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3,420,768

## MIDDLE DISTILLATE HYDROGEN TREATING PROCESSES

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4 Claims

### ABSTRACT OF THE DISCLOSURE

A process for the production of low nitrogen and sulfur middle distillates having pour points below 0° F. and -80° F., which comprises catalytically treating a high pour point middle distillate with low nitrogen and sulfur contents in the presence of hydrogen and a catalyst comprising alumina and a noble metal or a noble metal compound with the catalyst being essentially free of fluorine or aluminum fluoride, at temperatures of 700°-850° F., pressures of 200-2,000 p.s.i.g., and space velocities of 0.2-10. Platinum-on-alumina is the preferred catalyst. Hydrocracking precedes pour point reduction, and hydrofining may precede hydrocracking.

This invention relates to processes for producing low pour point oils from high pour point hydrocarbon oils. More particularly, the invention relates to the production of low pour point middle distillate fractions such as diesel fuel.

Middle distillate fractions, as the term is used herein, comprise those hydrocarbon oils boiling above the gasoline boiling range and at least partly above the kerosene boiling range, i.e. hydrocarbon distillates having end boiling points of from about 600° F. to about 800° F. with an initial boiling point of at least about 300° F. Middle distillates having end boiling points in the range 650-750° F. are particularly useful as diesel fuel provided they meet the other product requirements for such fuels. One such requirement where the diesel fuel is to be usable under cold weather conditions is that it have a low pour point of below 0° F., frequently specified as no greater than about -10° F., -20° F., or even lower. The requirement of a low pour point tends to dictate the use of oils having relatively low end boiling points, but it would be substantially more desirable that the oil have a higher end boiling point and a relatively low API gravity, preferably not over 39° API. The supply of straight run middle distillates having such a low pour point is quite limited. Dewaxing of high pour point fractions to obtain a suitable low pour point is expensive and difficult to accomplish with the distillate fractions. Numerous processes have been devised or proposed for producing larger amounts of low pour point middle distillates by hydrocracking processes applied to higher-boiling feedstocks. Low pour point middle distillate fractions are obtainable from such hydrocracking processes in relatively low yields, however, and operation of the hydrocracking processes to obtain higher middle distillate yields results

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in the production of oils having unsatisfactorily high pour points.

It has now been found how to lower the pour point of middle distillate fractions with minimal yield loss. By means of the process of the present invention larger amounts of low pour point middle distillate can be produced from heavy oils. Also, by the process of the invention there can be produced from high-boiling oils gasoline and low pour point middle distillate in nearly any desired relative amounts.

In accordance with the invention a heavy oil boiling at least partly above the middle distillate range, i.e. at least partly above 800° F., is contacted with hydrogen at hydrocracking reaction conditions in the presence of a solid catalyst having hydrogenation and cracking activity, and a sulfur-and-nitrogen-free middle distillate fraction is separated from the contacted oil. The middle distillate fraction is then contacted with hydrogen in the presence of a reforming catalyst at isomerization reaction conditions. The contacting with the reforming catalyst is effective to lower the pour point of the middle distillate fraction with minimal yield loss. At appropriate reaction conditions the API gravity of the middle distillate fraction can also be lowered.

In one embodiment a hetero-organic compound contaminated heavy oil boiling at least partly above the middle distillate range is contacted with hydrogen at hydrocracking conditions in the presence of a hydrofining catalyst, and the contacted oil is separated into fractions including a purified middle distillate fraction and a purified higher-boiling fraction. At least a portion of the purified middle distillate fraction is then contacted with the reforming catalyst to obtain the low pour point middle distillate product. All or a portion of the purified higher-boiling fraction can be recycled into contact with the hydrofining catalyst to form additional purified middle distillate fraction. Thus the hetero-organic compound contaminated oil can be recycle hydrocracked to extinction using the hydrofining catalyst to obtain middle distillate and lower-boiling fractions, all of which middle distillate fraction can be converted in high yield to low pour point middle distillate suitable as cold weather diesel fuel.

