March 17, 1964 K. TUPMAN ET AL **3,125,507**

HYDROFINING HYDROCARBON FRACTIONS

Filed Jan. 16, 1962 2 Sheets-Sheet 1

FIG. 1.

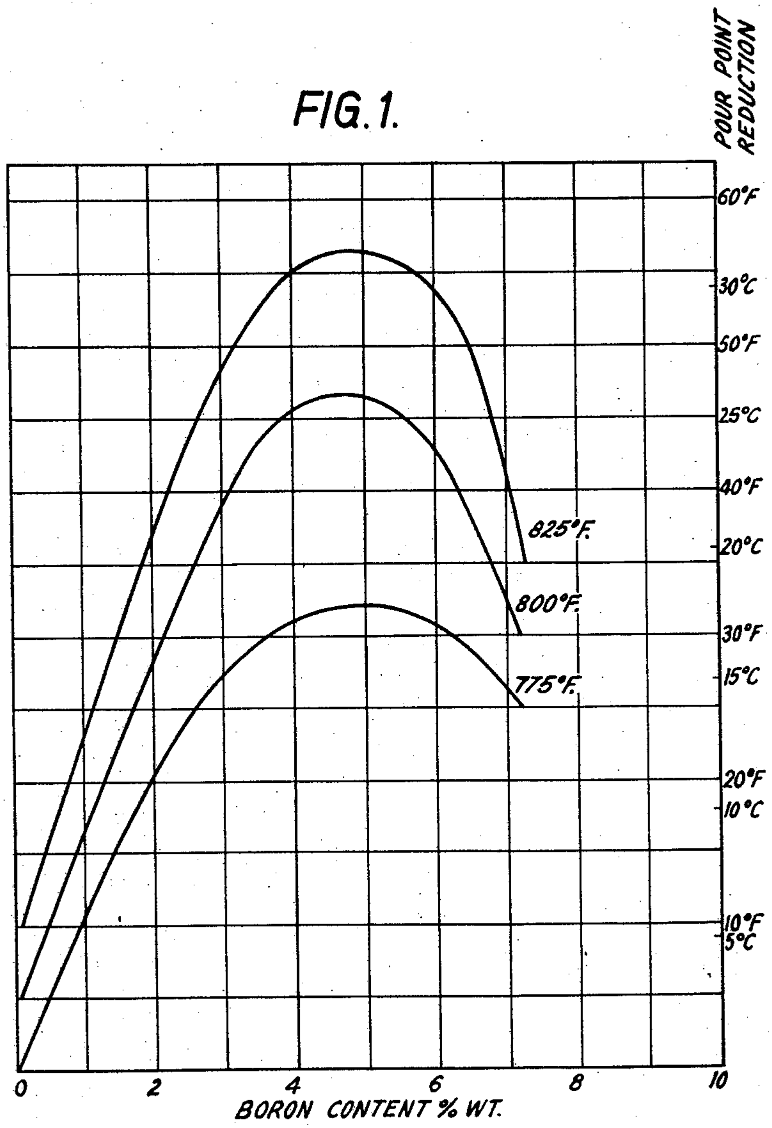

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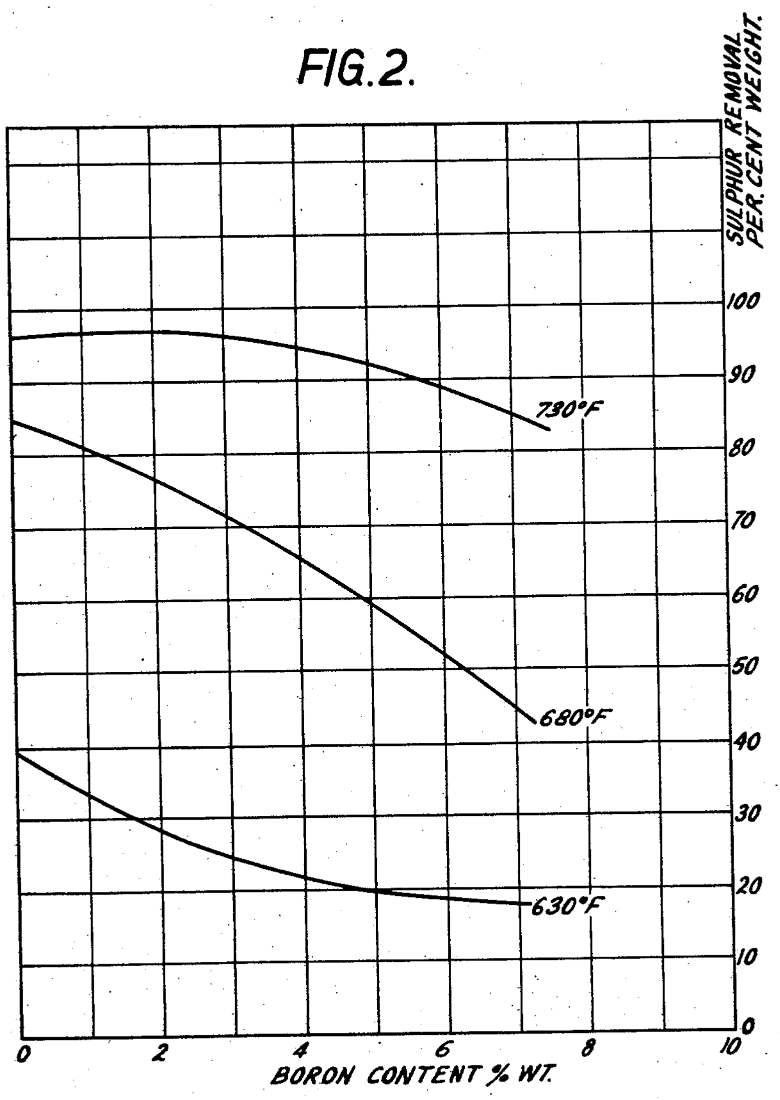
FIG. 2.



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HYDROFINING HYDROCARBON FRACTIONS

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Claims priority, application Great Britain Jan. 26, 1961
10 Claims. (Cl. 208—216)

This invention relates to the conversion of hydrocarbon fractions, particularly petroleum fractions, boiling above 150° C., and a 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. It is also an object to desulphurise hydrocarbon fractions containing sulphur simultaneously with the reduction in cloud, pour or freezing point.

According to the invention a hydrocarbon fraction boiling above 150° C. is contacted in the presence of hydrogen with a catalyst comprising a group VIa metal, a refractory oxide support and boron at a temperature of at least 700° F. but below that 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 pressure being correlated to give said lower pour point.

In the drawings:

FIG. 1 is a graph showing the effect of boron content and treating temperature on the pour point reducing activity of cobalt oxide-molybdenum oxide-alumina catalysts in the treatment of a hydrocarbon fraction according to the invention; and,

FIG. 2 is a graph showing the effect of boron content and treating temperature on the desulphurization activity of cobalt oxide-molybdenum oxide catalysts in the treatment of a hydrocarbon fraction according to the invention.

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.

The feedstock to the process may be substantially sulphur-free having for example less than 0.1% wt. of sulphur, but according to a preferred embodiment the feedstock contains 0.1% wt. or more of sulphur, the process effecting simultaneous desulphurisation as well as a reduction in cloud, pour, or freezing point.

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.

Some lower boiling material is likely to be produced by, for example, dehydrogenation, desulphurization and/or cracking and since the desired product boils above 150° C. this may be separated from the product, preferably by fractionation.

The boron content of the catalyst may be from 1 to 20% wt. by wt. of total catalyst but according to a particularly preferred embodiment the boron content is from 3–7% wt., preferably 4–6% wt.

