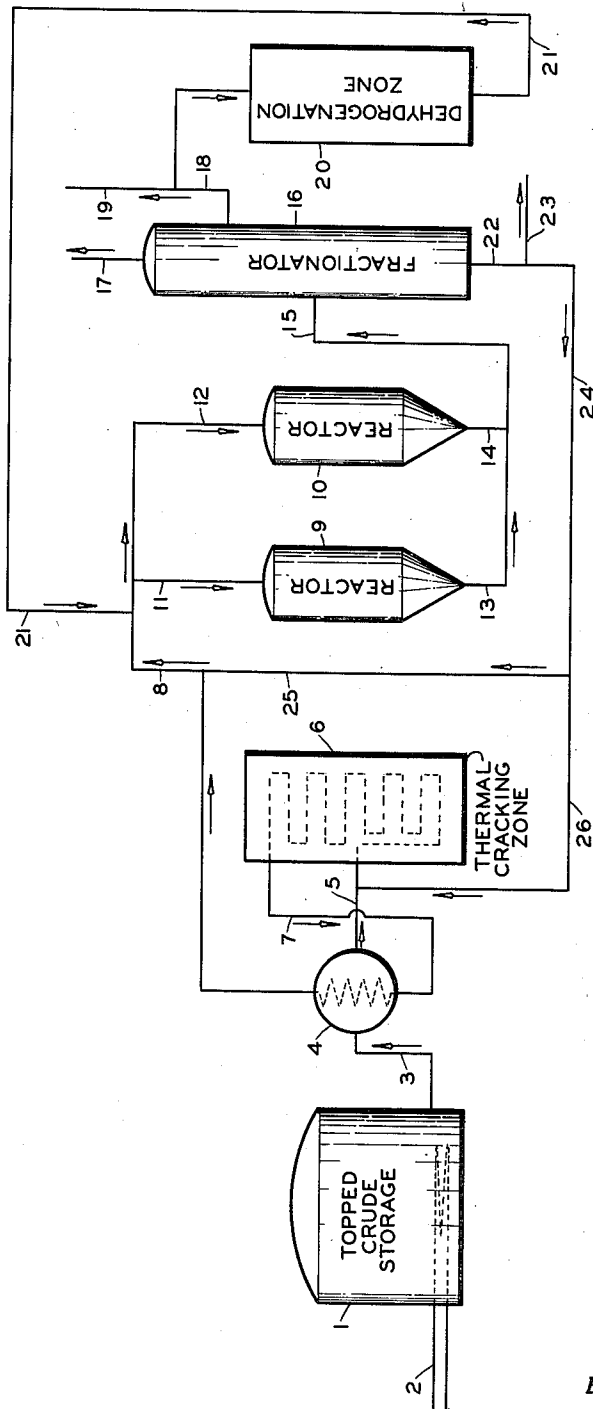


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P. H. JOHNSON
HYDROCARBON PROCESS FOR REDUCING THE
POUR POINT OF A TOPPED CRUDE OIL
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INVENTOR.
P. H. JOHNSON

BY *Hudson and Young*
ATTORNEYS

UNITED STATES PATENT OFFICE

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HYDROCARBON PROCESS FOR REDUCING
THE POUR POINT OF A TOPPED CRUDE OILPaul H. Johnson, Bartlesville, Okla., assignor to
Phillips Petroleum Company, a corporation of
Delaware

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This invention relates to a process for treating topped crude oils. In a specific aspect this invention relates to a process for reducing the pour point of a topped crude oil.

The problem of satisfactorily utilizing residual stocks boiling above 650° F. from petroleum refining is rapidly increasing in importance. In many instances, it is necessary to transport these stocks by tank car and/or pipe line and the like, or it is desirable to market these residual stocks as fuel oils. However, in order to transport these stocks or to market them as fuel oil it is necessary to reduce the pour point of these stocks to facilitate handling and/or to meet fuel oil specifications. One method of reducing the pour point involves cutting back the heavy residual stocks with a lighter hydrocarbon, i. e. gas oil. The gas oil is usually desired as a cracking stock or it can be utilized in a higher grade fuel oil commanding a higher market price. Also, some high pour point, waxy, residual stocks require considerable quantities of gas oil to effect the desired lowering of the pour point, but, when pour point lowering of such waxy stocks is effected in this manner, the viscosity of the resulting product is too low to meet fuel oil specifications. For example, the pour point of a waxy, residual stock can be lowered to meet the specification for a #6 fuel oil, but the amount of gas oil required lowers the viscosity of the product to the specification for a #5 fuel oil. Further addition of gas oil to lower the pour point effects further lowering of the viscosity. Thus, cutting back a residual stock with gas oil is frequently undesirable and it cannot always be employed to produce the desired product.

