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(54) **Removal of metallic contaminants from petroleum fractions.**

(57) A method for reducing the metal contaminant concentration in a petroleum fraction containing a metal contaminant is disclosed. The petroleum feedstock is contacted in a contacting zone (10) with SO_2 or a SO_2 precursor (14) at an elevated temperature after which the petroleum fraction is either deasphalted (Figure 6, 20) or vacuum distilled (Figure 7, 120). The petroleum fraction is thereby separated into a first fraction relatively lean in the metal contaminant and a second phase relatively rich in the metal contaminant.

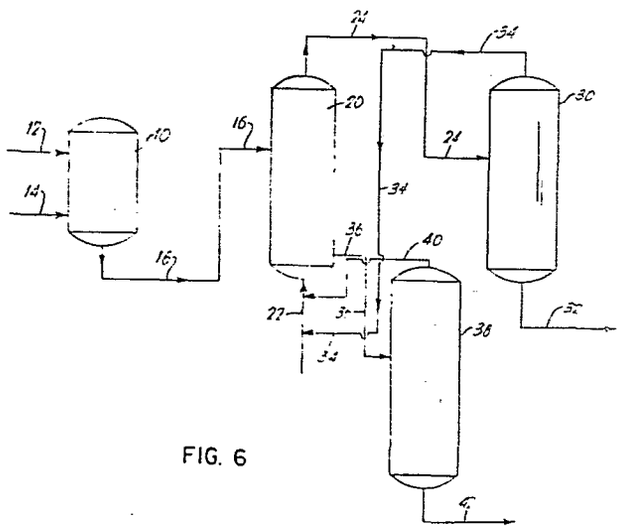

FIG. 6

EP 0 055 627 A1

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REMOVAL OF METALLIC CONTAMINANTS FROM PETROLEUM FRACTIONS.

The present invention generally relates to the removal of metallic contaminants from petroleum fractions. Specifically, the present invention relates to the removal of complex organo-metallic compounds, for example, of the porphyrin type, and particularly those compounds containing nickel and vanadium from residua by deasphalting or from vacuum gas oils. Petroleum gas oils normally contain iron, nickel, vanadium and other metallic contaminants which have an adverse effect upon petroleum processing operations. As the cut point, the atmospheric equivalent of the highest boiling material in the distillate increases, the fraction of the feed recovered as distillate increases. However, as the cut point is elevated, the metal concentration in the distillate also increases. In petroleum processing operations such as catalytic cracking the presence of these metallic contaminants in the petroleum feed; e.g., in a deasphalted oil, leads to rapid catalyst contamination by metals causing an undesirable increase in the hydrogen and coke makes, a loss in gasoline yield, a loss in conversion activity and a decrease in the catalyst life. The metal contaminant concentration generally is higher in the heavier feedstocks. Thus, the removal of metal contaminants is becoming more important as increasingly heavy feedstocks are being refined and as additional efforts are being directed at upgrading the residual petroleum fractions.

In the past, efforts have been directed at the removal of metal contaminants from petroleum fractions by a variety of methods including deasphalting processes, hydrotreating processes and HF extraction. U.S. Patent No. 2,926,129 is directed at the removal of organometallic compounds and the deasphalting of a petroleum fraction by heating the petroleum fraction at a temperature of (650-850°F) 343.3 to 454.4°C for 0.1 to 5 hours after which the fraction is contacted with an acidic material soluble

in the petroleum fraction, such as HCl, to coagulate the metallic contaminants. A sludging component, such as a liquid SO_2 is then added to the petroleum fraction at the rate of 0.1 to 3 volumes of SO_2 per volume of oil to promote precipitation of the asphaltene. A solvent also is added to the fraction preferably at the rate of 0.1 to 10 volumes per volume of oil to separate the asphaltene sludge fraction in a fractionating tower operated at temperatures of (30 to 300°F) and pressures of (25 to 500 psig). This patent also discloses in a table in column 5 that a less effective reduction in metals content in the recovered oil may be accomplished utilizing the solvent and liquid SO_2, without the acid. Use of the process described in this patent is not desirable, since relatively large quantities of sulfur dioxide in the liquid state are required, which necessitates operating at high vessel pressures if high temperatures are used and may necessitate the removal of the SO_2 from the recovered oil. Moreover, addition of an acid, such as HCl would require that the processing equipment be acid resistant. In addition, the presence of acidic compounds in the recovered oil would be injurious to catalysts used in subsequent processing.

U.S. Patent No. 3,294,678 is directed at a deasphalting process for the separation and removal of asphaltenic material including organo-metallic complexes of nickel and vanadium which comprises treating the petroleum fraction with an alkalinous bisulfide or bisulfite in aqueous solution under a pressure in the range of (150 to 2000 psig) in the presence of sufficient sulfur dioxide such that the partial pressure of the sulfur dioxide is within the range of about (150 to about 1500 psig). The asphaltenic material including organo-metallic compounds is converted into a water-soluble sulfonic acid salt which is subsequently extracted. This process is not desirable because of the additional steps of separating the water fraction from the petroleum fraction and

separating the sulfonic acid salts from the asphaltenic material.

U.S. Patent No. 2,969,320 discloses a method for removing tetraethyl lead from gasoline and other hydrocarbon liquids by injecting sulfur dioxide into the liquid to form an insoluble lead sulfide which may subsequently be removed by filtration. This method does not disclose or suggest removal of metals such as nickel and vanadium from petroleum fractions by heating in the presence of sulfur dioxide prior to deasphalting or distillation.

U.S. Patent No. 3,095,368 describes a method for selectively removing iron, nickel and vanadium from an asphaltic petroleum feedstock by deasphalting the oil and subsequently contacting the oil with a mineral acid to coagulate the metallic compound. The metallic compounds are then separated. This process requires the use of mineral acids which are corrosive and requires additional processing steps.

In a paper presented at the 1980 meeting of the Division of Petroleum Chemistry of the American Chemical Society, Bukowski and Gurdzinska disclosed a method for reducing the adverse catalytic effect of metal contaminants present in the distillate from atmospheric residuum. The method included the heat treating of the atmospheric residuum in the presence of cumene hydroperoxide (CHP) for up to six hours at 120°C. This step increased the distillate fraction obtained from the atmospheric residuum feed and decreased the metals content of the distillate which subsequently was used as feed for a catalytic cracking unit. This procedure is not advantageous due to the relatively high cost of the CHP required and the long treatment times involved.