This is because the degree of pour point reduction reaches its maximum within this range of boron contents, greater or lesser amounts giving a lesser degree of pour point reduction. This optimum content of boron is not related to the desulphurisation activity, and the desulphurisation activity declines steadily as the boron content increases from 0 to 7% wt. When deciding the most desirable boron content for any particular operation, therefore, the relative extents to which desulphurisation and pour point reduction are required should be considered. The temperatures normally used to obtain pour point reduction are, however, those which favour desulphurisation so that in practice it is likely that adequate desulphurisation will be achieved with boron contents within the range 3 to 7% wt., except in the case of feedstocks which are particularly difficult to desulphurise.

The refractory oxide support may be selected from the refractory oxides of metals of groups II, III, and IV of the periodic table. The preferred refractory oxide is alumina and the support may consist wholly of alumina or a mixture of refractory oxides having a major proportion of alumina and a minor proportion, preferably from 5–25% wt., of one or more other refractory oxides of metals of groups II, III, and IV. Examples of suitable supports thus include alumina, silica/alumina, titania/alumina, zirconia/alumina and beryllia/alumina.

The group VIa metal is preferably in the form of an oxide or sulphide. The catalyst may also contain a group VIII metal, preferably in the form of an oxide or sulphide, in addition to the group VIa metal. The presence of a group VIII metal is particularly desirable if it is desired to desulphurise as well as to reduce the pour point. The preferred group VIa metal is molybdenum and the preferred group VIII metal is an iron group metal, particularly cobalt. The molybdenum may be present in from 5 to 40% wt., calculated as the oxide MoO_3, by weight of total catalyst and the iron group metal from 0.1 to 10% wt., calculated as the divalent metal oxide, by weight of total catalyst. A particularly preferred catalyst contains the oxides of cobalt and molybdenum (as such, or in combined form, or both).

Active catalysts can be prepared using any convenient known technique, for example by the techniques generally known as co-precipitation, impregnation or milling. It has been found however that it is preferable to incorporate the boron at an early or intermediate point in the catalyst preparation rather than subsequently to impregnate the pre-formed catalyst particles. Preferably the boron is incorporated into a hydrogel of the hydrated refractory oxide. The group VIa metal and group VIII metal if used may be added subsequently by impregnation of the preformed support, but they are also preferably added to the hydrogel.

The boron may be added initially in the form of a boron compound for example in the form of a decomposable salt or in the form of an oxide or oxyacid. After calcination of the catalyst, the boron is believed to be in the form of boron oxide. Compounds used for adding the group VIa metal and the group VIII metal if used may be those conventionally used.

The catalyst may be employed as a fixed bed, a moving bed on 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 one having from 4–6% wt. of boron, 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. and may be at least 800° 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 from 0.5 v./v./hr. to 5.0 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

Alumina Preparation

1500 g. of aluminium nitrate was dissolved in 2 l. of de-ionised water and stirred for 30 mins. 780 ml. of 0.880 ammonia was added with continued stirring and a hydrogel was formed with a pH of 8.5. This mix was stirred a further 2 hrs., then aged in an oven at 70° C. for 16 hrs. After ageing, the hydrogen was filtered to a cake, the cake then reslurried with 2 l. of de-ionised water, stirred for 30 mins. and again filtered; this washing with de-ionised water was repeated twice more. The washed hydrogel was dried for 2 hrs. at 100° C., and calcined for 2 hrs. at 550° C. The calcined material was then pelleted to pellets of ⅛" x ⅛" dimensions. The pellets were calcined at 550° C. for 2 hrs.

Impregnation of the Pellets

100 g. of the pellets prepared as above were impregnated with a solution of 11.63 g. of ammonium molybdate dissolved in 55 ml. hot de-ionised water. The pellets were allowed to soak in this solution for 1 hr. before drying at 100° C. for 2 hrs. and calcining at 550° C. for 2 hrs.

The pellets were then impregnated with a solution of 12 g. boric acid dissolved in 55 ml. hot isopropyl alcohol. The pellets were allowed to soak in this solution for 1 hour before drying at 100° C. for 2 hrs. and calcining at 550° C. for 2 hrs. This impregnation was repeated twice more using the same quantities of boric acid and isopropyl alcohol. The pellets were dried at 100° C. for 2 hrs. and calcined at 550° C. for 2 hrs. after each impregnation.

