Sept. 3, 1968 S. E. TUNG ETAL 3,400,072

PROCESS FOR REDUCING THE POUR POINT OF CRUDE OIL AND THE LIKE

Filed March 24, 1965 3 Sheets-Sheet 1

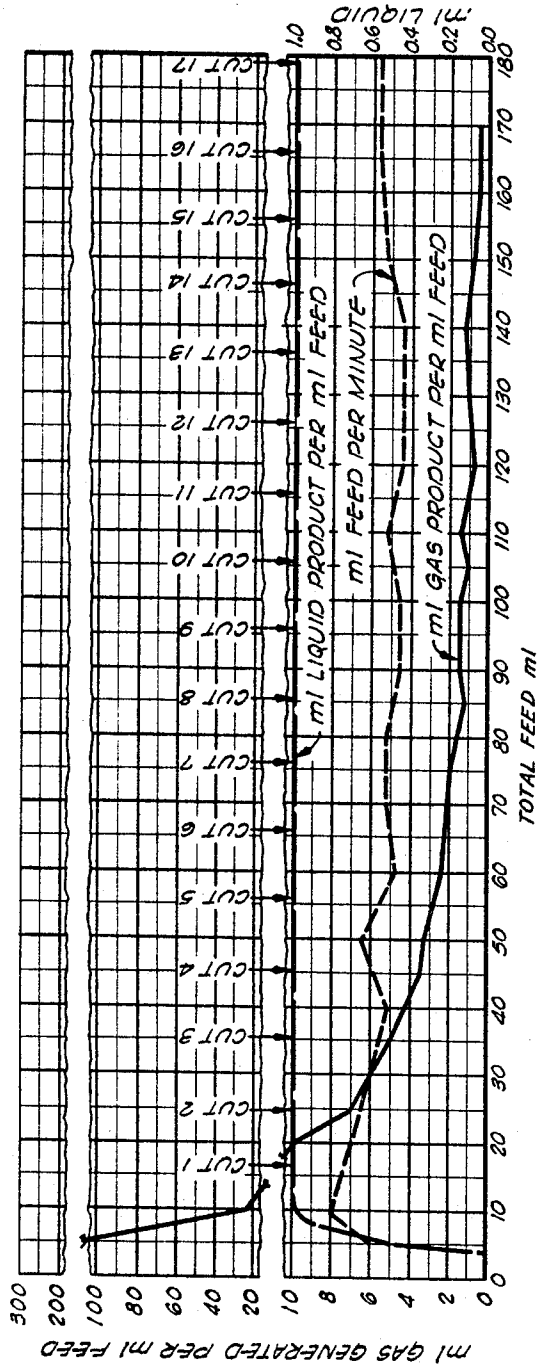


Fig. 4

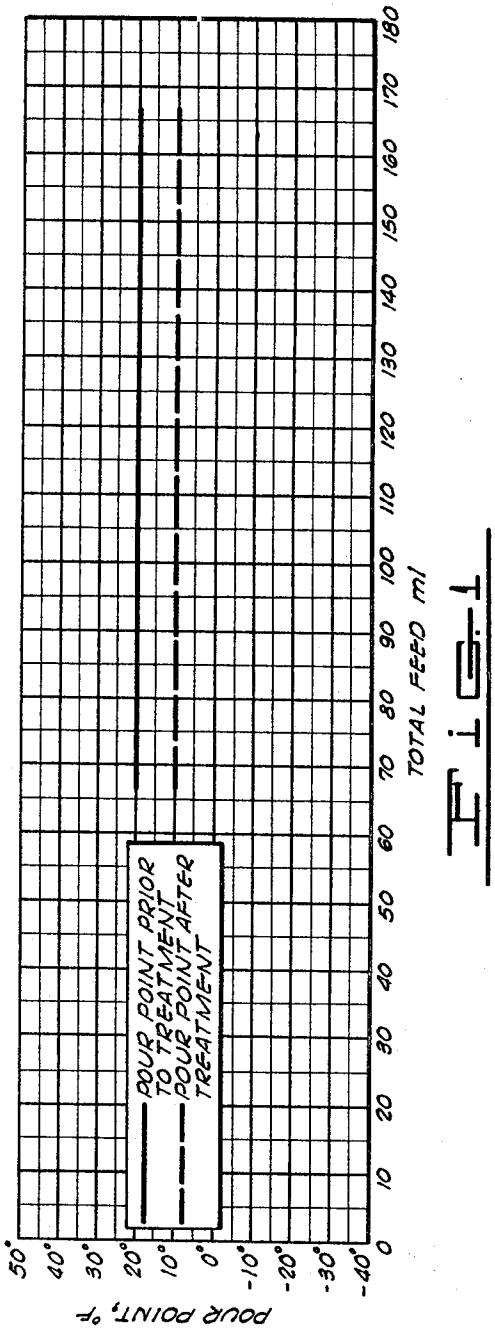