In another embodiment the higher-boiling fraction separated from the contacting of a hetero-organic compound contaminated heavy oil with a hydrofining catalyst is contacted with hydrogen in the presence of an acidic hydrocracking catalyst at hydrocracking reaction conditions to form gasoline and additional purified middle distillate fraction. Gasoline and low pour point middle distillate are then recovered as the principal liquid products of the process. When the middle distillate produced in the contacting with the hydrofining catalyst is converted to low pour point middle distillate by contacting with the reforming catalyst, and only the higher-boiling fraction is contacted with the acidic hydrocracking catalyst, the additional purified middle distillate fraction produced by the acidic hydrocracking catalyst contacting may have sufficiently low pour point that it can be blended directly with the product of the reforming catalyst treatment.

In another embodiment, a hetero-organic compound contaminated heavy oil boiling substantially above the middle distillate range is contacted in a first stage reaction zone with hydrogen in the presence of a hydrofining catalyst at hydrofining reaction conditions effective to substantially hydrogenate the hetero-organic compound contaminated heavy oil boiling substantially above the at least a high-boiling oil portion thereof, is then contacted with an acidic hydrocracking catalyst at hydrocracking reaction conditions to form products including gasoline and middle distillate which will be essentially free of sulfur and nitrogen compounds. As in conventional two-stage hydrocracking processes of the prior art, the oil effluent of the second stage is separated into fractions including gasoline, middle distillate, and a higher-boiling fraction. The higher-boiling fraction is recycled into contact with the acidic hydrocracking catalyst to form additional gasoline and middle distillate. The initial boiling point of the recycled fraction corresponds substantially to the end boiling point of the middle distillate fraction, and is referred to as the recycle cut point. In the process it is found that as the recycle cut point is raised in an effort to increase the yield of middle distillate fraction, the pour point of the middle distillate fraction becomes higher. In general, the middle distillate pour point is above  $-20^{\circ}\text{F}$ . at a recycle cut point which is still below  $650^{\circ}\text{F}$ . In accordance with this embodiment of the invention, the recycle cut point is maintained in the range  $650\text{--}750^{\circ}\text{F}$ ., and the high pour point middle distillate fraction recovered is passed to a pour point reducing zone wherein it is contacted with hydrogen in the presence of a reforming catalyst at isomerization reaction conditions, and there is recovered middle distillate having a low pour point of not in excess of  $-20^{\circ}\text{F}$ .

The attached drawing illustrates diagrammatically flow schemes suitable for carrying out the process of this invention, incorporating several of the above-mentioned alternate embodiments.

Referring to the drawing, a heavy oil feed such as a cracked or straight run heavy gas oil contaminated with hetero-organic compounds of sulfur and nitrogen is shown as comprising a heavy oil feed in line 11. The oil feed passes via line 12 to nitrogen and sulfur removal zone 13 wherein it is contacted with hydrogen, shown as added through line 14, in the presence of a sulfactive hydrogenation catalyst having hydrogenation and at least moderate hydrocracking activity. Suitable hydrofining catalysts comprise the transition metals and compounds thereof such as the oxides or sulfides, alone or associated with inorganic refractory oxide carriers. Preferred catalysts comprise the metals of Group VIII and those of Group VI, alone or in combination, such as combinations of nickel with tungsten or molybdenum, as sulfides. Suitable carriers comprise alumina, alone or in combination with silica, zirconia, titania, or magnesia, or various combinations thereof. Alumino-silicates of the molecular sieve type may also be used to advantage as carriers. The reaction conditions in zone 13 are such as to effect substantial conversion of the hetero-organic compounds to the hydrogenated inorganic by-products, such as  $\text{NH}_3$  and  $\text{H}_2\text{S}$ . The hydrofining reaction conditions include temperatures in the range  $600\text{--}850^{\circ}\text{F}$ . and pressures of  $1000\text{--}4000$  p.s.i.g., with hydrogen-rich gas throughputs of  $1,000\text{--}20,000$  s.c.f./bbl. and space velocities of  $0.2\text{--}10$  LHSV. Where hydrocracking reaction conditions are employed in zone 13, these will include temperatures of  $700\text{--}850^{\circ}\text{F}$ . and pressures of  $1000\text{--}4000$  p.s.i.g. At these conditions and in the presence of a hydrofining catalyst having at least moderate hydrocracking activity at least a portion of the heavy oil feed which boils above the middle distillate range is converted to middle distillate boiling range materials. Also, organic sulfur and nitrogen compounds are substantially eliminated by conversion to  $\text{H}_2\text{S}$  and  $\text{NH}_3$ .

The effluent of zone 13 passes via line 15 to a recovery zone 16, wherein any light gases formed are separated and removed through line 17, gasoline boiling range materials are withdrawn through line 18, and a middle distillate fraction is withdrawn through line 19, any remaining portion of the feed which still boils above the middle distillate end boiling point being withdrawn through line 20. At least a portion of the middle distillate fraction in line 19 is passed via lines 22 and 23 to pour point lowering zone 24, if the middle distillate fraction is nearly free of sulfur and nitrogen compounds. Specifically, the sulfur content of the oil should not exceed 50 p.p.m. by weight, and if the nitrogen content is below 10 p.p.m. by weight this sulfur limitation will usually be met. More desirably, the sulfur content is below 15 p.p.m.

In the pour point lowering zone 24 the middle distillate is contacted with hydrogen, introduced through line 25, in the presence of a catalyst effective for reforming gasoline boiling range hydrocarbons, at isomerization reaction conditions of  $700\text{--}850^{\circ}\text{F}$ . and  $400\text{--}4000$  p.s.i.g., with hydrogen-rich gas throughputs of  $1,000\text{--}20,000$  s.c.f./bbl. and space velocities of  $0.2\text{--}10$  LHSV. When the middle distillate of line 23 is essentially free of nitrogen and sulfur compounds, the reforming catalyst is effective in isomerizing paraffin constituents of the middle distillate to lower pour point isoparaffins with minimal conversion to lower boiling fractions. The pour point can be lowered by more than  $30^{\circ}\text{F}$ . with less than 10 percent conversion to gasoline and lighter products. Suitable catalysts comprise noble metals intimately associated with refractory oxide carriers of low cracking activity, a particularly suitable catalyst being platinum on alumina. While the platinum on alumina catalyst may be promoted with a small amount of halide, the introduction of acidic hydrocracking propensities into the catalyst is to be avoided. Thus, silica-alumina cracking catalyst carriers are not as suitable because at the elevated temperature conditions used in zone 24 there would be excessive conversion to gasoline. With a platinum-alumina reforming catalyst, the principal reaction appears to be isomerization. It will be noted that the temperature employed is generally lower than is normally used with the catalyst in reforming gasoline boiling range hydrocarbons. If pressures in the range  $400\text{--}900$  p.s.i.g. are employed, however, it is possible to aromatize a portion of the naphthenic compounds in the middle distillate whereby a lower gravity middle distillate product is obtained. Thus, on passing the effluent of pour point lowering zone 24 through line 26 to recovery facilities 27, there is obtained only a small amount of light products withdrawn through line 28 and a high yield of low pour point middle distillate withdrawn through line 29.

In one embodiment of the invention, as illustrated, the portion of the effluent of zone 13 which boils above the middle distillate end boiling point, in line 20, is recycled to extinction through line 21, returning to zone 13 via line 12. In another embodiment, all or a portion of this higher-boiling fraction in line 20 is passed via lines 31 and 32 to boiling point lowering zone 33 wherein it is contacted with hydrogen shown as added through line 34. In zone 33 there is provided an acidic hydrocracking catalyst and hydrocracking reaction conditions effective to convert the high boiling oil to gasoline and additional middle distillate fraction. Suitable catalysts comprise the Group VIII metals or compounds thereof intimately associated with refractory oxide carriers having acidic properties, such as an active cracking catalyst. The Group VIII metal may be one of the iron group metals or compounds such as the sulfide, particularly cobalt or nickel sulfide, or it may be a noble metal of the platinum-palladium group. Cracking catalysts consisting of or comprising alumino-silicates of the molecular sieve type provide a very effective acidic carrier for these metals when free of alkali metal.

Hydrocracking reaction conditions usable in zone 33 include temperatures of 400–900° F. and pressures of 1000–4000 p.s.i.g., with hydrogen-rich gas throughputs of 1,000–20,000 s.c.f./bbl. and space velocities of 0.2–10 LHSV. Lower temperatures of 400–750° F. can be employed if the high-boiling oil in line 32 is essentially free of nitrogen and sulfur compounds, i.e. less than 10 p.p.m. nitrogen by weight. If the oil still contains a significant amount of hetero-organic compound contaminants such as organic nitrogen, or by-product  $\text{NH}_3$ , higher temperatures of above 650° F. are used in zone 33.

The effluent of zone 33 passes via line 35 to recovery facilities 36 wherein it is separated into fractions comprising light gases in line 37, gasoline boiling range materials in line 38, a middle distillate fraction in line 40 and a higher-boiling fraction in line 41. Optionally, a kerosene product fraction may be taken off through line 39. Generally, the higher-boiling fraction in line 41 will be recycled back to zone 33 via line 32. If the high-boiling fraction of line 20 and the other constituents of the oil in line 32 comprise only materials boiling above the middle distillate end boiling point, and if the material in line 32 is essentially free of nitrogen compounds, the middle distillate product of line 40 will have a low pour point such that it can be blended directly with the low pour point of the middle distillate product of line 29 by passing through line 43. If, however, the oil of line 32 contains nitrogen compounds on particular, or includes materials boiling in the middle distillate range, the pour point of the middle distillate in line 40 will be higher than desired in the ultimate product. The middle distillate will, however, be essentially free of sulfur and nitrogen. Accordingly, this middle distillate can be passed via line 42 and line 23 to the pour point lowering zone 24.

Thus, the relative amounts of middle distillate and gasoline products in the over-all process can be adjusted in a variety of manners. In one approach, all or a portion of the middle distillate fraction of line 19 is combined with the bottoms fraction of line 20 by passing through line 30. Instead of recycling the bottoms through line 21, the broad boiling range oil is passed through lines 31 and 32 to boiling point lowering zone 33. The recycle cut point, i.e. the initial boiling point of recycled oil in line 41, is maintained in the range 650–750° F., and the resulting high pour point middle distillate recovered in line 40 is passed via lines 42 and 23 to pour point lowering zone 24. A minimal yield of middle distillate can be obtained by employing a relatively low recycle cut point. When even greater yield of middle distillate is desired than can be obtained by using the maximum recycle cut point, a greater portion of middle distillate is taken from line 19 of recovery zone 16 and passed through lines 22 and 23 to the pour point lowering zone 24. The maximum yield of middle distillate is obtained by maximizing the amount which is withdrawn from the first stage through line 19 and passed to the pour point lowering zone, because the boiling point lowering accomplished in zone 33 always results in the production of substantially more gasoline per barrel of feed than is obtained in nitrogen and sulfur removal zone 13.

Catalysts usable respectively in zones 13, 24, and 33 may be prepared by a variety of suitable methods described in detail in the art. A universally suitable method comprises impregnating a preformed inorganic oxide carrier with a solution of a hydrogenation-dehydrogenation promoting metal compound followed by drying and calcining. For example, a low silica content alumina-silica carrier may be impregnated with solutions of nickel nitrate or chloride and ammonium molybdate to form a catalyst suitable for use in zone 13; activated alumina may be impregnated with platinum chloride to form a catalyst for zone 24; and an acidic silica-alumina cracking catalyst carrier may be impregnated with nickel nitrate or other salt to form a catalyst for zone 33. Other techniques such as coprecipitation or cogellation of all or part of the

carrier with all or part of the promoting metal can be used. When aluminosilicate zeolites are employed as carriers, all or part of the promoting metal may be based exchanged for alkali metal or alkaline earth metal cations in the molecular sieve either directly or after first exchanging for other cations.

The contacting of oil with hydrogen in the presence of the catalysts in the respective zones may be carried in a variety of methods including passing the oil and hydrogen concurrently upwards or downwards, or countercurrently, through fixed beds of catalyst particles contained within pressure vessel reactors. Other techniques such as the use of moving beds of catalyst particles, fluidized beds of finely divided catalyst particles, and reactor systems wherein the catalyst particles are suspended as a slurry in the oil may also be used. The most preferred technique from the standpoint of design convenience and ease of operation is to pass preheated oil and hydrogen downwards through one or more fixed beds of catalyst particles within a high pressure reactor, cool the effluent to condense at least a portion of the oil and separate hydrogen-rich gas for recycling from the oil, and then separate the oil portion into fractions which are recovered or further treated in the other zones.

It will be recognized that the recovery zones 16, 27, and 36 may each comprise one or more distillation columns for obtaining better separation between and among the respective fractions. Further, in some instances zone 16 and zone 36 may be combined into a single unit or complex of units. For example, when the higher boiling material in the effluent of zone 13 is to be further converted to middle distillate in zone 33, and the middle distillates produced in zones 13 and 33 are to be further treated for pour point lowering in zone 24, the effluents of zone 13 and zone 33 may pass to a common distillation column for separation of a gasoline boiling range fraction, a middle distillate fraction to be further treated, and a higher-boiling recycle fraction.

In the following examples concurrent downflow of oil and hydrogen through fixed catalyst beds was employed, with separate fractionation of the effluents of the respective zones and recycle of hydrogen-rich gas in each zone. The first example illustrates that high yields of middle distillate can be produced by hydrocracking heavier oils with a hydrofining catalyst, but the middle distillate pour point is unsatisfactorily high.

#### Example 1

A heavy straight-run Arabian gas oil boiling from about 700° F. to about 1030° F. was recycle hydrocracked to gasoline and middle distillate fractions by contacting with a nickel sulfide-tungsten sulfide silica-magnesia sulfactive hydrogenation catalyst having moderate hydrocracking activity at 750° F., 2000 p.s.i.g., 1.0 LHSV, with 5,000 s.c.f./bbl. of recycle hydrogen. A middle distillate fraction boiling from about 300° F. to about 700° F. was recovered in 85 volume percent yield. This middle distillate fraction contained less than 1 p.p.m. nitrogen and less than 10 p.p.m. sulfur after washing to remove ammonia and  $\text{H}_2\text{S}$ , but had a pour point of 0° F.

The following example illustrates the pour point lowering obtainable by treating the purified middle distillate with a reforming catalyst at elevated pressure.

#### Example 2

The sulfur-and-nitrogen-free middle distillate of the above example was contacted with 1.0 percent platinum on alumina catalyst at 780° F., 1800 p.s.i.g., 1.0 LHSV, with 6,000 s.c.f.  $\text{H}_2$ /bbl. Ninety-three volume percent of the liquid product from contacting the platinum-alumina reforming catalyst still boiled from 350° F. to 640° F., and had a pour point of –70° F. as compared to the

pour point of 0° F. determined for the nitrogen-and-sulfur-free middle distillate feed.

The next example shows that API gravity can also be lowered while lowering the pour point of middle distillate, in accordance with the invention.

#### Example 3

The sulfur-and-nitrogen-free middle distillate having a pour point of 0° F. prepared as in Example 1 was contacted with the platinum-alumina catalyst at 780° F. and a pressure of only 550 p.s.i.g. at 1.0 LHSV. Ninety percent of the liquid product boiled from 350° F. to 650° F. and had a pour point of -60° F. In this case the gravity of the low pour point product was lower than that of the nitrogen-and-sulfur-free middle distillate feed, 38.8° API as compared to 41.3° API, and the oil contained about 30 volume percent aromatics as compared to 10 volume percent aromatics in the feed.

Inspections of the feed and products in the foregoing examples are summarized in the following Table I. The low cloud points of the isomerized oils are particularly to be noted, as it is desirable that the cold weather diesel fuel have a cloud point of not in excess of 0° F.

TABLE I

	Feed Heavy Gas Oil	Example 1 Hydro- cracked Middle Distillate	Example 2 (1,800 p.s.i.g.) Product	Example 3 (550 p.s.i.g.) Product
Yield, vol. percent of				
Feed	100	85	79	76
Gravity, ° API	23.2	41.3	44	38.8
Aniline Point, ° F.	181.1	175.2	179.3	145.6
Pour Point, ° F.	+95	0	-70	-65
Cloud Point, ° F.		+8	-32	-27
Analysis:				
Paraffins		39.7	43.7	42.2
Naphthenes		50.2	51.8	28.0
Aromatics		10.0	4.5	29.8
Distillation, ASTM				
D-86:				
Start	658	300	344	350
5%	694		378	375
95%	1,004		627	644
EBP	1,031	700	640	657
Nitrogen, p.p.m.	874			
Sulfur, wt. percent	2.8			

The next example illustrates that the hydrocracking process itself is not capable of achieving the low pour points obtainable on contacting with the platinum-alumina reforming catalysts and, further, that the low pour point oil obtainable is obtained at a lower yield.

#### Example 4

A heavy straight-run gas oil boiling from about 700° F. to 1030° F. was contacted with a nickel sulfide-molybdenum sulfide-alumina-silica sulfactive hydrogenation catalyst having moderate hydrocracking activity at 760° F. and 2270 p.s.i.g. on a once-through basis at 0.8 LHSV with 5,000 s.c.f. H<sub>2</sub>/bbl. About 70 volume percent of the feed was converted to materials boiling below 700° F., including about 56 volume percent boiling between 300 and 700° F. The 300-700° F. middle distillate fraction had a gravity of 35.9° API and a pour point of -45° F.

The next example illustrates the concurrent production of gasoline and low pour point middle distillate by hydrocracking a purified higher-boiling fraction with an acidic catalyst.

#### Example 5

The unconverted 30 volume percent of the oil in the above Example 4, boiling entirely above 700° F., was contacted with a nickel sulfide on acidic silica-alumina hydrocracking catalyst at 570° F., 1200 p.s.i.g., and 0.8 LHSV with extinction recycle of material in the effluent

boiling above 650° F. (recycle cut point). In this hydrocracking operation most of the oil was converted to gasoline and lower-boiling distillates, only a 30 volume percent yield of 300-650° F. middle distillate being obtained. The middle distillate, however, has a very low pour point of below -60° F. The over-all yield of low pour point middle distillate obtainable from the combination of once-through hydrocracking-hydrofining as in Example 4, and then recycle hydrocracking the bottoms as in this Example 5, amounts to about 64 volume percent of middle distillate having a pour point of about -50° F.

The following example illustrates the embodiment of the invention wherein the middle distillate fraction is produced by two-stage hydrocracking, and shows the effect of recycle cut point on middle distillate pour point recovered from distillation in a single still of the effluents of both stages.

#### Example 6

A straight-run heavy gas oil boiling from about 600° F. to about 850° F. was contacted with a nickel sulfide-molybdenum sulfide alumina hydrofining catalyst at 700° F., 1430 p.s.i.g., and 0.5 LHSV on a once-through basis to essentially eliminate organic sulfur and nitrogen contaminants. The sulfur-and-nitrogen-free liquid product was distilled to recover a middle distillate fraction boiling from 300° F. to the recycle cut point of the subsequent hydrocracking stage, and the bottoms fraction boiling above the recycle cut point was then contacted with a nickel sulfide-silica-alumina acidic hydrocracking catalyst in a recycle operation at about 520° F. and 1400 p.s.i.g. The effluent from contacting the acidic hydrocracking catalyst was combined with the first-stage effluent for distillation into gasoline and lower-boiling fractions, the middle distillate fraction, and the higher-boiling fraction which was the feed to the second stage. With a recycle cut point of 590° F. there is obtained as the middle distillate fraction an oil boiling from 300 to 590° F. with a pour point of about -49° F. in a yield of about 51 volume percent. At a recycle cut point of 650° F., however, the middle distillate boils from about 300° F. to 650° F. and has a pour point of +2° F. while the yield has increased to only 62 volume percent. At a recycle cut point of 630° F., the yield is 57 volume percent and the pour point is -10° F.

It is to be noted that the middle distillate has a low pour point when the recycle cut point is below the feed initial boiling point. As the cut point is raised above the feed initial boiling point, the product pour point becomes higher due in part to the inclusion of unconverted feed in the product, as the feed boils partly within and partly above the middle distillate boiling range.

The next example illustrates the improvement of obtaining a greater yield of lower pour point middle distillate by adding a pour point lowering stage and changing the operation of the two-stage process of Example 6.

#### Example 7

In accordance with the invention, the recycle cut point in the acidic hydrocracking stage of Example 6 is maintained at 650° F. or above, and the middle distillate fraction having a pour point of +2° F. or above is then contacted with the platinum-alumina reforming catalyst at 750-800° F. and 1500-2000 p.s.i.g., whereby there is obtained middle distillate having a pour point well below -20° F. with minimal yield loss.

The yields and middle distillate pour points obtainable in the foregoing examples are further summarized for comparison in the following Table II.

TABLE II

Example	Description	Middle Distillate Produced	
		Yield, vol. percent	Pour Point, ° F.
1-----	Extinction recycle hydrocracking in nitrogen and sulfur removal zone.	85-----	0
2-----	Pour point lowering of product of Ex. 1 using reforming catalyst at 1,800 p.s.i.g.	93 (79% over-all)-----	-70
3-----	Same as Ex. 2, at 550 p.s.i.g.	90 (76% over-all)-----	-65
4-----	Once-through hydrocracking in nitrogen and sulfur removal zone.	56-----	-45
5-----	Recycle hydrocracking 700+° F. bottoms of Ex. 4 in boiling point lowering zone, 650° F. RCP*.	30 (9% over-all)-----	~-60
6-----	Two-stage recycle hydrocracking with single recovery still:		
	(a) 590° F. RCP-----	51-----	-49
	(b) 610° F. RCP-----	53.5-----	-38
	(c) 630° F. RCP-----	57-----	-10
	(d) 650° F. RCP-----	62-----	+2
7-----	Pour point lowering of product (d) of Ex. 6 using same catalysts reform.	93 (58% over-all)-----	-60

\* RCP=recycle cut point.