The composition of the finished catalyst was:

Molybdenum oxide (expressed as MoO_3)	9% wt.
Boron oxide (expressed as B_2O_3)	18% wt. (equivalent to 5.6% wt. boron).
Alumina	Balance.

Use of the Catalyst

The catalyst was tested for pour point reducing activity using as feedstock a desulphurised heavy gas oil having an ASTM boiling range of 298–395° C., a cloud point of +60° F. and a pour point of +50° F. The process conditions used were:

Pressure	500 p.s.i.g.
Space velocity	1.0 v./v./hr.
Once-through gas rate	5000 s.c.f. of H_2/b.
Temperature	775, 800 and 825° F.
Duration	4 hours at each temperature.

At the conclusion of the first test period (using all three temperatures) the catalyst was regenerated. The initial regeneration gas contained 2% oxygen and the remainder inert gas and the final treatment was with neat air. Throughout the regeneration the temperature of the catalyst was kept below 550° C. After the regeneration the catalyst was tested again with the same feedstock and under the same conditions, then regenerated again and tested again.

The results obtained are given in Table 1 below.

TABLE 1

Catalyst		Activity Test Temperature 775° ° F.	800° ° F.	825° ° F.	Feedstock
Fresh Catalyst	Cloud Point, ° F.	+24	+26	+26	+60
	Pour Point, ° F.	+20	+20	+10	+50
After 1st regeneration	Cloud Point, ° F.	+30	+28	+20	-------
	Pour Point, ° P.	+20	+20	+15	-------
After 2nd regeneragion	Cloud Point, ° F.	+32	+26	+26	-------
	Pour Point, ° F.	+25	+20	+15	-------

Similar results to those given in Table 1 were also obtained with a catalyst consisting of 10% wt. molybdenum oxide, 9.4% wt. boron oxide (equivalent to 3% wt. boron) and the balance alumina.

EXAMPLE 2

A catalyst containing 1.84% wt. cobalt, 10% wt. molybdenum and 5% wt. boron on a base of alumina was prepared in a similar manner to the catalyst described in Example 1.

The catalyst was used to treat a gas oil having an ASTM boiling range of 250 to 360° C., a sulphur content of 1.2% wt., a pour point of +15° F. and a cloud point of +18° F. under the following conditions:

Pressure	p.s.i.g.	600
Space velocity	v./v./hr.	1.0
Hydrogen:hydrocarbon mole ratio		7.5:1
Temperature	° F.	750

The product, after processing for 50 hours on stream, had a sulphur content of 0.01% wt., a pour point of 0° F. and a cloud point of 5° F.

EXAMPLE 3

Preparation of Catalysts

2030 g. of aluminium nitrate was dissolved in 2.5 l. of de-ionised water and stirred for 30 minutes. 1040 ml. of 0.880 ammonia was added with continued stirring and a hydrogel was formed with a pH of 8.5. This mix was stirred a further 2 hours, then aged in an oven at 70° C. for 16 hours. After ageing, the hydrogel was filtered to a cake, the cake then reslurried with 2.5 l. of de-ionised water, stirred for 30 minutes and again filtered; this washing with de-ionised water was repeated twice more.

The cake of hydrogel was divided into 4 equal portions which were treated as follows:

Catalyst A.—A solution was made up by dissolving 19.3 g. of ammonium molybdate in 50 ml. of de-ionised water and to this was added a solution of 9.8 g. cobaltous nitrate dissolved in 20 ml. de-ionised water and the mixed solutions slurried with one portion of the alumina hydrogel. The mix was then dried at 110° C. for 16 hours, calcined for 2 hours at 550° C. and the calcined material pelleted to form ⅛" x ⅛" pellets.

The calcined pellets were then impregnated with a solution of 24.3 g. of boric acid dissolved in 100 ml. of de-ionised water. The impregnated pellets were then dried at 105° C. for 2 hours and calcined for 2 hours at 550° C.