Fig. 1

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PROCESS FOR REDUCING THE POUR POINT OF CRUDE OIL AND THE LIKE

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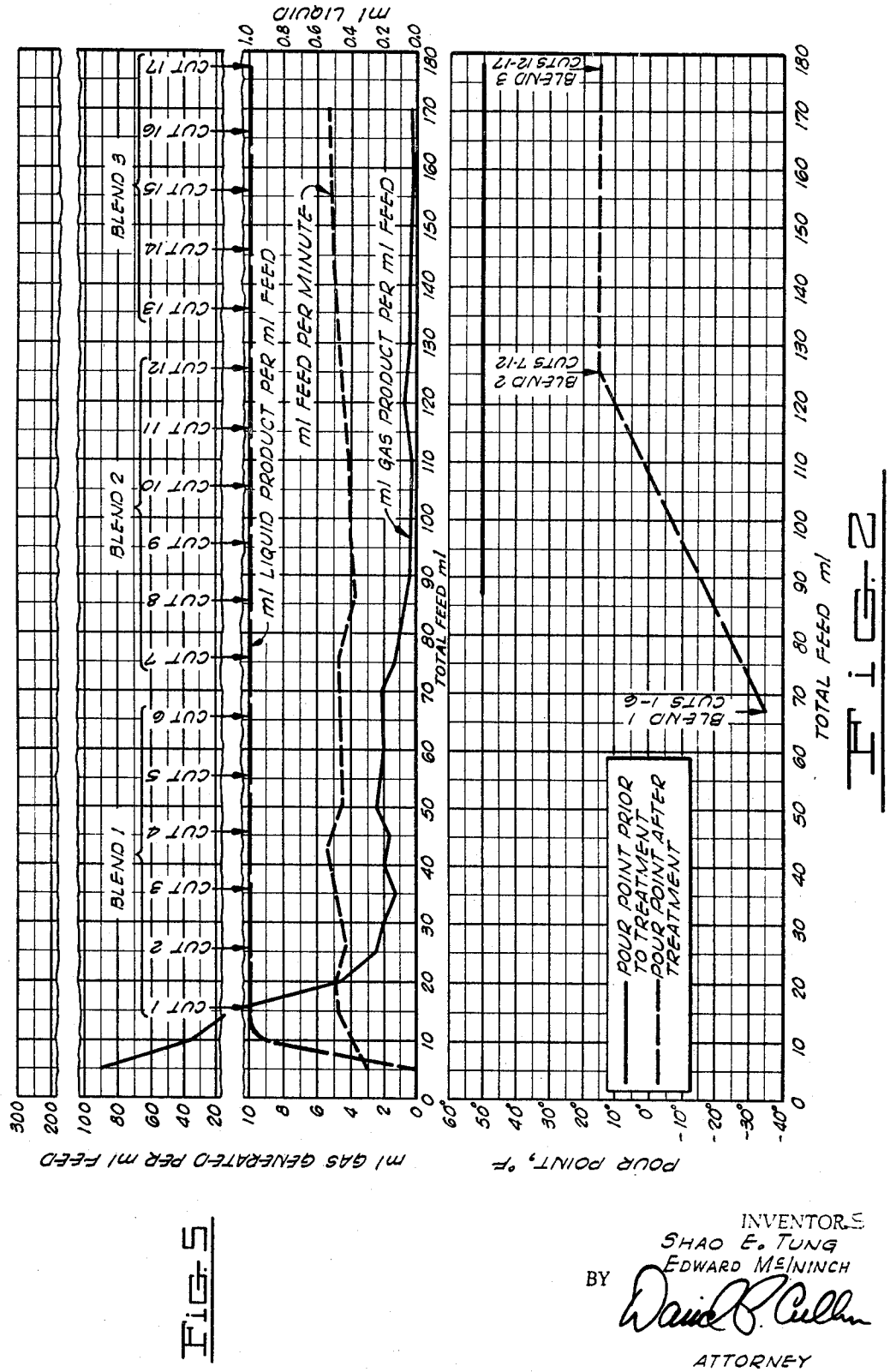