British Patent Application No. 2,031,011 describes a method for reducing the metals and asphaltene content of a heavy oil by hydrotreating the oil in the

presence of a catalyst including a metal component from Group Ib, IIb, IIIa, Va, VI, and VIII of the Periodic Table followed by deasphalting. This process is not preferred since relatively large quantities of hydrogen are required in addition to a large investment in hydrotreating reactors and process equipment.

Accordingly, it is desirable to provide a process which reduces the metals concentration in petroleum feedstocks to sufficiently low levels without the addition of large amounts of acidic materials.

It is also advantageous to provide a process which will reduce the metals concentration in the petroleum fraction without an excessive amount of equipment and without the addition of a large number of additional processing operations.

SUMMARY OF THE INVENTION

The subject invention is directed at a method for reducing the metal contaminant concentration in a petroleum fraction containing the metal contaminant and which may contain an asphaltenic component comprising the steps of:

a. contacting the petroleum fraction in a contacting zone with an effective amount of a metal rejection agent selected from the class consisting of sulfur dioxide and precursors of sulfur dioxide at an elevated temperature; and

b. thereafter either:

I. contacting the petroleum fraction with a deasphalting agent to form a first fraction relatively lean in asphaltene and metal contaminant and a second fraction relatively rich in asphaltene and the metal contaminant, after which the first and second fractions are separated; or,

II. passing the petroleum fraction into a vacuum separation zone wherein the petroleum fraction containing the metal contaminant is separated into a distillate having a relatively low metal contaminant

concentration and a bottoms having a relatively high metal contaminant concentration.

In a preferred embodiment the petroleum fraction, comprising atmospheric distillation column bottoms, is passed into a contacting zone maintained at a temperature ranging between about 200°C and 450°C for about 0.01 to about 5 hours, said contact time varying inversely with temperature in the presence of about 0.5 to about 5.0 weight percent sulfur dioxide in the vapor phase, based upon the weight of the petroleum fraction. The petroleum fraction is then deasphalted or vacuum distilled. In deasphalting the petroleum fraction is contacted in a deasphalting zone with an effective amount of a deasphalting agent or solvent such as propane, butane, pentane or hexane and then separated into a first fraction relatively lean in asphaltene and metal contaminant and a second fraction relatively rich in asphaltene and metal contaminants. Solvent from said first and second fractions preferably is recovered and recycled to the deasphalting zone. For example, when propane is used as the solvent, the solvent to feed ratio typically ranges from about 2:1 to 6:1. The actual solvent to feed ratio used will be a function of the solvent and the feed characteristics. These ratios are known by those skilled in the art.

In vacuum distillation, the petroleum fraction, after passing through the contacting zone, is transferred to a vacuum distillation column where the fraction is separated into a distillate relatively low in metals content having at least one component boiling above about 520°C at atmospheric pressure, preferably above about 565°C and most preferably above about 590°C and a bottoms having a relatively high metals content.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a plot of the equilibrium weight percent of the nickel on cracking catalyst as a function of the parts per million of nickel in the feed at typical

fluid catalytic cracking conditions.

Figure 2 is a plot of the weight percent of the feed which is converted to hydrogen as a function of the nickel content of the catalyst under typical catalytic cracking conditions.

Figure 3 is a plot of nickel and vanadium content in a distillate produced from a typical heavy feed as a function of the cut point.

Figure 4 illustrates the volume percent of a typical feed which is distilled as a function of the cut point.

Figure 5 is a plot of the weight percent of the feed which is converted to coke as a function of the nickel content on the catalyst under typical catalytic cracking operating conditions.

Figure 6 is a simplified process flow diagram illustrating one method for practicing the subject invention.

Figure 7 is a simplified process flow diagram illustrating another method for practicing the subject invention.

DETAILED DESCRIPTION OF THE INVENTION

Figures 1-5 graphically illustrate the importance of reducing the nickel and vanadium content of catalytic cracking feedstocks. Generally, vanadium is considered to exhibit about one-quarter of the adverse catalytic effect of nickel on a weight equivalent basis. The adverse catalytic effect of nickel and vanadium is discussed in an article by Cimbalo, Foster and Wachtel in "Oil and Gas Journal" May 15, 1972, pages 112-122, the disclosure of which is incorporated herein by reference.

Figure 1 illustrates the relationship between the nickel content of the feed and the corresponding nickel content of the catalyst under typical cat cracking conditions. Figure 2 illustrates the weight percent of the feed converted to hydrogen as a function of the

nickel concentration of the catalyst. Figure 3 illustrates the increase in vanadium and nickel content of the distillate from a typical residual petroleum fraction as a function of the cut point where the subject invention has not been practiced. Typically, in the production of vacuum gas oils, the cut point is limited to a maximum temperature of approximately 565°C. Above this temperature the metals concentration in the distillate increases sharply as shown by the curves for the nickel and vanadium concentrations. Figure 4 illustrates the percent of a typical heavy petroleum feed which is distilled into a vacuum gas oil distillate as a function of the cut point. It should be noted that, as the cut point increases, the volume percent of the feed recovered as distillate increases. Use of the subject invention results in reduced metals content in the distillate at a given cut point or increased yield with substantially the same metals content utilizing a higher cut point. Figure 5 illustrates the weight percent of the feed converted to coke as a function of the nickel content on the catalyst. While Figures 1, 2 and 5 are directed at the detrimental effects of nickel on hydrogen and coke production, vanadium and other metals, such as iron and copper may also be present in petroleum fractions. These metals are less catalytically active, but also may contribute to excessive hydrogen and coke production. As used herein the term "metal contaminant" is defined to include all of the aforementioned metals.

In the data shown in Figures 2 and 5 a commercially available silica-alumina zeolite catalyst sold under the tradename CBZ-1, manufactured by Davison Division, W.R. Grace and Company was used. The CBZ-1 catalyst used was first steamed at 760°C for 16 hours after which the catalyst was contaminated with the indicated metals by laboratory impregnation, followed by calcining at about 540°C for four hours. Tests were run using a microcatalytic cracking (MCC) unit. The MCC

unit comprised a captive fluidized bed of catalyst kept at a cracking zone temperature of 500°C. Tests were run by passing a vacuum gas oil having a minimum boiling point of about 340°C and a maximum boiling point of about 565°C through the reactor for two minutes and analyzing for hydrogen and coke production. It can be seen that as the nickel concentration on the catalyst increases, the undesired hydrogen and coke yields also increase. Thus, it can be appreciated that a process which would provide a cat cracking feedstock of lower metals content would be particularly useful.

