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# TREATMENT OF PETROLEUM FRACTIONS TO LOWER THE POUR POINT

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6 Claims. (Cl. 208—143)

This invention relates to the treatment of hydrocarbon fractions, particularly petroleum fractions, boiling above 150° C., and the principal object of the invention is to provide a process by means of which the cloud point, pour point or freezing point of such fractions may be lowered.

According to the invention a hydrocarbon fraction boiling above 150° C. is contacted in the presence of hydrogen with a catalyst comprising a platinum group metal on a support containing a major proportion of alumina but less than 1% wt. of halogen at a temperature of at least 700° F. but below the temperature at which substantial cracking occurs, a pressure of at least 100 p.s.i.g., and a space velocity not exceeding 8.0 v./v./hr. and a product boiling above 150° C. having a pour point at least 5° F. lower than the pour point of the feedstock is recovered, the temperature and space velocity being correlated to give said lower pour point.

For the purposes of the present specification substantial cracking is understood to occur when more than 20% wt. of the feedstock is converted to material boiling below 150° C. Preferably not more than 15% wt. of the feedstock is so converted.

The term "fraction" as used in this specification includes both fractions which are distillable at normal or reduced pressure, for example, gas oils and waxy distillates and also residues and portions thereof, for example deasphalted residues. Particularly suitable fractions for use as feedstocks are distillate fractions boiling within the range 150 to 450° C. and more particularly within the range 250 to 450° C.

It has been found that it is not necessary to desulphurise the feedstock prior to submitting it to the pour point reduction process, although such a preliminary desulphurisation may be given if desired. When operating with a sulphur-containing feedstock (for example one with more than 0.1% wt. of sulphur) the process will normally effect considerable desulphurisation simultaneously with the lowering of the cloud point, pour point or freezing point. It has also been found that the process can be operated in the presence of considerable quantities of hydrogen sulphide, so that, for example, the process can be operated on the total effluent of a previous hydrocatalytic desulphursation process.

If desired a part only of a particular fraction may be treated by the process according to the invention and the resulting product blended with the untreated portion to give a final product of reduced pour point.

The platinum group metal content of the catalyst may be within the range 0.01 to 5.0 percent weight preferably 0.1 to 1.0 percent weight. The preferred platinum group metals are platinum and palladium. The catalyst support material contains, as stated above, at least a major proportion of alumina and it may also contain a minor proportion of one or more of the oxides of metals of groups II, III and IV of the periodic table. Preferably the amount of the group II, III or IV metal oxides is from 5–25% wt. of the support. Examples of suitable supports include alumina, silica/alumina, titania/alumina, zirconia/alumina and beryllia/alumina. A support of alumina and from 5 to 25/ wt. of silica is particularly preferred. The support material may also contain a minor proportion of one or more compounds (including oxides) of non-metallic elements in groups III, IV and V for example boron or phosphorus, which may if desired be combined or mixed with any of the metal oxides of groups II, III and IV. Preferably the amount of the compounds of the non-metallic elements is from 5 to 25% wt. of the support, a support of alumina and from 5 to 25% wt. of the support of boron oxide (calculated as $B_2O_3$) being particularly preferred. As stated above if halogen, for example chlorine or fluorine, is present is should not exceed 1% wt. of the support.



The catalyst may be employed as a fixed bed, a moving bed or a fluidised bed.

An essential requirement to obtain pour point reduction with any given catalyst and operating conditions employed is a correlation of temperature and space velocity. In general the higher the temperature, the higher the space velocity that can be employed, the upper limit of temperature, at any given space velocity, being determined by the amount of cracking occurring. The feedstock used, the activity of the catalyst used and the reduction of pour point required should also be taken into account when selecting the process conditions. When treating the heavier feedstocks, for example, the operating conditions may be more severe (i.e. conditions of higher temperature and/or lower space velocity) than when treating lighter feedstocks. When using a more active catalyst, for example those having silica-alumina or boria-alumina supports, less severe conditions may be used, an equivalent reduction in pour point being obtainable at a lower temperature and/or higher space velocity. In practice the temperature will not normally exceed 950° F. and it is preferably at least 750° F. The pressure may be from 100 to 1500 p.s.i.g. and the hydrogen:hydrocarbon mole ratio from 1:1 to 20:1. In practice the space velocity will not normally be less than 0.1 v./v./hr. and it is preferably not less than 0.5 v./v./hr.