FIG. 2

FIG. 5

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PROCESS FOR REDUCING THE POUR POINT OF CRUDE OIL AND THE LIKE

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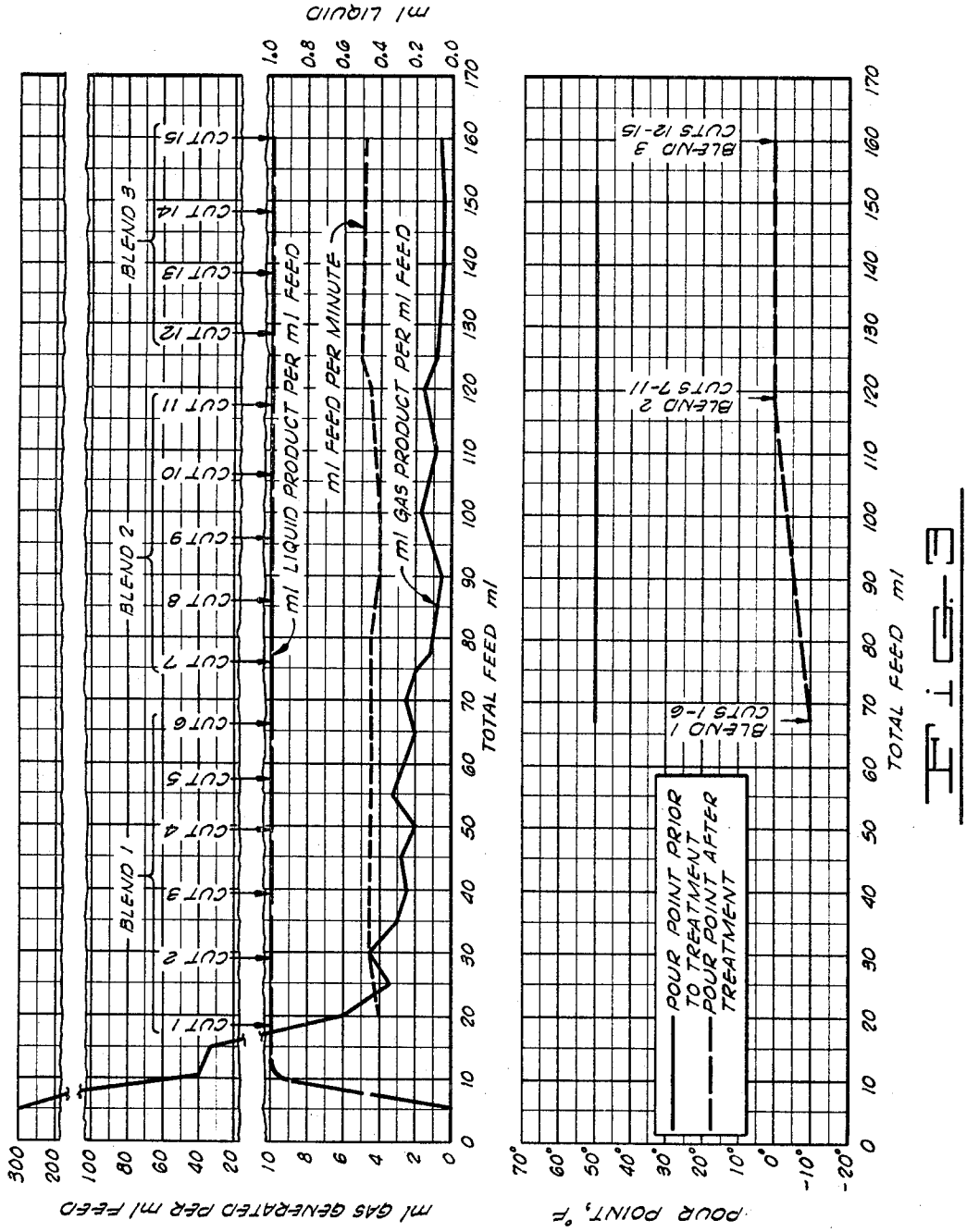