Referring to Figure 6, one method for practicing the subject invention is shown. In this figure valves, pumps, piping, instrumentation and equipment not essential to the understanding of the subject invention have been eliminated for clarity. A petroleum fraction is shown entering contacting zone 10 through line 12. A metals rejection agent is added to zone 10 through line 14. Typically contacting zone 10 will comprise a process vessel whose size is a function of the feed rate through line 12 and the desired residence time. After the requisite residence time in zone 10, the petroleum fraction is transferred through line 16 to a deasphalting zone 20 which comprises a countercurrent mixing tower, in which the petroleum fraction is contacted with a solvent entering through line 22 to form a first fraction relatively lean in metal contaminant and asphaltene and a second fraction relatively rich in metal contaminant and asphaltene. The first fraction comprising a deasphalted oil and solvent mixture is then transferred from the top of tower 20 through line 24 to a separation zone 30, comprising a flash distillation tower, in which the mixture is separated into a deasphalted oil fraction relatively low in asphaltenic and metal compounds exiting zone 30 through line 32 and a solvent fraction which exits zone 30 through line 34 and is recycled to zone 20 through line 22. The second fraction comprising a molten

asphaltene fraction containing a small amount of solvent is withdrawn from the bottom of tower 20 and fed via line 36 to flash separation zone 38 wherein the mixture is separated into an asphalt stream, exiting through line 42, and a solvent stream which is returned via lines 40 and 22 to mixing zone 20. The operating conditions for deasphalting operations are dependent upon the type of solvent, solvent to oil ratio and the characteristics of the feedstock to the deasphalting operation. These variables are known by those skilled in the art. A discussion of deasphalting operations in general may be found in Advances in Petroleum Chemistry and Refining, volume 5, pages 284-291, John Wiley and Sons, New York, New York (1962), the disclosure of which is incorporated herein by reference.

Referring to Figure 7, another method for practicing the subject invention is shown. A petroleum fraction is shown entering contacting zone 110 through line 112. A metal rejection agent is added to zone 110 through line 114. Typically contacting zone 110 will comprise a process vessel whose size is a function of the feed rate through line 112 and the desired residence time. After the requisite residence time in zone 110 the petroleum fraction is transferred through line 116 to a vacuum separation zone 120 in which the feedstock is separated into a distillate 122 and a bottoms product 124.

The composition of the petroleum feedstock passed into contacting zones 10 and 110 is not critical. Typically this will comprise the bottoms from an atmospheric distillation having an initial atmospheric boiling point of above about 285°C which has a total elemental metal contaminant content ranging between about 1 and about 2000+ parts per million by weight (WPPM), although other feedstocks having high metal content may also be used. To avoid unnecessary product contamination as well as to minimize costs, the amount of metal rejection agent used should be the lowest amount which will give effective

results at the desired operating conditions. The amount of metal rejection agent required will be a function of the specific agent used and the metal content of the feed. The metal rejection agent may be selected from the class consisting of vapor phase sulfur dioxide and precursors of vapor phase sulfur dioxide, such as sulfurous acid, ammonium bisulfite and alkyl metal bisulfites. Of these, the most preferred compound based upon cost and effectiveness is sulfur dioxide. Typically, the concentration of SO_2 added to the high metals feed will range from about 0.5 to about 5.0 weight percent of the feed, preferably about 1 to about 3 weight percent. If a precursor of SO_2 is used, the precursor concentration should be sufficient to furnish SO_2 concentrations of from 0.5 to 5.0 weight percent of the feed, and preferably 1-3 weight percent of the feed.

The residence time of the petroleum fraction in contacting zone 10 must be sufficient to provide adequate contacting between the metal rejection agent and the petroleum fraction. The residence time in zones 10 and 110 is a function of the specific metal rejection agent utilized, the process conditions in zones 10 and 110 and the metal contaminant content of the petroleum fraction. Typically, the contacting time in zones 10 and 110 ranges between 0.01 and 5 hours. The temperature in zones 10 and 110 is above the critical temperature of SO_2, approximately 157.7°C and typically may range between about 200°C and about 450°C, preferably between about 250°C and about 400°C, while the gauge pressure may range between about 1.406 and 28.123 kg/cm² (20 and about 400 psig), preferably between 3.5155 and 14.0612 kg/cm² (about 50 and about 200 psig).

In the process shown in Figure 6 the temperature in deasphalting zone 20 generally may range between about 25 and 250°C, while the gauge pressure may range between 0 and 42.184 kg/cm² (about 0 and 600 psig). The deasphalting agent or solvent added may be any solvent effective for deasphalting the petroleum fraction. Typically, an organic solvent,

preferably an alkane, is added to mixing zone 20 in a ratio of solvent to petroleum fraction of from about 1:1 to about 20:1 by volume. Among the preferred alkane solvents are propane, butane, pentane and hexane, with the most preferred being propane. Deasphalting zone 20 may comprise conventional mixing equipment such as a countercurrent contacting tower. Separation zones 30 and 38 comprise means by which the deasphalted oil and asphaltene fractions, respectively, are separated from solvent. Typically, these separation zones comprise flash distillation towers. The operating conditions for separation zones 30 and 38 are well known by those skilled in the art. When propane is used as the deasphalting agent, the gauge pressure in separation zones 30 and 38 typically ranges between about 17.5769 and 21.0921 kg/cm² (250 and about 300 psig). The temperatures in zone 30 typically may range between 150 and 175°C, which the temperature in zone 38 may range between about 225°C and about 325°C.

In the process shown in Figure 7, vacuum separation zone 120, generally comprising a distillation column may be of conventional design. The specific operating conditions are a function of the feed composition entering through line 116 and the desired distillate composition exiting through line 122. The design of the distillation column is not critical and would be determined by conventional design techniques. Typically, the absolute pressure measured at the top of zone 120 will range between about 10 and about 100 mm Hg, and the temperature at the base of zone 120 will range between about 370°C and about 450°C. The cut point of the distillate normally will be at least 550°C and may range as high as 590°C or above.