The process may be operated with or without a net hydrogen consumption. A net hydrogen consumption is generally favoured by increase in pressure, and for any given temperature and space velocity the pressure at which the hydrogen consumption and hydrogen production are in balance is known as the equilibrium pressure. It is generally preferred to operate at or above this pressure because this results in an increase in the on stream time before catalyst regeneration or replacement is necessary. Another advantage of this type of operation is, for example, that when processing feedstocks such as gas oils for the production of diesel oils reduction of the diesel index is minimized or avoided. The principal advantages of operating below the equilibrium pressure are that a reduction in the specific gravity of the distillate is minimised or avoided, and that hydrogen is produced, this hydrogen being then available for use in other hydrogen-consuming processes.

Operation of the process using a fixed bed of catalyst is carried out in the normal manner, which is to increase the temperature gradually as the run continues in order to maintain the quality of the product at the desired level.

The process of the present invention will normally lower all the three points specified viz. cloud point, pour point and freezing point. Which point is taken as the criterion for any particular operation will depend on the feedstock used and the use to which the product is to be put. The freezing point is normally only of importance with the lower boiling feedstocks.

The invention is illustrated by the following examples:

## EXAMPLE 1

A gas oil having a boiling range of 250–360° C. ASTM was hydrocatalytically desulphurised to reduce the sulphur content from 1.25% wt. to 0.04% wt. The conditions used were as follows.

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Pressure, p.s.i.g. | | | 500 | 500 | 500 | 750 | 1,000 | 750 | 750 | 750 |
| Temperature, ° F. | | | 800 | 825 | 825 | 825 | 825 | 825 | 825 | 825 |
| Space Velocity, v./v./hr. | | | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Gas Rate (Recycle), s.c.f./b. | | | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 5,000 | 2,500 |
| Recycle Gas $H_2$ content, percent vol. | | | 92 | 89 | 90 | 89 | 93 | 89 | 85 | 85 |
| $H_2$ Make | | | yes | yes | yes | yes | | yes | yes | yes |
| $H_2$ Consumption | | | | | | | yes | | | |
| Product (Unstabilised): | | | | | | | | | | |
| Cloud Point, ° F. | | | 8 | −2 | | | | | | |
| Pour Point, ° F. | | | 8 | −10 | −10 | −20 | −5 | −20 | −25 | −20 |
| Product (Boiling >150° C.): | | | | | | | | | | |
| Yield, percent wt. | | | 97 | 94.5 | 93.5 | 93.5 | 95 | 93.5 | 92.5 | 93.5 |
| | Raw Feed | Hydrofined Feed | | | | | | | | |
| SG at 60° F./60° F. | 0.842 | 0.829 | 0.834 | 0.836 | 0.840 | 0.835 | 0.829 | 0.835 | 0.833 | 0.837 |
| Diesel Index | 60 | 66 | 59 | 55 | 54 | 56 | 62 | 56 | 57 | 54 |
| Cloud Point, ° F. | 18 | 18 | 6 | −2 | | −8 | | −8 | −4 | −8 |
| Pour Point, ° F. | 15 | 15 | 5 | −5 | −5 | −15 | 0 | −15 | −10 | −15 |



A series of runs was carried out to determine the effect of process variables. The process conditions used and the results obtained are given in Table 1 below.

*Table 1*

The first set of results at 500 p.s.i.g. shows the advantage of operating at the higher temperature of 825° F. The second set of results at 825° F. shows the effect of pressure and indicates that the equilibrium pressure for the feedstock and conditions used lies between 750 and 1000 p.s.i.g. The third set of results shows that for the feedstock and conditions used the results are independent of recycle rate within the range 10,000–2,500 s.c.f./b.

## EXAMPLE 2

The hydrofined gas oil of Example 1 was processed over the catalyts of Example 1 in an extended run to assess the length of processing period obtainable. The process conditions used and the results obtained are given in Table 2 below.

*Table 2*

| | Raw Feed | Hydrofined Feed | Hours on Stream | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 80 | 140 | 164 | 224 | 284 | 308 | 368 | 428 | 512 | 572 | 632 |
| Pressure, p.s.i.g. | | | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 |
| Temperature, ° F. | | | 820 | 820 | 825 | 825 | 825 | 830 | 830 | 830 | 845 | 845 | 845 |
| Space Velocity, v./v./hr. | | | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Gas Rate (recycle), s.c.f./b. | | | 2,500 | 2,560 | 2,500 | 2,560 | 2,640 | 2,630 | 2,510 | 2,560 | 1,080 | 1,000 | 980 |
| Recycle Gas Density | | | 0.196 | 0.199 | 0.200 | 0.222 | 0.200 | 0.200 | | 0.182 | 0.222 | 0.236 | 0.242 |
| Recycle Gas $H_2$ Content, percent vol. | | | 87.0 | 88.0 | 88.5 | 89.0 | 88.5 | 88.5 | 88.2 | 89.5 | 81.0 | 85.0 | 84.0 |
| Recycle Gas $H_2S$ Content, percent vol. | | | Nil | Nil | Nil | Nil | Nil | Nil | Nil | Nil | Nil | Nil | Nil |
| Exit Gas Make, s.c.f./b. | | | | 159 | 183 | 161 | 132 | 117 | 175 | 151 | 125 | 39 | 30 |
| Product Gas Make, s.c.f./b. | | | 53 | 58 | 60 | 57 | 43 | 60 | 28 | 54 | 73 | 78 | 74 |
| Liquid Recovery, percent wt. | | | 101.1 | 99.8 | 99.2 | 99.7 | 99.2 | 99.2 | 100.9 | | 103.6 | 98.7 | 99.2 |
| Product (Unstabilised): | | | | | | | | | | | | | |
| Cloud Point, ° F. | | | −10 | −2 | −4 | −4 | −2 | −4 | −2 | 0 | −2 | 2 | 4 |
| Pour Point, ° F. | | | −15 | −10 | −10 | −5 | −10 | −10 | −10 | −10 | −10 | −10 | −10 |
| Product (Boiling >150° C.): | | | | | | | | | | | | | |
| Yield, percent wt. | | | 93.3 | 94.1 | 93.9 | 94.4 | 93.9 | 93.6 | 94.0 | 94.0 | 90.9 | 91.8 | 92.8 |
| Cloud Point, ° F. | 18 | 18 | 2 | 0 | 0 | −2 | 0 | 0 | 0 | 2 | 2 | 8 | 4 |
| Pour Point, ° F. | 15 | 18 | −10 | −5 | −5 | −5 | −5 | −5 | −5 | −5 | −10 | −5 | −10 |

| | |
|---|---|
| Temperature, °F. | 780. |
| Pressure, p.s.i.g. | 1000. |
| Space velocity, v./v./hr. | 8.0. |
| Recycle gas rate, s.c.f./b. | 4000. |
| Catalyst: | |
| Molybdenum oxide ($MoO_3$) | 14.3% wt. |
| Cobalt oxide (CoO) | 2.4% wt. |
| Alumina | Balance. |

The hydrofined product was then processed over a platinum catalyst to reduce its pour point. The catalyst composition was:

| | Percent weight |
|---|---|
| Platinum | 0.75 |
| Fluorine | 0.35 |
| Chlorine | 0.35 |
| Alumina | Balance |

After the processing the product was stabilised to remove a small proportion of material boiling below 150° C. and give a gas oil of the required flash point (150° C.).

These results show that a stabilised product was obtained in a yield of about 93%/94% wt. with a pour point at least 20° F. below that of the feedstock. The process was operated at a fixed recycle rate and fixed pressure below the equilibrium pressure giving a net production of hydrogen. However in spite of this the rate of loss of catalyst activity was low. Between 428 and 512 hours on stream the recycle rate was reduced voluntarily to show that operation at low recycle rates was possible. The run was ended voluntarily at 800 hours while the catalyst still had considerable activity. Regeneration of the catalyst restored the activity completely.

## EXAMPLE 3

A heavy gas oil was hydrocatalytically desulphurised over a catalyst of 2.4% wt. cobalt oxide and 14.3% wt. molybdenum oxide on alumina. The process conditions used and inspection data on the feed and product are given in Table 3 below.

*Table 3*

| Catalyst | CoMo/Alumina | |
|---|---|---|
| Operating conditions: | | |
| Pressure, p.s.i.g. | 1,000 | |
| Temperature, ° F. | 730 | |
| Space Velocity, v./v./hr. | 2.0 | |
| Gas Recycle Rate, s.c.f./b. | 1,000 | |
| | Feed | Product |
| Results: | | |
| Specific Gravity at 60° F./60° F. | 0.876 | 0.850 |
| ASTM Distillation, ° C.: | | |
| IBP | 298 | 146 |
| 10% Vol. Recovered at | 320 | 278.5 |
| 50% Vol. Recovered at | 345 | 333 |
| 90% Vol. Recovered at | 380 | 371 |
| FBP | 395 | 391 |
| Sulphur Content, percent wt. | 1.91 | 0.08 |
| Diesel Index | 57/58 | 62/63 |
| Cloud Point, ° F. | 58 | 60 |
| Pour Point, ° F. | 50 | 50 |

The desulphurised heavy gas oil was then processed to reduce its pour point over a platinum catalyst having the composiiton given in Example 1.

The process conditions used and the results obtained are given in Table 4 below.

*Table 4*

| | Feed | Hours on Stream | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 100 | 200 | 250 | 300 | 350 | 400 | 450 | 500 |
| Pressure, p.s.i.g. | ------- | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 |
| Temperature, ° F. | ------- | 830 | 860 | 860 | 860 | 860 | 860 | 860 | 860 |
| Space Velocity, v./v./hr. | ------- | 1.0 | 1.0 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Gas Recycle Rate, s.c.f./b. | ------- | 5,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 |
| Recycle Gas $H_2$ Content, percent vol. | ------- | 86 | 86 | 85 | 85 | 83 | 82 | 81 | 80 |
| Recycle Gas Density, g./l. | ------- | 0.200 | 0.250 | 0.250 | 0.250 | 0.250 | 0.25 | 0.320 | 0.265 |
| Exit Gas Make, s.c.f./b. | ------- | 50 | 75 | 50 | 50 | 50 | 50 | 30 | 25 |
| $H_2$ Consumption, s.c.f./b. | ------- | Nil | Nil | Nil | Nil | Nil | Nil | Nil | Nil |
| Product Gas Make, s.c.f./b. | ------- | 40 | 50 | 70 | 75 | 75 | 75 | 80 | 85 |
| Product (Unstabilised): | | | | | | | | | |
| Cloud Point, ° F. | ------- | 52 | 46 | 40 | 40 | 40 | 42 | 42 | 44 |
| Pour Point, ° F. | ------- | 45 | 40 | 30 | 30 | 35 | 35 | 35 | 35 |
| Product (Boiling >150° C.): | | | | | | | | | |
| Yield, percent wt. | 100 | ------- | 94 | ------- | ------- | 92.5 | ------- | 93.5 | ------- |
| Diesel Index | 62/63 | ------- | 56 | ------- | ------- | 55 | ------- | 55 | ------- |
| Cloud Point, ° F. | 60 | ------- | 48 | ------- | ------- | 44 | ------- | 44 | ------- |
| Pour Point, ° F. | 50 | ------- | 45 | ------- | ------- | 40 | ------- | 40 | ------- |

The table shows the effectiveness of the platinum alumina catalyst for reducing the pour point of heavy gas oils over a processing period of at least 500 hours. It also shows that lowering the space velocity at a given temperature gives a further reduction in the pour point.

## EXAMPLE 4

The catalyst used in Example 3 was regenerated by burning off the deposits formed in an oxygen-containing gas. It was then re-used to process a further quantity of the desulphurised heavy gas oil used in Example 3.

The process conditions used and the results obtained are given in Table 5 below.



The results show that the regenerated catalyst had an activity comparable to a fresh catalyst and that it was capable of reducing the pour point of a heavy gas oil over a processing period of at least 1100 hours. Alterations in the process conditions made at 840 hours on stream and after were made for the purposes of assessing the effect of increased temperature and space velocity and not to compensate for a decline in catalyst activity, and they show that increased temperatures give a further reduction in pour point and allow the use of higher space velocities.

## EXAMPLE 5

A light gas oil was hydrocatalytically desulphurised over a catalyst of 2.4% wt. cobalt oxide and 14.3% wt. molybdenum oxide on alumina under the following conditions:

| | |
|---|---|
| Temperature | 820° F. |
| Pressure | 750 p.s.i.g. |
| Space velocity | 8.0 v./v./hr. |
| Gas rate | 8000 s.c.f. of hydrogen/b. |

The gas oil feedstock had an ASTM boiling range of 250–360° C., a sulphur content of 1.25% wt., a cloud point of +18° F. and a pour point of +15° F. Previous experiments on the desulphurisation of such a feedstock under these process conditions showed a reduction of sulphur content to 0.04% wt. but no reduction of the cloud or pour point.

The total effluent from the hydrocatalytic desulphurisation, including all the $H_2S$ produced was then contacted with a platinum alumina catalyst having the following composition:

| | Percent weight |
|---|---|
| Platinum | 0.75 |
| Fluorine | 0.35 |
| Chlorine | 0.35 |
| Alumina | Balance |

*Table 5*

| | Feed | Hours on Stream | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 100 | 200 | 250 | 300 | 350 | 400 | 450 | 500 | 550 | 600 | 800 | 815 | 840 | 846 | 950 | 1,100 |
| Pressure, p.s.i.g. | ------ | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 | 750 |
| Temperature, ° F. | ------ | 830 | 860 | 880 | 880 | 880 | 880 | 880 | 880 | 890 | 890 | 890 | 900 | 925 | 950 | 950 | 950 |
| Space Velocity, v./v./hr. | ------ | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 2.0 | 2.0 |
| Gas Recycle Rate, s.c.f./b. | ------ | 5,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 | 10,000 |
| Recycle Gas $H_2$ Content, percent vol. | ------ | 90 | 86 | 81 | 79 | 78 | ------ | ------ | ------ | 81 | ------ | 79 | 75 | 65 | 50 | 59 | ------ |
| Recycle Gas Density, g./l. | ------ | 0.175 | 0.200 | 0.250 | 0.260 | 0.280 | ------ | ------ | ------ | 0.280 | ------ | 0.290 | 0.300 | 0.375 | 0.500 | 0.480 | ------ |
| Exit Gas Make, s.c.f./b. | ------ | 40 | 50 | 25 | 10 | Nil | Nil | Nil | Nil | Nil | Nil | Nil | Nil | Nil | Nil | Nil | Nil |
| $H_2$ Consumption, s.c.f./b. | ------ | Nil | Nil | Nil | Nil | Nil | Nil | 25 | 25 | ------ | 75 | 100 | 140 | 175 | ------ | ------ | 195 |
| Product Gas Make, s.c.f./b. | ------ | 40 | 55 | 75 | 80 | 85 | 85 | 85 | 85 | 95 | 100 | 100 | 110 | 220 | 400 | 250 | 260 |
| Product (Unstabilised): | | | | | | | | | | | | | | | | | |
| Cloud Point, ° F. | ------ | 50 | 46 | 38 | 42 | 38 | 42 | 42 | 44 | 42 | 40 | 42 | 38 | 26 | 12 | 32 | 28 |
| Pour Point, ° F. | ------ | 45 | 40 | 30 | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 35 | 30 | 10 | −10 | 20 | 20 |
| Product (Boiling >150° C.): | | | | | | | | | | | | | | | | | |
| Yield, percent wt. | 100 | ------ | 94 | 91.5 | 92.5 | ------ | 91.5 | 93 | 93 | ------ | 92 | ------ | ------ | ------ | ------ | ------ | ------ |
| Diesel Index | 62/63 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| Cloud Point, ° F. | 60 | ------ | 46 | 42 | 44 | ------ | 44 | 44 | 42 | ------ | 42 | ------ | ------ | ------ | ------ | ------ | ------ |
| Pour Point, ° F. | 50 | ------ | 45 | 40 | 40 | ------ | 40 | 40 | 40 | ------ | 40 | ------ | ------ | ------ | ------ | ------ | ------ |