Fig. 3

Fig. 6

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3,400,072

PROCESS FOR REDUCING THE POUR POINT OF CRUDE OIL AND THE LIKE

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15 Claims. (Cl. 208—120)

This invention relates to a process for reducing the pour point of hydrocarbon mixtures derived from petroleum and including crude petroleum, and straight-run and cracked fractions of petroleum. More particularly, the present invention relates to a method for catalytically converting a relatively high pour point mixture of petroleum-derived hydrocarbons to a mixture of hydrocarbons having a lower pour point than the mixture prior to subjection to such catalytic conversion.

An important property of crude petroleum and certain distillates derived therefrom is the pour point. The pour point is the temperature at which the mixture of hydrocarbons will begin to flow under gravitational influence and with certain standard conditions applied. Its value, when considered conjunctively with other selected properties, can provide an indication of the end products which can be derived from hydrocarbon mixtures. The pour point is also indicative of the ease with which the crude petroleum or distillate fraction can be pumped through pipelines under various environmental conditions.

As an example of the important significance of the pour point characteristic of crude petroleums, the oils produced in the majority of the Libyan fields have pour points which range from 25° F. to 45° F. The Middle East crudes, on the other hand, have a substantially lower pour point, averaging about 10° F. In keeping with the correlation between pour point and end products to which reference has been made, a larger portion of the Middle East crude oil can be economically converted to distillate suitable for Diesel fuel, etc., than the portion of Libyan crude which can be converted to such oils at the same or a comparable cost. Stated differently, a greater portion of the Middle East crudes, can be economically converted to distillate than in the case of the Libyan crudes.

Since the demand of the European market is primarily for distillate, the Libyan crude oils presently suffer an economic disadvantage relative to the Middle East petroleum. It is therefore desirable to investigate methods of more economically converting a larger portion of the Libyan and other crudes to distillate stocks. One such method which we have discovered entails treating the high pour point crude oil or a fraction thereof to reduce the pour point. A significantly larger portion of the product resulting from our process can be economically converted to distillate and such pour point reduction further serves to make the treated crude oil or hydrocarbon mixture more susceptible to pipeline transport in cold climates.

The process of the present invention is a catalytic conversion procedure by which the overall molecular makeup of a complex mixture of hydrocarbons, such as crude oil, is changed so as to yield a mixture of hydrocarbons having a reduced pour point. Broadly described, the present invention comprises contacting, at a temperature in the range of from about 350° F. to about 850° F., a petroleum-derived mixture of hydrocarbons selected from the group consisting of crude pertoleum and fractions thereof with a catalyst comprising a crystalline aluminosilicate material in which the crystalline structure is a three-dimensional framework containing cation sites and SiO_4 and AlO_4 tetrahedra bonded through oxygen in regular orientation and forming an intracrystalline pore system having an average pore size of from about 6 A to about 14 A., the silicon to aluminum ratio in said aluminosilicate material being from about 1:1 to about 4:1, said crystalline structure being further characterized by the absence of monovalent cations from some of the available cation sites in said theree-dimensional structure.