The following examples demonstrate the effectiveness of the subject invention in reducing the metals content from a deasphalted petroleum fraction. Comparative experiments were conducted using as the feedstock a Tia Juana atmospheric residuum having an

initial boiling point of about 260°C, a nickel content of 34 parts per million by weight (wppm) and a vanadium content of 273 wppm. In these examples 300 g. of the Tia Juana residuum was charged to a one liter Hastelloy-C autoclave with 6.3 g. (2.1 weight percent on feed) of gaseous sulfur dioxide. The autoclave then was heated to about 340°C for stirred contact for the indicated time during which time the gauge pressure reached about 8.7884 kg/cm² (125 psig). Upon cooling to 150°C, the pressure was released and the autoclave was flushed with nitrogen while cooling further to room temperature. The resultant treated residuum was contacted with 16 volumes of pentane per volume of residuum, mixed for 0.5 hour at 60°C in a stirred autoclave and then cooled to room temperature. The resulting mixture was filtered using a #2 Whatman paper to recover an asphaltene fraction relatively rich in asphaltene and metal and a deasphalted oil fraction relatively lean in asphaltene and metal. The results of these experiments for sulfur dioxide pretreatments of 60 and 100 minutes are shown in Table 1 below designated as samples 1 and 2, respectively. Sample 3 of Table 1 illustrates that when the same petroleum feedstock did not have the aforementioned sulfur dioxide pretreatment prior to deasphalting in a manner similar to that of samples 1 and 2, the resulting deasphalted oil had a higher metals content.

TABLE 1

EFFECT OF SO_2 PRETREATMENT ON METALS REJECTION

Sample No.	1	2	3
Sulfur Dioxide Pretreatment Time (Minutes)	60	100	0
Deasphalted Oil; Weight Percent on Feed	86.2	83.1	90.2
Deasphalted Oil Metal Contents			
wppm Nickel	3.5	5.2	9.4
wppm Vanadium	28.4	42.3	72.4

From Table 1 it may be seen that the SO_2 pretreatment step resulted in a decreased yield of deasphalted oil, but the resulting deasphalted oil had a substantial reduction in metals content for a 60 minute and a 100 minute pretreatment as compared with no pretreatment.

Another test was conducted on an identical sample of Tia Juana atmospheric residuum to determine if the heat treatment step would be effective in reducing the metals content in deasphalted oil if sulfur dioxide in the vapor phase were not present during the heat treating step. Both samples were heat treated for the same time and were deasphalted in a similar manner. As shown in Table II below, heat treating alone did not reduce the metals content of the deasphalted oil significantly.

TABLE II

EFFECT OF PRETREATMENT ON METALS REJECTION

Sample No.	1	4
Pretreatment Time @ 343°C, Minutes	60	60
Weight Percent SO_2 on Feed	2.1	0
Deasphalted Oil; Weight Percent on Feed	86.2	89.6
Deasphalted Oil Metal Content		
wppm Nickel	3.5	10.0
wppm Vanadium	28.4	85.0

It should be noted that the atmospheric residuum used in these tests contained organo-sulfur compounds. Thus, the presence of organo-sulfur compounds in the petroleum feedstock processed even in combination with heat treatment is ineffective in significantly reducing the metals content of deasphalted oil.

Similar comparative experiments were conducted to determine the effectiveness of the subject invention in reducing the metals content of a vacuum gas oil. Comparative experiments were made using as feed a Tia Juana

atmospheric residuum having an initial boiling point of about 260°C, a nickel content of 34 parts per million by weight (wppm), and a vanadium content of 273 wppm. Results are given in Table III below. In this example, sample number five, 300 g. of Tia Juana residuum, was charged to a one liter autoclave of Hastelloy-C construction, along with 6.3 g. (2.1 weight percent on feed) of gaseous sulfur dioxide. The autoclave was then heated to 343°C for a one hour stirred contact, during which time the gauge pressure reached 8.788 kg/cm² (125 psig). Upon cooling to 150°C, the pressure was released and the autoclave was flushed with nitrogen while cooling further to room temperature. The resultant treated residuum was then batch distilled at 0.05 cms. (500 microns) absolute pressure ~~vacuum~~ on a column having one theoretical plate to obtain a vacuum residuum bottoms fraction and a vacuum gas oil (VGO) fraction of maximum boiling point 315°C, which corresponds to an atmospheric equivalent boiling point of 565°C. With sample number six, the SO_2 pretreatment step was omitted. The Tia Juana residuum feed was distilled in a manner similar to that of sample number 5 to recover a 565°C atmospheric equivalent boiling point vacuum gas oil and a 565+°C vacuum residuum bottoms. As can be seen from Table III, the vacuum gas oil obtained from the SO_2 treated sample contained significantly less metals. Expressed in terms of reduction in the equivalent nickel content of the vacuum gas oil (VGO), SO_2 treating is seen to give about a 66 percent reduction in metals content relative to the VGO from the untreated residuum sample.

TABLE III

EFFECT OF SO_2 PRETREAT ON REDUCING THE METALS CONTENT OF A 565°C END POINT VACUUM GAS OIL

Sample No.	5	6
Sulfur Dioxide Pretreatment	Yes	No
Volume Percent 565°C on Feed	57	58
VGO Metals Content		
wppm Nickel	0.02	0.10
wppm Vanadium	0.28	0.62

Percent Reduction in Equivalent Nickel* Content of VGO	66

*Equivalent Nickel = wppm Nickel + $\frac{\text{wppm Vanadium}}{4}$

Another set of comparative experiments were made also using a Tia Juana residuum feed identical to that previously used. The SO_2 treatment used in the experiment, designated as sample seven, was similar to that used in the previous test in Table III. However, the vacuum distillation of the treated oil in sample number 7 and of the untreated feed, designated as sample number 8, was carried to a higher temperature to isolate a vacuum gas oil of final atmospheric equivalent boiling point of 593°C.

As shown by the data in Table IV, the 593°C cut point VGO obtained from the SO_2 treated resid, sample number 7, contained significantly less metals than the untreated sample, sample number 8.

TABLE IV

EFFECT OF SO_2 PRETREAT ON REDUCING THE METALS CONTENT OF A 593°C END POINT VACUUM GAS OIL

Sample No.	7	8
Sulfur Dioxide Pretreatment	Yes	No
Volume Percent 593°C VGO on Feed	61	64
VGO Metals Content		
wppm Nickel	0.13	0.20
wppm Vanadium	1.00	1.70
Percent Reduction in Equivalent Nickel Content of VGO	40	-

A final test was run to determine if residuum heat soaking in the absence of SO_2 would result in a lower metals content in the VGO product. The procedure used was exactly that described for sample number 8 of the previous example, except that SO_2 was omitted and the contact time at 343°C was extended to two hours in order to give heat soaking the best possible chance to effect a lowering of metals content in the VGO product.