Another manner of reducing the pour point of a residual stock is to convert the residual stock by thermally cracking or visbreaking, topping the effluent, and recovering product of lower pour point which can be transported or will meet the fuel oil specifications with or without addition of light oil. By such a process, at least a part of the originally required light oil is made available for other uses. In this process, however, the production of gas and relatively low grade gasoline is quite high, and reforming of the gasoline to upgrade it to a more useful quality level thus involves a further expense and a further high loss to gas. Thus, the overall loss to gas is substantially more than that of the visbreaking operation alone. Also, to obtain the desired pour point by such a process it is necessary to reduce the viscosity of the fuel oil below the required maximum desired value.

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It is an object of this invention to provide a novel process for treating topped crude oils.

It is another object of this invention to provide a novel process for reducing the pour point of a topped crude oil.

It is a further object of this invention to provide a novel process for producing from a topped crude oil, having a high pour point, a fuel oil of substantially lower pour point.

It is a further object of this invention to provide a novel process for reducing the pour point of a topped crude oil without the addition of lower-boiling hydrocarbons, such as gas oil, to the topped crude oil.

Further and additional objects of my invention will be readily manifest from the disclosure hereinafter.

I have found that a waxy topped crude oil, having a high pour point, can be treated to produce a fuel oil of substantially lower pour point by the novel process of thermally cracking the topped crude oil to convert a portion of the feed stock to a highly olefinic gasoline, passing the cracking effluent into contact with a hydrogen exchange catalyst, and subsequently recovering a fraction having a pour point substantially lower than the pour point of the topped crude oil feed stock.

The accompanying drawing is a schematic diagram of one method for carrying out my invention. Conventional equipment, such as valves, pumps, compressors, temperature and pressure controls, and the like, has not been included in this drawing to facilitate the understanding of my invention, but the inclusion of such equipment is within the scope of my invention.

In practicing my invention a heavy, high pour point, residual stock is subjected to a visbreaking or a mild thermal cracking operation to produce a relatively small amount of highly olefinic gasoline. The effluent is passed over a hydrogen exchange catalyst at such conditions that hydrogen is transferred from the high-boiling hydrocarbons to the lower-boiling olefinic hydrocarbons. In this manner the unsaturation of the hydrocarbons boiling in the fuel oil range is increased with a resulting reduction in the pour point of those hydrocarbons. Thermal visbreaking or mild cracking operations have been employed in the prior art to reduce the pour point of a topped crude oil, but the operations have produced only low yields of low pour point fuel oil. Also, the gasoline fractions resulting from such processes have only a low octane number, and they require an upgrading treatment to improve the quality. In my process improved yields

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of low pour point fuel oil are obtained with a consequent reduction in the yields of lower-boiling fractions, particularly the low grade gas fraction.

Referring now to the accompanying drawing, topped crude oil from a crude oil topping or reducing operation (not shown) is stored in topped crude storage zone 1. Zone 1 is provided with heating coil 2 through which steam or other fluid heating medium is passed in order to heat the topped crude oil and thus facilitate the passage of the topped crude oil via line 3 to heat exchanger 4. After being heated in heat exchanger 4 the topped crude oil passes via line 5 to visbreaking or thermal cracking zone 6. Zone 6 is operated at a temperature within the range of 800 to 1100° F. and at a pressure within the range of 0 to 100 pounds per square inch gauge. Space velocities of 0.5 to 5.0 liquid volumes of topped crude oil per volume of reaction space per hour are employed. The operating conditions in zone 6 are such that from 5 to 25, preferably not more than 15, weight per cent of the feed is converted to a fraction boiling within the gasoline boiling range, usually not above 400° F. The operating conditions are such that the fraction boiling below 400° F. is highly olefinic, and, consequently, this fraction has a high hydrogen accepting capacity. The effluent from zone 6 passes via line 7 into heat exchanger 4 where it passes in heat exchange relation with the topped crude oil feed to zone 6. Thence, the total effluent from zone 6 passes via line 8 into reactors 9 and 10 via lines 11 and 12, respectively.

Reactors 9 and 10 are shown as being operated in parallel, and, it is possible to have both reactors on stream at the same time. However, the reactors may be employed in a manner that only one reactor is on stream while the other reactor is not in operation for various reasons, such as catalyst regeneration, catalyst replacement, equipment repairs, and the like. If desired, reactors 9 and 10 may also be connected for series operation. Reactors 9 and 10 are provided with a suitable hydrogen exchange catalyst to promote the transfer of hydrogen from the heavy hydrocarbons in the cracking zone effluent to the lighter olefinic hydrocarbons in the same effluent. Suitable hydrogen exchange catalyst are coprecipitated silica-alumina and silica gel impregnated with alumina, but other catalysts may be employed. With these catalysts in reactors 9 and 10, temperatures within the range of 650 to 900° F., atmospheric or slightly superatmospheric pressures and space velocities of 0.5 to 5.0 liquid volumes of feed per volume of catalyst per hour are employed. The effluent from reactors 9 and 10 is withdrawn via lines 13 and 14, respectively, and thence passes via line 15 to fractionator 16. In place of a fractionator any suitable means, such as a flashing chamber, may be employed to separate the fuel oil from lower boiling fractions.

From fractionator 16 hydrocarbons containing no more than four carbon atoms per molecule are withdrawn via line 17. Hydrocarbons boiling within the gasoline boiling range, i. e. those hydrocarbons containing at least five carbon atoms per molecule and boiling below 400° F. are withdrawn via line 18 and separated from the system via line 19. Gasoline thus separated may be passed to additional processing steps for upgrading the gasoline to improve the octane rating thereof. If desired, a gas oil fraction can be withdrawn from fractionator 16 and mixed with some topped crude oil from zone 1 to lower the

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pour point of that crude oil and thus improve the yield of fuel oil of lowered pour point obtainable from my process.

If it is desired to reduce the severity of the cracking conditions in zone 6, gasoline is passed from fractionator 16 via line 18 to dehydrogenation zone 20 where the highly paraffinic gasoline is dehydrogenated to a highly olefinic gasoline. A suitable dehydrogenation catalyst, such as chromia-alumina, may be employed in zone 20 to effect the desired dehydrogenation. With this type of catalyst temperatures within the range of 900 to 1300° F. and atmospheric pressure are satisfactory operating conditions. Dehydrogenated effluent from zone 20 is withdrawn via line 21 and recycled to reactors 9 and 10 where it serves as a hydrogen acceptor and reacts with and lowers the pour point of heavy highly paraffinic hydrocarbons entering reactors 9 and 10.

Fuel oil having a pour point lower than the charge stock to the system is withdrawn from fractionator 16 as bottoms product via line 22, and product fuel oil is withdrawn from the system via line 23. If it is desired to lower further the pour point of the fuel oil, bottoms product from fractionator 16 is recycled to reactors 9 and 10 via lines 22, 24, 25 and 8. Alternatively, the fuel oil may be recycled to visbreaking zone 6 via lines 22, 24, 26 and 5, and in this manner the pour point of the fuel oil is further reduced by passage through the system already described.

The pour point of the fuel oil produced in accordance with my invention will depend upon various factors such as the pour point of the topped crude oil feed stock, the depth of cracking in zone 6, the reaction conditions in reactors 9 and 10, and the like. In experimental work, as represented by the examples hereinbelow, wherein the feed stock had a pour point of 130° F., the resulting fuel oil had a pour point of 110° F. This pour point could have been reduced further by employing more severe cracking conditions and by employing recycle operations similar to those in the accompanying diagram. In general, with my process pour point reductions of at least 10° F. and as high as 30° F. and higher can be effected.