The process conditions used were the same as for the hydrocatalytic desulphurisation except that the space velocity was 1.0 v./v./hr. The results obtained are given in Table 6 below:

*Table 6*

| | Feed to desulphuriser | Hours on Stream | | | |
|---|---|---|---|---|---|
| | | 50 | 75 | 100 | 125 |
| Cloud Point, ° F | +18 | −6 | −6 | −8 | −4 |
| Pour Point, ° F | +15 | −15 | −15 | −15 | −15 |
| S content, percent wt | 1.25 | 0.01 | 0.01 | 0.01 | 0.01 |

## EXAMPLE 6

The gas oil of Example 5 was contacted without any previous desulphurisation, with a platinum-alumina catalyst having the following composition:

| | Percent weight |
|---|---|
| Platinum | 0.57 |
| Chlorine | 0.81 |
| Alumina | Balance |

The process conditions used were:

| | |
|---|---|
| Temperature | 820° F. |
| Pressure | 750 p.s.i.g. |
| Space velocity | 1.0 v./v./hr. |
| Gas rate | 2,500 s.c.f. of hydrogen/b. |

The results obtained are given in Table 7 below:

*Table 7*

| | Feedstock | Hours on Stream | | | |
|---|---|---|---|---|---|
| | | 50 | 75 | 100 | 125 |
| Cloud Point, ° F | +18 | −4 | −4 | −2 | 0 |
| Pour Point, ° F | +15 | −15 | −10 | −10 | −10 |
| S content, percent wt | 1.25 | 0.02 | 0.02 | 0.02 | 0.02 |

## EXAMPLE 7

A gas oil of 250–350° C. ASTM boiling range containing 1.25/ wt. sulphur and having a pour point of 20° F. was processed over the catalyst of Example 1. A series of runs was carried out at 750 p.s.i.g. and a gas rate of 10,000 s.c.f. of hydrogen/b., the temperature and space velocity being varied to indicate the correlation required to reduce the pour point of the feedstock. The results obtained are given in Table 8 below and are in each case the initial results obtained with fresh catalyst.

*Table 8*

| Temperature, ° F | 700 | | 800 | | 900 | | |
|---|---|---|---|---|---|---|---|
| Space velocity, v./v./hr. | 0.5 | 1.0 | 1.0 | 2.0 | 1.0 | 4.0 | 8.0 |
| Product >150° C.: | | | | | | | |
| Yield, percent wt. | 98.5 | 98.5 | 93.5 | 97 | 75 | 91 | 97.5 |
| Pour Point, ° F | 20 | 20 | 5 | 15 | <−70 | −10 | 20 |
| Sulphur, percent wt | 0.02 | 0.05 | 0.02 | 0.04 | <0.01 | <0.01 | ------ |

The results show, while substantially complete desulphurisation was obtained under all conditions, pour point reduction was not always obtained. There is thus no connection between desulphurisation and pour point reduction.

With the particular catalyst 700° F. is below the minimum practicable temperature. Pour point reduction is not obtained even at 0.5 v./v./hr. and a very low space velocity would be necessary to obtain pour point reduction. Raising the temperature to 800° F. gives pour point reduction and allows a higher space velocity to be used. At 900° F. a space velocity of 4 v./v./hr. gives a good reduction but 8 v./v./hr . is the limiting space velocity at that temperature and with the catalyst used. A space velocity of 1 v./v./hr. at 900° F. gives a large reduction in pour point, but the amount of cracking exceeds that which is desirable.



## EXAMPLE 8

The gas oil of Example 7 was processed over three different catalysts. These were:

(1) The catalyst of Example 1, viz. 0.75% wt. platinum, 0.35% chlorine, 0.35% wt. fluorine and the balance alumina.

(2) A catalyst of 1% wt. platinum on a support of 10% wt. silica and 90% wt. alumina.

(3) A catalyst of 0.54% wt. platinum, 0.75%wt. chlorine, 9.0% wt. boron oxide ($B_2O_3$) and the balance alumina.

The process conditions in each case were:

| | |
|---|---|
| Temperature | 775, 800 and 825° F. |
| Pressure | 500 p.s.i.g. |
| Space velocity | 1.0 v./v./hr. |
| Gas rate | 5000 s.c.f. of hydrogen/b. |

The results obtained are given in Table 9 below:

*Table 9*

| Catalyst | Pour Point | | | |
|---|---|---|---|---|
| | Feed | 775° F. | 800° F. | 825° F. |
| 1. Pt/alumina | 20 | 20 | 10 | 0 |
| 2. Pt/silica-alumina | 20 | 0 | −5 | −30 |
| 3. Pt/boria-alumina | 20 | −55 | −60 | −65 |

The results show the much greater activity of the silica- and boria-containing catalysts. This greater activity allows considerably wider variation in the correlation of temperature and space velocity, a given reduction in pour point being obtainable at lower temperature and/or higher space velocity.

We claim:

1. A process for the treatment of distillate petroleum fractions boiling within the range 150–450° C. to lower the pour point at least 5° F. without material reduction in the specific gravity and diesel index of said distillate fractions, comprising contacting the distillate fraction as feedstock in a treating zone and in the presence of hydrogen with a catalyst comprising a platinum group metal on a support containing a major proportion of alumina, from 5–25% by weight of the support of a material selected from the group consisting of group II metal oxides, group III metal oxides, group IV metal oxides, and group III non-metallic oxides, group IV non-metallic oxides, and group V non-metallic oxides, and mixtures of the foregoing, and less than 1% wt. of halogen, the hydrogen to hydrocarbon mole ratio being from 1 to 1 to 20 to 1; maintaining a selected temperature and a selected space velocity in said zone, said selected temperature in said zone being maintained at least at 700° F. but not higher than about 950° F. and being a temperature at which, at said selected space velocity, not more than 20% wt. of the feedstock is converted to material boiling below 150° C. and said selected space velocity being at least 0.01 v./v./hr. but not higher than 8.0 v./v./hr. at which, at said selected temperature, not more than 20% wt. of the feedstock is converted to material boiling below 150° C.; maintaining a selected pressure in said zone in the range 100–1500 p.s.i. ga., said selected temperature and said selected space velocity being correlated to reduce the pour point of the feedstock such that the pour point of the material of the treated distillate fraction boiling above 150° C. is at least 5° F. lower than the pour point of the feedstock, and recovering the treated distillate fraction.

2. A process in accordance with claim 1 wherein the

platinum group metals is present in an amount from 0.01 to 5.0% wt.

3. A process as claimed in claim 1 wherein the fraction is sulphur-containing.

4. A process as claimed in claim 1 wherein the platinum group metal is platinum.

5. A process as claimed in claim 1 wherein the metal oxide is silica.



6. A process as claimed in claim 1 wherein the selected compound is boron oxide.

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| 2,967,147 | Cole | Jan. 3, 1961 |

# UNITED STATES PATENT OFFICE
# CERTIFICATE OF CORRECTION

Patent No. 3,125,505

March 17, 19

Kenneth Tupman et al.

It is hereby certified that error appears in the above numbered pat
ent requiring correction and that the said Letters Patent should read a
corrected below.

Column 2, line 7, for "5 to 25/wt." read -- 5 to 25%
wt. --; columns 3 and 4, Table 1, under the column headed
"Raw Feed", line 1 thereof, for "0.842" read -- 0.843 --; colu
7, line 42, for "1.25/wt." read -- 1.25% wt. --.

Signed and sealed this 25th day of January 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNEF
Commissioner of Patents