After heat soaking, a vacuum distillation was carried out to produce a vacuum gas oil having an atmospheric equivalent boiling point of 593°C. Results are shown in Table V and are compared in the table with the results obtained for sample number 8 which had no pretreatment at all. As is apparent from the data, heat soaking alone at 343°C does not give any appreciable reduction in the metals content of the VGO product.

TABLE V

EFFECT OF HEAT SOAK ON REDUCING THE METALS CONTENT OF A 593°C END POINT VACUUM GAS OIL

Sample No.	9	8
Heat Soak Pretreatment	Yes	No
Volume Percent 593°C VGO on Feed	62	64
VGO Metals Content		
wppm Vanadium	1.36	1.70
wppm Nickel	0.30	0.20
Percent Reduction in Equivalent Nickel Content of VGO	Negligible	-

It should be noted that the atmospheric residuum used in these tests also contained organo-sulfur compounds. Thus, the presence of organo-sulfur compounds in the petroleum feedstock processed even in combination with heat treatment is ineffective in significantly reducing the metals content of the vacuum gas oil.

While the invention has been described with respect to a specific embodiment, it will be understood that this disclosure is intended to cover any variations, uses or adaptations of the invention including such departures from the present disclosure as come within known or customary practice in the art to which the invention pertains and as fall within the scope of the invention.

CLAIMS

1. A method for reducing the metal contaminant concentration in a petroleum fraction containing the metal contaminant, the method being characterized by comprising:

(a) contacting the petroleum fraction in a contacting zone (10) with an effective amount of a metal rejection agent (14) selected from sulfur dioxide in the vapor phase and precursors of vapor phase sulfur dioxide at an elevated temperature; and

(b) thereafter either:

(i) contacting the petroleum fraction in a contacting zone (Fig. 6, 20) with a deasphalting agent (Fig. 6, 22) to form a first fraction (24) relatively lean in asphaltene and metal contaminant and a second fraction (36) relatively rich in asphaltene and the metal contaminant, after which the first and second fractions are separated; or

(ii) passing the petroleum fraction into a vacuum separation zone (Fig. 7, 120) wherein the petroleum fraction containing the metal contaminant is separated into a distillate (122) having a relatively low metal contaminant concentration and a bottoms (124) having a relatively high metal contaminant concentration.

2. The method of claim 1 characterized by the metal rejection agent being selected from sulfur dioxide, sulfurous acid, ammonium bisulfite and alkali metal bisulfites.

3. The method of claim 1 or claim 2 characterized by the metal rejection agent being sulfur dioxide.

4. The method of any one of claims 1 to 3 characterized in that the temperature of the contacting zone (20) is maintained above the critical temperature of sulfur dioxide.

5. The method of any one of claims 1 to 4 characterized by effecting the contacting at a temperature between about 200°C and about 450°C.

6. The method of any one of claims 1 to 5 characterized by effecting the contacting at a pressure being maintained between about 1.4062 and 28.124 kg/cm^2 gauge (20 psig and about 400 psig).

7. The method of any one of claims 1 to 6 characterized by the effective concentration of sulfur dioxide in the contacting zone being in the range of from about 1 to about 3 weight percent based upon the weight of the petroleum fraction.

8. The method of any one of claims 1 to 7 characterized by the residence time of the petroleum fraction in the contacting zone being maintained between about 0.01 and about 5 hours.

9. The method of any one of claims 1 to 8 characterized by the petroleum fraction being a distillate having a cut point of at least 520°C.

10. The method of any one of claims 1 to 9 characterized in that the said petroleum fraction is a distillate obtained by distillation of a feedstock, and the petroleum fraction is not treated, prior to step (a) by the addition thereto of at least one of the following: an acidic material; an acid material which is soluble in the fraction; water, an aqueous solution of an alkaline bisulfide and/or bisulfite, a solvent which is selective for non-asphaltenic material.

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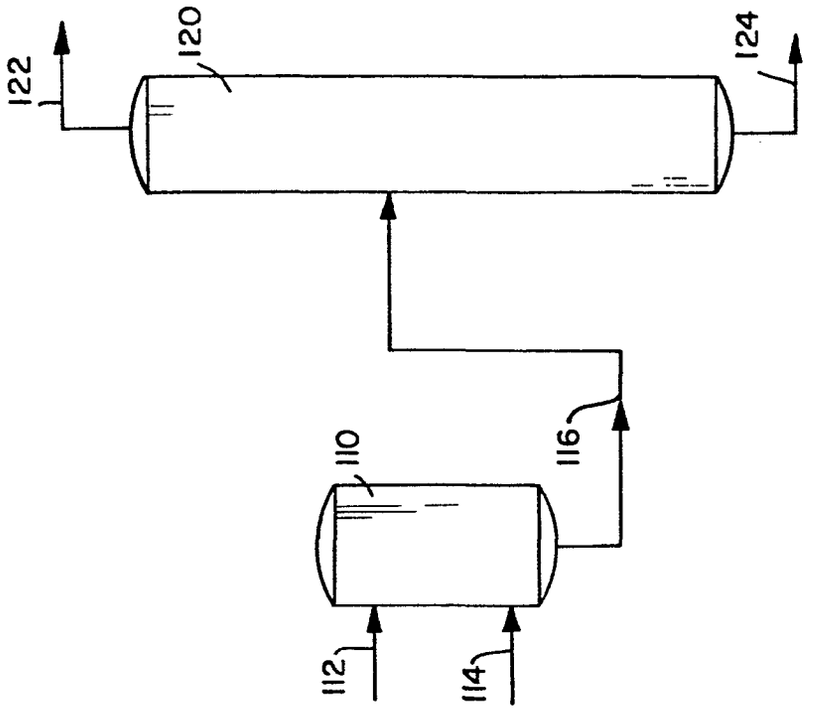