The following examples demonstrate the improved results obtainable with my process when compared with prior art processes of visbreaking a topped crude oil to reduce its pour point.

Example I

A topped crude oil with a pour point of 130° F. and an initial boiling point of 683° F. was passed through a 100 cc. quartz chip-filled thermal visbreaking zone. The rate of topped crude oil charging was 206 cc. per hour, the pressure was atmospheric, and the outlet temperature of the visbreaking zone was 850° F. The effluent from the visbreaking zone was passed to a 350 cc. hydrogen exchange zone filled with silica-alumina catalyst comprising about 2 per cent Al_2O_3 deposited on silica gel. The inlet temperature of the hydrogen exchange zone was 850° F. and the average temperature throughout the zone was 700° F. The effluent from the hydrogen exchange zone contained 81 volume per cent heavy residuum boiling at 400° F. and higher and having a pour point of 110° F., 13.5 volume per cent gasoline, and 5.5 volume per cent C_4 and lighter gases. The viscosity of the heavy residuum was within the range of 10 to 15 Saybolt Furol seconds at 122° F.

Example II

A topped crude oil, similar to that employed in Example I, was passed through a thermal vis-breaking zone operated at an average inlet temperature of 906° F. and an average outlet temperature of 1051° F. and at a pressure of 50 pounds per square inch gauge. The space velocity was 4.3 volumes of feed per volume of reaction space per hour. The heavy residuum boiling at 400° F. and higher from this operation had a pour point of 110° F., and a yield of heavy residuum of 66.5 volume per cent was obtained. The gasoline yield was 19.4 volume per cent, and the remainder of the effluent was 14.1 volume per cent C₄ and lighter gases. The viscosity of the heavy residuum was 12 Saybolt Furol Seconds at 122° F.

From a comparison of the results set forth in these two examples it is seen that a considerably higher yield of heavy residuum of lowered pour point is obtained by the process of my invention and that the yields of the less desirable gases and the low grade gasoline are correspondingly decreased.

Numerous modifications of my process within the scope of my invention will be apparent to those skilled in the art.

I claim:

1. The process for reducing the pour point of a topped crude oil which comprises thermally cracking said topped crude oil at a temperature within the range of 800 to 1100° F. and at a pressure within the range of 0 to 100 pounds per square inch gauge and converting from 5 to 15 per cent of said topped crude oil to lower boiling hydrocarbons within the gasoline boiling range, passing the total effluent from said thermal cracking step into contact with a silica-alumina catalyst at a temperature within the range of 650 to 900° F. and at atmospheric pressure to effect a transfer of hydrogen from the higher boiling to the lower boiling components of said effluent, separating from the effluent from the hydrogen transfer step a highly paraffinic fraction within the gasoline boiling range, dehydro-

drogenating said highly paraffinic fraction to form a highly olefinic fraction, passing said olefinic fraction to the above-named hydrogen exchange step, and recovering from the process a fuel oil having a pour point 10 to 30° F. lower than the pour point of the topped crude oil feed.

2. The process for reducing the pour point of a topped crude oil which comprises thermally cracking said topped crude oil at a temperature within the range of 800 to 1100° F. and at a pressure within the range of 0 to 100 pounds per square inch gauge and converting from 5 to 15 per cent of said topped crude oil to lower boiling hydrocarbons within the gasoline boiling range, passing the total effluent from said thermal cracking step into contact with a silica-alumina catalyst at a temperature within the range of 650 to 900° F. and at atmospheric pressure to effect a transfer of hydrogen from the higher boiling to the lower boiling component of said effluent, fractionally distilling the effluent from the hydrogen transfer step to obtain a highly paraffinic fraction within the gasoline boiling range and a fuel oil fraction, dehydrogenating said highly paraffinic fraction to form a highly olefinic fraction, passing said olefinic fraction to the above-named hydrogen exchange step, passing a portion of said fuel oil fraction to the above-named hydrogen exchange step, and recovering from the process a fuel oil having a pour point 10 to 30° F. lower than the pour point of the topped crude oil feed.

PAUL H. JOHNSON.

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