As shown, the maximum yield of low pour point middle distillate is obtained by recycle hydrocracking a heavy oil in a single stage and then contacting the middle distillate fraction produced, having a high pour point, with a reforming catalyst. Where a greater yield of gasoline of higher quality is desired concurrently with low pour point middle distillate, this can be accomplished by once-through hydrocracking in a sulfur-and-nitrogen removal zone followed by once-through or recycle hydrocracking in a boiling point lowering zone with separation of a middle distillate fraction either from both stages or only from the second stage. In either case, a high yield of lower pour point product is then obtainable by further treating the middle distillate with a reforming catalyst in the pour point lowering zone.

It will be appreciated that a pour point as low as -60° F. is not always needed or even desired in diesel fuel or other middle distillate products. Operating conditions in the pour point lowering zone can be adjusted to obtain a desired pour point in the range between 0° F. and -80° F. An extremely low pour point product can be blended with other higher pour point oils. Also, the usual stabilizing additives, including pour point depressants, can be incorporated into the finished product.

What is claimed is:

1. In a process for producing a middle distillate product boiling in the range of 300°-800° F., containing no more than 10 p.p.m. organic nitrogen and 50 p.p.m. organic sulfur, and having a pour point between 0° F. and -80° F., comprising catalytically treating a hydrocarbon fraction boiling within said middle distillate range but having a pour point substantially higher than said middle distillate in a pour point reducing zone in the presence of hydrogen and a catalyst, at elevated temperatures and pressures, the improved method of operating said pour point reduction zone which comprises:

(a) using as said hydrocarbon fraction a fraction substantially comprising a portion of the effluent of a previous hydrocracking step wherein hydrocarbon feed boiling at least partly above 800° F. was hydrocracked, said portion being further characterized by an organic nitrogen content of no more than 10

p.p.m. and an organic sulfur content of no more than 50 p.p.m.;

(b) reducing the pour point of said hydrocarbon fraction by at least about 60° F. by contacting said fraction in said pour point reducing zone with hydrogen in the presence of a catalyst comprising alumina and a noble metal or noble metal compound, said catalyst being essentially free of any halide, at pour point reduction conditions within the range of 700°-850° F., 400-2,000 p.s.i.g., and 0.2-10 LHSV; and

(c) recovering from said zone a middle distillate product having an organic nitrogen content of no more than 10 p.p.m., an organic sulfur content of no more than 50 p.p.m., and a pour point in the range of 0° F. to -80° F., said pour point being at least about 60° F. lower than the pour point of said hydrocarbon fraction used as the feed to said zone.

2. The process of claim 1, wherein said catalyst comprises platinum on alumina.

3. The process of claim 1, further characterized in that the feed to said hydrocracking step contains more than 10 p.p.m. organic nitrogen and more than 50 p.p.m. organic sulfur, and said nitrogen and sulfur contents are reduced in said hydrocracking step to less than 10 p.p.m. and less than 50 p.p.m., respectively, by catalytic hydrofining accomplished concurrently with catalytic hydrocracking.

4. The process of claim 1, further characterized in that said feed to said hydrocracking step has been previously subjected to a catalytic hydrofining step to reduce the organic nitrogen content to no more than 10 p.p.m. and the organic sulfur content to no more than 50 p.p.m.

#### References Cited

##### UNITED STATES PATENTS

3,125,511	3/1964	Tupman et al.	208-264
3,172,838	3/1965	Mason et al.	208-60

DELBERT E. GANTZ, *Primary Examiner*.

A. RIMENS, *Assistant Examiner*.

U.S. Cl. X.R.

208-60, 89

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,420,768

January 7, 1969

Ben G. Bray et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 7, cancel "contaminated heavy oil boiling substantially above the" and insert -- contaminants. The entire effluent from this contacting, or --.

Signed and sealed this 31st day of March 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.  
Attesting Officer

WILLIAM E. SCHUYLER, JR.  
Commissioner of Patents