FIG. 7

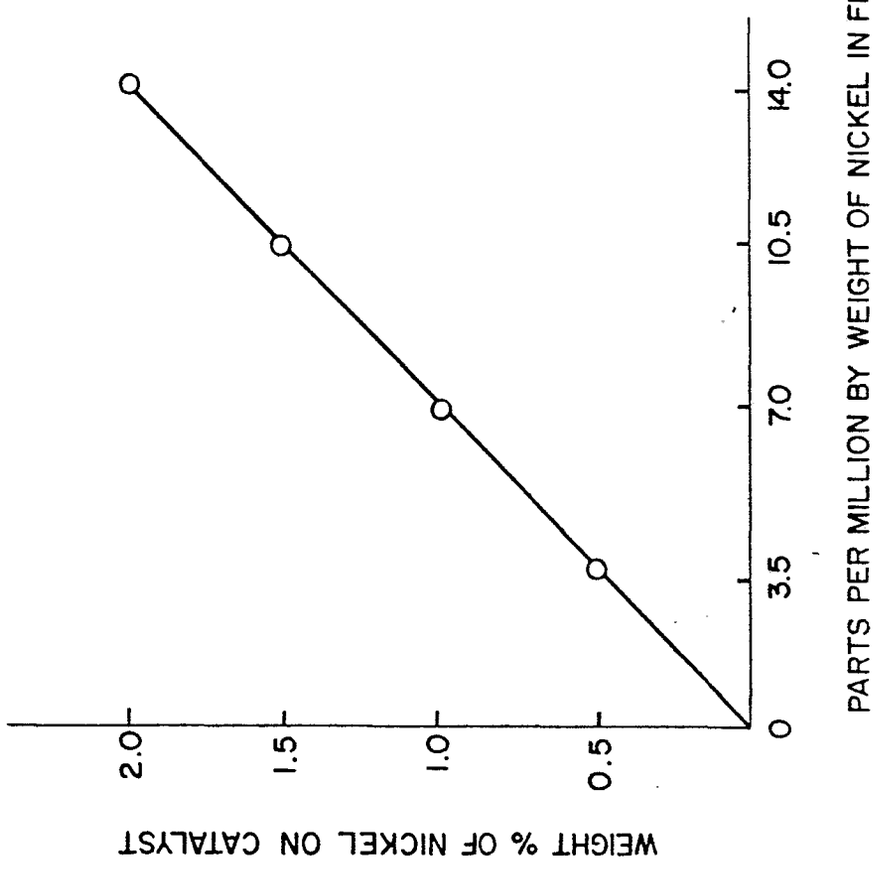

FIG. 1

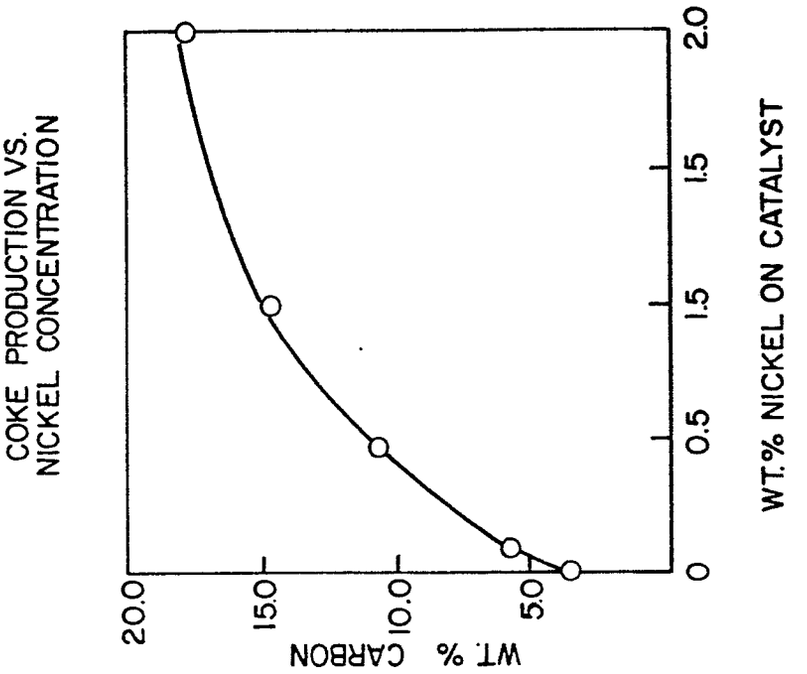
COKE PRODUCTION VS.
NICKEL CONCENTRATION
WT. % CARBON
20.0
15.0
10.0
5.0
0
0.5
1.5
2.0
WT.% NICKEL ON CATALYST

FIG. 5

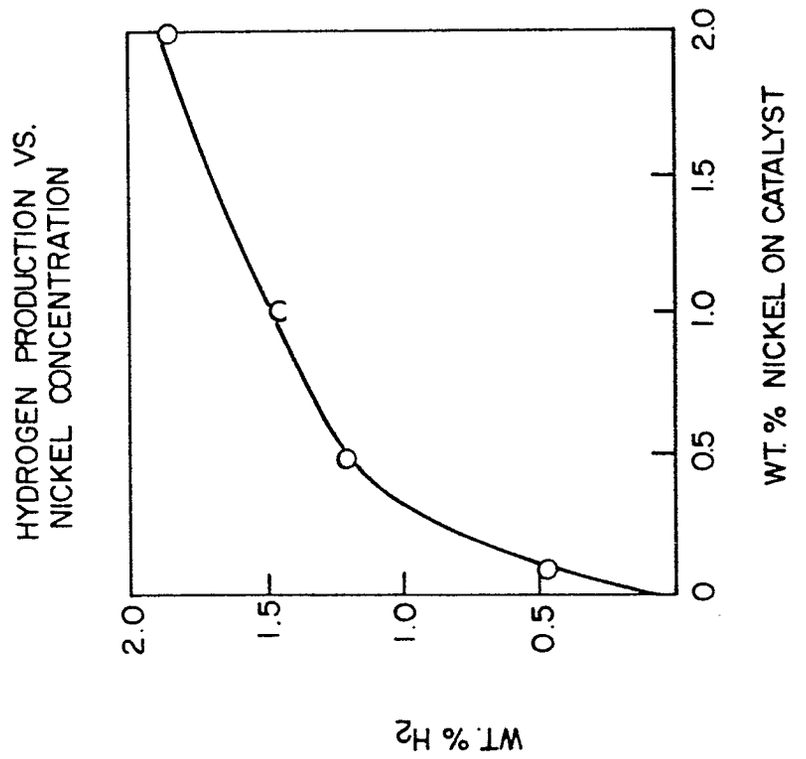
HYDROGEN PRODUCTION VS.
NICKEL CONCENTRATION
WT. % H2
2.0
1.5
1.0
0.5
0
0.5
1.0
1.5
2.0
WT.% NICKEL ON CATALYST

FIG. 2

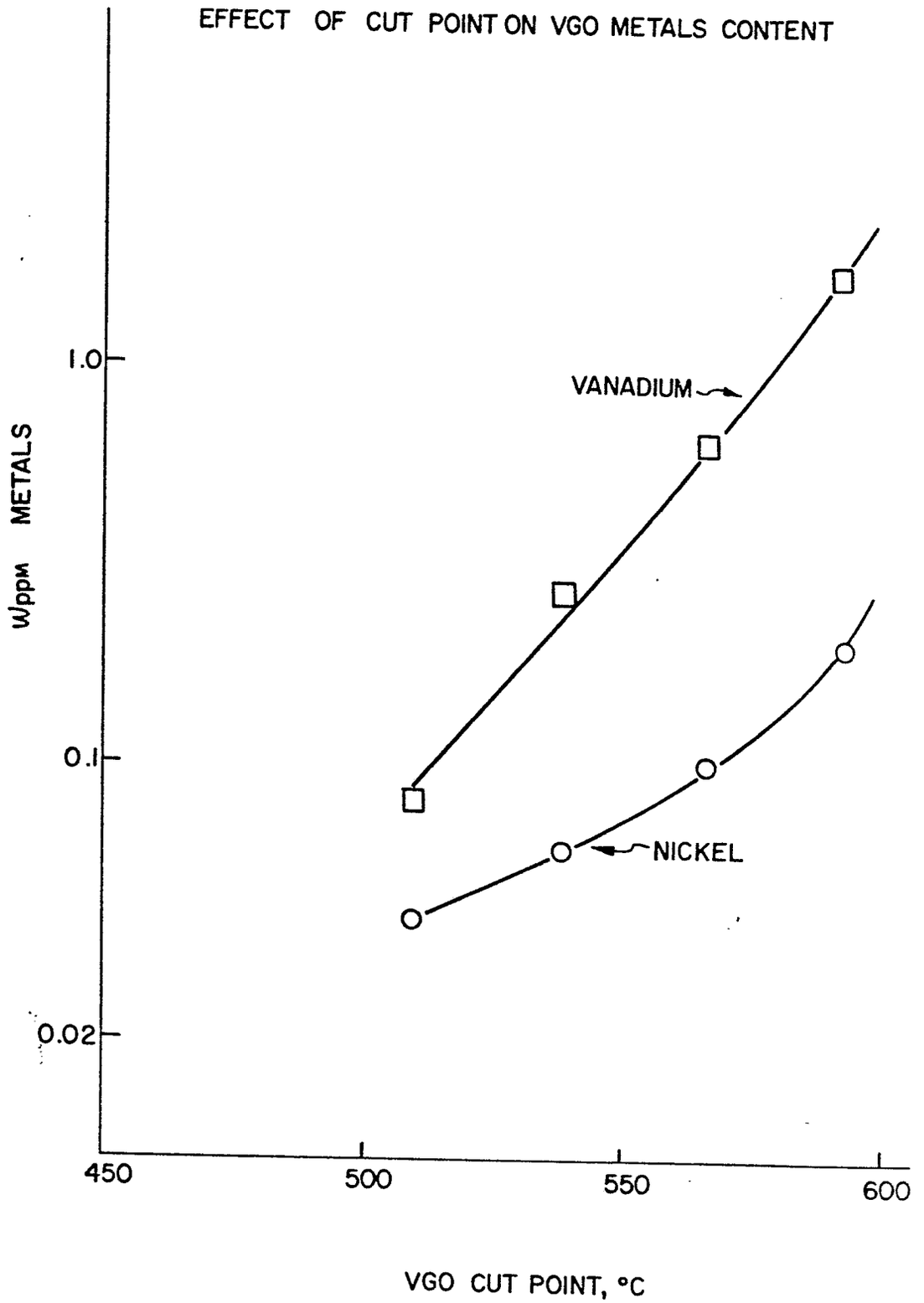
EFFECT OF CUT POINT ON VGO METALS CONTENT
Wppm METALS
1.0
0.1
0.02
VANADIUM
NICKEL
450
500
550
600
VGO CUT POINT, °C

FIG. 3

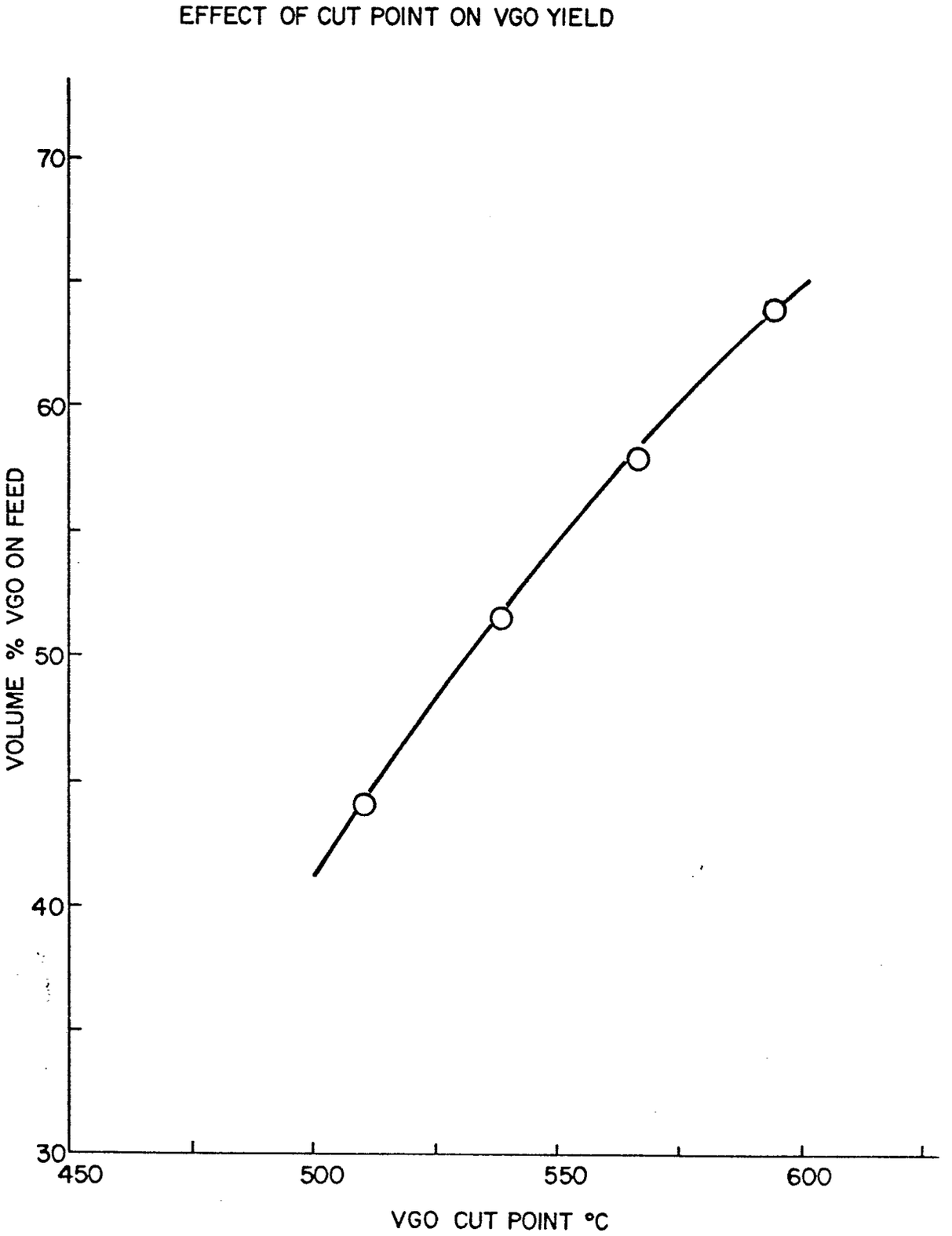
EFFECT OF CUT POINT ON VGO YIELD
VOLUME % VGO ON FEED
70
60
50
40
30
450
500
550
600
VGO CUT POINT °C