Catalyst B.—A second portion of the alumina hydrogel was slurried with a solution of boric acid made up by dissolving 24.3 g. boric acid in 100 ml. of de-ionised water. The mix was then dried at 110° C. for 2 hours and calcined for 2 hours at 550° C., the calcined material was formed into ⅛" x ⅛" pellets, which were then impregnated with a solution made up by dissolving 19.3 g. ammonium molybdate in 50 ml. of de-ionised water and mixing this solution with a solution of 9.8 g. cobaltous nitrate dissolved in 20 ml. de-ionised water. The impregnated pellets were dried at 105° C. for 2 hours and calcined for 2 hours at 550° C.

Catalyst C.—A further portion of the alumina hydrogel was slurried with 24.3 g. boric acid dissolved in 100 ml. de-ionised water and stirred for 15 minutes, after which 19.3 g. of ammonium molybdate dissolved in 50 ml. de-ionised water was added and stirred in; 9.8 g. of cobaltous nitrate dissolved in 20 ml. de-ionised water was then added and the whole mix stirred for 2 hours, before drying at 110° C. for 16 hours, calcining for 2 hours at 550° C. and then forming into ⅛" x ⅛" pellets.

Catalyst D.—The final portion of alumina hydrogel was slurried with solutions of boric acid, ammonium molybdate and cobaltous nitrate in the same proportions and manner as for catalyst C and after drying the mix at 100° C. for 16 hours it was pelleted to ⅛" x ⅛" pellets before calcining at 550° C. for 2 hours.

The composition of each of the finished catalysts was:

	Percent wt.
Molybdenum (expressed as MoO_3)	15.75
Cobalt (expressed as CoO)	2.54
Boron (expressed as B_2O_3)	12.73
Alumina	Balance

Testing of the Catalysts

Each catalyst was tested for pour point reducing activity using as feedstock a desulphurised heavy gas oil having an ASTM boiling range of 298–395° C., a cloud point of +60° F. and a pour point of +50° F. The process conditions used were:

Pressure	500 p.s.i.g.
Space velocity	1.0 v./v./hr.
Once-through gas rate	5000 s.c.f./b. of H_2.
Temperature	775, 800, 825° F.
Duration	4 hr. at each temp.

The results of these tests are given in Table 2.

TABLE 2

Catalyst		Activity Test Temperature			Feedstock
		775° F.	800° F.	825° F.	
A	Cloud Point, ° F	+24	+26	+20	+60
	Pour Point, ° F	+20	+20	+10	+50
B	Cloud Point, ° F	+26	+24	+18	
	Pour Point, ° F	+20	+20	+10	
C	Cloud Point, ° F	+20	+18	+10	
	Pour Point, ° F	+15	+10	0	
D	Cloud Point, ° F	+18	+10	+2	
	Pour Point, ° F	+10	0	−10	

These data show that a wide variety of techniques can be employed for preparing active catalysts. However, it is clear that the activity of the finished catalyst can be greatly affected by the particular technique employed and that of the four techniques described, that for catalyst D is preferable.

Example 4

A desulphurised gas oil had the following inspection data.

Specific gravity at 60° F./60° F	0.850
ASTM distillation:	
IBP, ° C	146
10% vol. recovered at ° C	278.5
50% vol. recovered at ° C	333
90% vol. recovered at ° C	371
FBP, ° C	391
Sulphur, percent wt	0.08
Cloud point, ° F	60
Pour point, ° F	50

Portions of this feedstock were treated to reduce their pour point under the following conditions:

Temperature, ° F	775, 800, 825
Pressure, p.s.i.g	500
Space velocity, v./v./hr	1.0
Once through gas rate, s.c.f. of H_2/b	5000

12 runs were carried out using cobalt oxide-molybdenum-oxide-alumina catalysts having different boron contents within the range 0–7.2% wt. and the results obtained are shown on the accompanying graph, FIGURE 1. The results show a clear optimum content of boron of about 5% wt. for maximum pour point reduction.