The pressure which is applied to the system as the hydrocarbon mixture is contacted with the catalyst can vary from atmospheric pressure up to about 2,000 p.s.i.g.

The hydrocarbon mixtures may be contacted with the catalyst in several ways, such as by using a fluidized bed of the catalyst, or using a fixed bed. The fixed bed procedure is presently preferred, however, and when this technique is employed, the space velocity utilized in passing the hydrocarbon mixture through the catalyst bed can range from about 0.5 pound of the hydrocarbon mixture per pound of catalyst per hour to about 7 pounds of the hydrocarbon mixture per pound of catalyst per hour.

The type of catalyst materials which are preferably employed are dervived from aluminosilicate materials of the type known as zeolites. The zeolites may be of natural or synthetic origin, provided that the pore size and silicon to aluminum ratio are as hereinbefore defined, and provided that some of the available cation sites in the zeolite crystalline structure have either been divested of cations (decationized), or that a portion of the cation sites is occupied by polyvalent cations, as opposed to monovalent cations.

By passing the hydrocarbon mixture through a catalyst bed of the character described and at a rate within the range indicated, a substantial reduction in the pour point of the mixture can be effected. Thus, with typical Libyan crude oils, we have been successful in reducing the pour point of the crude oil by as much as 55° F. in a single pass of the crude oil through a fixed catalyst bed.

From the foregoing description of the invention, it will have become apparent that it is a major object of the invention to provide a process for reducing the pour point of petroleum-derived mixtures of hydrocarbons.

Another object of the invention is to provide a simple procedure for economically converting a greater portion of crude petroleums to hydrocarbon mixtures having properties and economic value similar to distillate fractions of petroleum.

An additional object of the present invention is to render petroleum-derived mixtures more suitable for pipeline transport, especially in winter or in colder climates.

Another object of the invention is to provide a catalytic conversion process which can be very easily

practiced by operating personnel of relatively little technical training, and which can be used to reduce the pour point of crude oil and fractions derived therefrom.

Additional objects and advantages of the invention will become apparent as the following detailed description of the invention is considered in conjunction with the accompanying drawings which graphically depict typical results obtained in the practice of the invention.

In the drawings:

FIGURES 1 and 4 are two graphs illustrating some of the process conditions employed, and results obtained, when a crude oil distillate fraction was subjected to the process of the present invention and employing one of the types of catalyst suitable for use in the invention.

FIGURES 2 and 5 are two graphs similar to those depicted in FIGURES 1 and 4, but based upon the results obtained when a Libyan crude oil was subjected to the process of the invention and using a different catalyst from that employed in the procedure which yielded the results graphically portrayed in FIGURES 1 and 4.

FIGURES 3 and 6 are two graphs similar to those shown in FIGURES 1, 2, 4, and 5, but depicting results obtained when a Libyan crude oil was subjected to catalytic conversion using yet a different type of catalyst in the process of the invention.

Before considering certain specific examples of the practice of the invention, and the accompanying drawings, which graphically depict the results obtained from such practice, the materials used in the process and the conditions employed therein will be specifically considered.

The types of hydrocarbon mixtures to which the invention is applicable will first be described. In general, any crude oil or a straight-run or cracked fraction of the crude oil can be subjected to the catalytic conversion process. Since a major object of the invention is to a reduction in pour point of the hydrocarbon mixture, the starting mixture of hydrocarbons preferably has a pour point of at least 15° F. as determined by ASTM D–97. As a general proposition, the higher the pour point of the starting material, the greater the reduction in pour point which can be achieved by the use of the invention.

Whether raw crude oil will be directly subjected to the process, or will instead first be topped, and the distillate and residual cuts then subjected to the catalytic conversion process of the invention to achieve pour point reduction, will depend upon the plant facilities available, and the process economics dictated by the market and other factors. For example, where a low pour point distillate is in greater demand than fuel oil as hereinbefore described, and it is desired to increase the yield of the former material without an uneconomic increase in the cost of such production, the crude oil which is available and of undesirably high pour point may be treated in any one of three ways. First, the entire uncut crude oil may be contacted with the catalyst used in the invention to reduce the pour point of the crude, and thus impart to it a character permitting a higher distillate fraction to be yielded upon ultimate refining. Alternatively, the crude oil may be topped and the entire topped fraction may then be subjected to contact with the catalyst to adjust the pour point.

As a final alternative, the distillate fraction from the crude may be further fractionated to remove the higher boiling portion thereof and this higher boiling fraction can be subjected to catalytic conversion. The converted higher boiling fraction is then blended back with the lower boiling portion of the topped crude oil. This blend is then a distillate having the desired properties, including a relatively low pour point.

A typical crude oil of Libyan origin to which the present invention may be effectively applied to increase the yield of distillate has the following properties:

Gravity, ° A.P.I.	38.6
Pour point, ° F.	40

Kinematic viscosity @ 70° F., centistokes	7.5
Total sulfur, wt. percent	0.32
ASTM D–86 distillation, vol. percent received @ 760 mm. Hg:	
I.B.P.	115
5	181
10	227
15	270
20	310
25	350
30	393
35	433
40	473
45	514
50	554
55	592
60	630
65	666
70	708

A crude distillate fraction derived from the Libyan crude oil which has been used in the practice of the present invention has the following properties:

Gravity, ° A.P.I.	36.8
Pour point, ° F.	20
Kinematic viscosity @ 100° F., centistokes	3.873
ASTM D–86 distillation, vol. percent received @ 760 mm. Hg:	
I.B.P.	464
5	482
10	491
20	504
30	516
40	530
50	545
60	562
70	581
80	601
90	614
95	639
E.P.	651

The properties of the crude oil and distillate fraction as set forth above are based upon accepted tests of the American Standards for Testing Materials as follows—gravity, ASTM D–287; pour point, ASTM D–97; kinematic viscosity, ASTM D–445; and distillation, ASTM D–86.

In other terms, the typical Libyan crude oils which I have found can be particularly beneficially subjected to the process of the invention are, by the U.S. Bureau of Mines method of classification, intermediate types, grading toward paraffinic in the gas oil and residual fractions.

The catalyst used in the process of the invention comprises an aluminosilicate material of crystalline structure. This crystalline structure is a three-dimensional framework containing a plurality of cation sites and containing SiO_4 and AlO_4 tetrahedra bonded to each other through oxygen in regular orientation so as to form a uniform intracrystalline pore system. The pores of the crystal lattice have an average diameter of at least about 6 A. when the cation sites are actually occupied by cations to permit the passage of the hydrocarbon molecules therethrough. Preferably, the pore size is at least about 8 A., and best results to date have been obtained using a crystalline structure having a pore size of about 10 A. Crystalline structures in which the diameter of the pores is as high as about 14 A. can be used effectively.

The crystalline aluminosilicate employed is further characterized by a Si to Al ratio of from about 1:1 to about 4:1. Preferably, this ratio exceeds 1 to 1, and at the present time, a silicon to aluminum ratio of about 2.5:1 is considered the preferred proportion of these two major elemental types in the crystalline structure.

At this point it should be pointed out that though the catalyst preferably consists essentially of the described crystalline form of aluminosilicate, large amounts of amorphous aluminosilicate can also be included in the catalyst, though the predominantly amorphous material containing only very small amounts of the crystalline catalyst does not at this time appear to give as great a reduction in pour point. Where amorphous aluminosilicate is present in the catalyst, it preferably contains silicon and aluminum in the ratio of from about 3:1 to about 4:1.

The crystalline structure present in the catalyst may be further and differently described as containing silicon and aluminum atoms in fourfold coordination and bonded to each other through oxygen atoms so as to form the SiO_4 and AlO_4 tetrahedra hereinbefore mentioned. In this arrangement, the negative charge on each of the AlO_4 tetrahedrons is normally balanced, both in the naturally occurring crystalline aluminosilicates and in synthetic materials of this type, by the inclusion of an electropositive cation. Thus, a number of cation sites exist throughout the crystalline structure.

An important characteristic of the aluminosilicate crystals suitable for use in the catalyst in the process of the present invention is that the cation sites in the crystal be either vacant (that is, not occupied by any cation whatsoever), or be occupied by a polyvalent cation. Stated differently, the crystalline structure used in the catalyst of the invention is characterized by the absence of monovalent cations from a portion of the available cation sites in the three-dimensional crystalline structure.

The extent to which monovalent cations are absent from the available cation sites in the crystalline structure is of some importance. In general, the greater the number of the cation sites which have been either decationized and are therefore vacant, or, alternatively, have been filled with polyvalent cations by a process of ion exchange, the greater the activity of the catalyst in pour point reduction. It has been observed that the activity of the catalyst increases substantially when it has been decationized to the extent of about 10 percent (that is, all ions have been removed from at least about 10 percent of the available cation sites in the crystalline structure). It has also been found that a substantial increase in catalytic activity occurs when at least about 30 percent of the monovalent alkali metal cations which generally occupy the cation sites in naturally occurring aluminosilicates, and in most of the synthetic aluminosilicates now made, have been replaced by polyvalent cations. Further, the catalytic activity of the crystals increases as an increasing proportion of the cation sites are either decationized or occupied by polyvalent cations. Preferably, the aluminosilicate crystalline structure has either been at least about 40 percent decationized, or has at least about 70 percent of the cation sites occupied by polyvalent cations. At the 70 percent level of polyvalent cation occupancy, the remaining monovalent ion content, expressed as sodium, may amount to about 3 weight percent of the catalyst.

Where the cation sites are occupied to a substantial degree by polyvalent cations to activate the catalyst, divalent cations are the polyvalent cations which are preferably employed, and of this ionic type, it is preferred to employ magnesium, calcium and barium as the polyvalent cation in the crystalline structure.

Some additional advantage may be gained by including in a minor portion of the total available cation sites, cations derived from the metals of Group VIII of Mendeleev's periodic table. Of this group of metals, it is preferred to include the ions of platinum, iridium, ozmium, palladium, rhodium and nickel in the crystalline structure in an amount ranging from about 0.1 weight percent to about 10 weight percent of the crystalline structure. The most preferred Group VIII ionic species are derived from platinum and palladium.

The described aluminosilicate structures embrace, but are not limited to, the natural and synthetic zeolites, and these materials have been found to be especially well suited for use in the invention. They have been either partially decationized to remove the monovalent cations which are usually included in the crystalline lattice, or are subjected to ion exchange to replace a portion of the monovalent cations with the polyvalent cationic types hereinbefore described. In general, the zeolite crystalline structure will include the SiO_4 and AlO_4 tetrahedra hereinbefore described, and will further include in association with such tetrahedra, alkali metal cations which satisfy or balance the negative charge on each of the AlO_4 tetrahedrons. To prepare the catalyst used in the present invention, these alkali metal cations may be removed by decationization procedures well understood in the art, or may be replaced by polyvalent cations using ion exchange techniques equally well understood. It is reiterated that all of the alkali metal cations need not be removed from the crystalline lattice or replaced by polyvalent cations. Catalytic activity commences to be perceptible as soon as a small number of the alkali metal ions are removed or replaced, and increases as an increasing number of the cation sites in the crystal are either vacated or filled with polyvalent cations.