FIG. 4

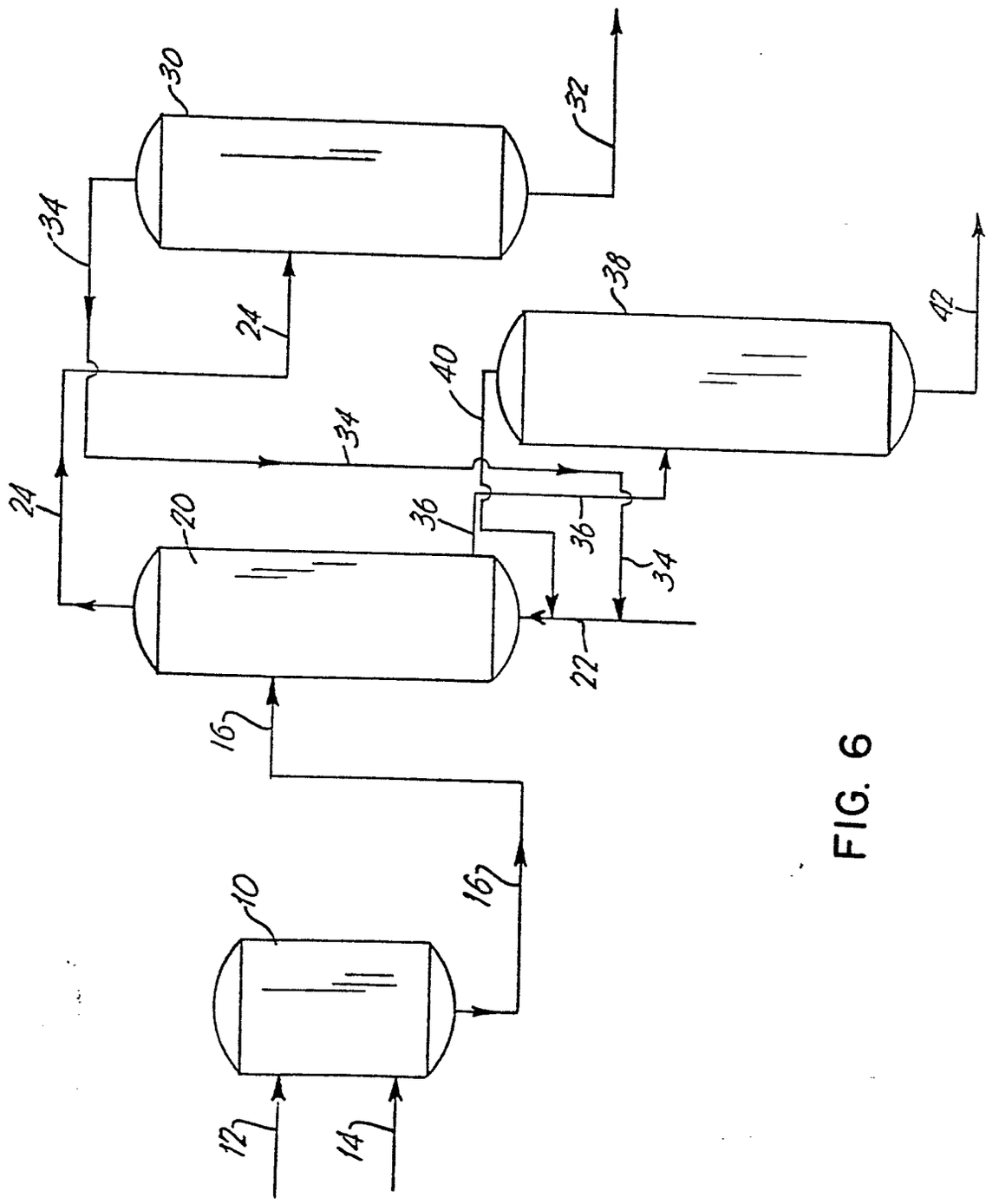

FIG. 6

European Patent Office

EUROPEAN SEARCH REPORT

0055627
Application number
EP 81306170.2

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A	US - A - 4 035 287 (WILTON F. ESPENSCHEID AND TSOUNG-YUAN YAN) * Claims; column 2, lines 5-21 *	1-3,6
A	US - A - 3 511 774 (R.B. LONG et al.) * Claims; column 1, lines 42-53; column 2, lines 1-63; column 3, lines 1-75 *	1-5
D,A	US - A - 2 969 320 (A. SHAPIRO et al.) * Claims; column 1, lines 55-67; column 2, lines 1-55; column 3, lines 58-71 *	1-3
D,A	US - A - 2 926 129 (C.N. KIMBERLIN JR. et al.) * Claims; column 1, lines 50-72; column 2, lines 1-53 *	1-3

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

C 10 G 17/08
C 10 G 21/06

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 10 G 21/00
C 10 G 17/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
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T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	05-04-1982	STÖCKLMAYER