Other characteristics of the catalysts were also varied. Thus the cobalt content varied from 1.2 to 2.6% wt., the molybdenum content from 7.2 to 15.2% wt., and both ⅛" pellets and 8–12 mesh granules were used. This resulated in some slight departures from the curves shown in FIG. 1, but the trend was not in any way affected, indicating that the contents of cobalt and molybdenum and the form of the particles were not critical in determining the extent of pour point reduction.

Similar trends and curves were found for the relationship between boron content and cloud point reduction.

Example 5

A series of experiments similar to those of Example 3 was carried out to investigate the effect of boron content on the desulphurisation activity of cobalt oxide-molybdenum oxide catalysts. The feedstock used was a straight-run gas oil having the following inspection data.

Specific gravity at 60° F./60° F	0.850
ASTM distillation:	
IBP, ° C	232
10% vol. recovered at ° C	263.5
50% vol. recovered at ° C	289
90% vol. recovered at ° C	331
FBP, ° C	359
Sulphur, percent wt	1.25
Cloud point, ° F	18
Pour point, ° F	15

The process conditions used were:

Temperature, ° F	630, 680, 730
Pressure, p.s.i.g	500
Space velocity, v./v./hr	5.0
Once through gas rate, s.c.f. of H_2/b	1000

Again a variety of catalysts were tested having boron contents ranging from 0–7.2% wt. and the results obtained are shown in the accompanying graph, FIG. 2.

The results show the decreasing desulphurisation activity with increasing boron content and the increasing degree of desulphurisation with increase of temperature. At the preferred operating temperatures of above 750° F. for pour point reduction it is clear that a high degree of desulphurisation would occur even with 7% wt. of boron.

As would be expected, the degree of desulphurisation tended to increase with increase in the content of cobalt and molybdenum and with decrease of the size of the catalyst particles.

No reduction in the cloud or pour point of the feed stock was obtained in any of the experiments. This illustrates the necessity of correctly correlating the temperature and space velocity, a space velocity of 5 v./v./hr. being too high at temperatures of 730° F. or below to obtain cloud or pour point reduction.

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 group VIa metal, a refractory oxide support, and from 3–7%, by weight of total catalyst, of boron, the hydrogen to hydrocarbon mole ratio being from 1 to 1 to 20 to 1; maintaining a selected temperature and a selected space velocty in said zone, said selected temperature in said zone being maintained at least about 750° 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 equal to the space velocity at which at said selected temperature not more than 20% wt. of the feedstock is converted to material boiling below 150° C. but not exceeding 8.0 v./v./hr.; maintaining a selected pressure in said zone in the range of 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 as claimed in claim 1 wherein the fraction contains at least 0.1% wt. of sulphur.

3. A process as claimed in claim 1 wherein the catalyst contains from 4 to 6% wt. of boron by weight of total catalyst.

4. A process as claimed in claim 1 wherein the group VIa metal is molybdenum, present in an amount calculated as the oxide MoO_3, of from 5 to 40% by weight of total catalyst.

5. A process as claimed in claim 1 wherein the catalyst contains also a group VIII metal.

6. A process as claimed in claim 5 wherein the group VIII metal is an iron group metal, present in an amount, calculated as the divalent metal oxide, of from 0.1 to 10% wt., by weight of total catalyst.

7. A process as claimed in claim 6 wherein the iron group metal is cobalt.

8. A process as claimed in claim 1 wherein the refractory oxide support is alumina.

9. A process as claimed in claim 1 wherein the refractory oxide support is a mixture containing a major proportion of alumina and a minor proportion of at least one other refractory oxide of a metal selected from groups II, III and IV of the periodic table.

10. A process as claimed in claim 1 wherein the space velocity is from 0.5 to 5 v./v./hr.

References Cited in the file of this patent

UNITED STATES PATENTS

2,878,180 Watkins ---------------- Mar. 17, 1959

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,125,507 March 17, 1964

Kenneth Tupman et al.

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

Column 2, line 62, for "on" read -- or --.

Signed and sealed this 15th day of February 1966.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents