

In onal Application No
PCT/ZA 02/00101

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10G33/04 C10G33/06 C10G1/04

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)
IPC 7 C10G C10C B01D

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, API Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 264 453 A (MRAOVICH GEORGE) 28 April 1981 (1981-04-28) claims 1,7,8,10; figure column 1, line 16-34 column 2, lines 3-8 and 51-56 column 3, line 24-39 column 3, line 67 -column 4, line 3 ---	1,4,5, 11-13
X	EP 0 283 584 A (RUETGERSWERKE AG) 28 September 1988 (1988-09-28) claims 1,2; example 1 page 2, line 27-36 page 3, line 40-43 --- -/--	1,2,4-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 31 October 2002	Date of mailing of the international search report 18/11/2002
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Harf, J

INTERNATIONAL SEARCH REPORT

Int onal Application No
PCT/ZA 02/00101

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 019 888 A (MISHRA SURENDRA K ET AL) 1 February 2000 (2000-02-01) claims 1,8,12-17; figure 1 column 1, lines 16-23 and 56-61 column 2, line 23-27 column 5, lines 15-25 and 54-61 column 6, line 51-65 ---	1-3,5,6, 8-14,17, 19,25
X	DE 42 33 584 A (PREUSSAG NOELL WASSERTECH) 16 September 1993 (1993-09-16) claims 1-3; figures 1,2 column 1, lines 6-12 and 46-51 column 2, lines 2-7, 21-25 and 63-67 column 3, line 7-25 ---	1,2,5,8, 9,14-17, 23,24,31
X	DE 42 08 182 A (PREUSSAG NOELL WASSERTECH) 16 September 1993 (1993-09-16) claims 1,3; figure column 1, lines 7-12 and 41-50 column 2, lines 12-16 and 26-34 column 2, line 66 -column 3, line 1 column 4, line 42-45 ---	1,5,6,8, 9,14,15, 20,31
X	US 3 684 699 A (KEATON MICHAEL JOHN ET AL) 15 August 1972 (1972-08-15) claims 1,2,4; figure 1; example column 1, line 50-58 column 2, lines 7-16, 31-43 and 49-56 column 3, line 72 -column 4, line 3 column 6, lines 32-34 and 67-70 ---	1,2,5,7, 14,17, 18, 20-23, 26-30
X	US 4 812 225 A (CORTI ALDO ET AL) 14 March 1989 (1989-03-14) claims 1,4-7,9,15; figures 1,2 column 1, line 20-22 column 1, line 67 -column 2, line 20 column 2, line 37-52 column 3, line 43-63 column 4, line 43-50 ---	1,3-5, 14,15, 20,21, 23,24,31
A	US 5 989 436 A (IIJIMA MASAKI ET AL) 23 November 1999 (1999-11-23) column 5, line 6-13 -----	9

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 32-35

Present claims 32-35 relate to an extremely large number of possible methods. In fact, the claims contain so many options that a lack of clarity and conciseness within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible. Consequently, the search has been carried out for those parts of the application which do appear to be clear and concise, namely the method of reducing the solid particulate matter content of a crude tar feed consisting of a hydrocarbon fluid fraction, a water fraction and a solid particles fraction by introducing a solvent into the feed to remove at least a portion of the hydrocarbon fluid coating the solid particles and decrease the crude tar density well below that of water and solids (claims 1-31).

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/ZA 02/00101

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 32-35
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

In onal Application No
PCT/ZA 02/00101

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 4264453	A	28-04-1981	CA	1152927 A1	30-08-1983
			EP	0032420 A2	22-07-1981
EP 0283584	A	28-09-1988	DE	3709465 A1	06-10-1988
			CS	8800837 A2	14-08-1990
			DE	3764637 D1	04-10-1990
			EP	0283584 A1	28-09-1988
			JP	63254187 A	20-10-1988
			PL	271346 A1	06-02-1989
US 6019888	A	01-02-2000	NONE		
DE 4233584	A	16-09-1993	DE	4233584 A1	16-09-1993
			CA	2091508 A1	13-09-1993
DE 4208182	A	16-09-1993	DE	4208182 A1	16-09-1993
			CA	2091502 A1	13-09-1993
US 3684699	A	15-08-1972	CA	940853 A1	29-01-1974
US 4812225	A	14-03-1989	CA	1313836 A1	23-02-1993
US 5989436	A	23-11-1999	JP	9208967 A	12-08-1997
			US	6165360 A	26-12-2000