As previously indicated herein, the mixture of hydrocarbons can be contacted with the aluminosilicate catalyst material either by a fluidized catalytic process, or by passing the hydrocarbon mixture through a fixed bed of the catalyst. Where the fixed bed procedure is employed, the size of the catalyst pellets can vary widely. For example, a particle size diameter of from about $\frac{1}{16}$ inch up to about $\frac{1}{4}$ inch can be very conveniently employed, and the preferred particle size range is from about $\frac{1}{8}$ inch to about $\frac{3}{16}$ inch in diameter. Where a portion of the cation sites in the aluminosilicate crystalline structure are occupied by ions derived from one of the Group VIII metals, as hereinbefore described, the catalyst is preferably pre-treated to reduce them to their lowest valence state by passing hydrogen gas through the catalyst and in contact therewith for a substantial period of time prior to commencement of the process of the invention. For example, the catalyst may be conditioned for use by passing hydrogen gas through the bed at a temperature of 1,000° F. for about 4 hours prior to commencing the process.

The conditions applied to the system as the hydrocarbon mixture is contacted with the catalyst are of some importance. The temperature of the catalyst at the time of contact is from about 350° F. to about 850° F. Preferably, the temperature employed during the catalytic conversion is from about 550° F. to about 700° F. The pressure employed can range from atmospheric pressure to about 2,000 p.s.i.g. Where the system is maintained under pressure during the catalysis, such pressure is preferably maintained by utilizing hydrogen gas under pressure in contact with the catalyst. The space velocity utilized in passing the hydrocarbon mixture through the catalyst bed can range from about 0.5 pound of the hydrocarbon mixture per pound of the catalyst per hour to about 7 pounds of the hydrocarbon mixture per pound of the catalyst per hour. Preferably, from about 2 to about 5 pounds of the hydrocarbon mixture per pound of catalyst per hour is the space velocity employed.

In order to maintain the activity and extend the life of the catalyst, it is preferable to include with the liquid hydrocarbon mixture passed in contact with the catalyst, entrained hydrogen gas, with the mole ratio of the hydrogen gas to the hydrocarbon liquid feed stock being from about 1:1 to about 10:1. A hydrogen to feed stock mole ratio of from about 3:1 to about 7:1 is preferably employed.

In order to further describe and more clearly illustrate the practice of the present invention, a number of examples of such practice are hereinafter set forth.

EXAMPLE I

A Libyan crude oil of the following properties was subjected to the catalytic conversion process of the present invention:

Property	Test Method	Value		
Gravity, °A.P.I.	ASTM D-287	38.6		
Gravity, Specific, 60/60° F.	ASTM D-1250	0.8319		
Density at 15° C., Kg./Liter	ASTM D-1250	0.8315		
		Kinematic	Saybolt Univ.	Engler Degrees
Viscosity:				
At 70° F. (21.1° C.)	ASTM D-445	7.50	50.33	1.61
At 100° F. (37.8° C.)	ASTM D-445	4.64	41.20	1.37
At 122° F. (50.0° C.)	ASTM D-445	3.52	37.74	1.27
At 130° F. (54.4° C.)	ASTM D-445	3.21	36.77	
Characterization Factor			11.90	
Mean Molecular Weight			212	
Water and Sediment, Vol. Percent	ASTM D-96		0.24	
Water by Distillation, Wt. Percent	ASTM D-95		0.0	
Acidity, Total, Mg. KOH/Gm.	ASTM D-664		0.17	
Carbon Residue, Ramsbottom, Wt. Percent.	ASTM D-524		1.83	
Asphaltenes, Wt. Percent	IP-43		0.71	
Sulfur, Total, Wt. Percent	ASTM D-1522		0.32	
Ash, Wt. Percent	ASTM D-482		0.007	
Metallic Elements, p.p.m.:				
Iron			1.8	
Nickel			4.9	
Vanadian			1.4	
Pour Point	ASTM D-97		40	
Chlorides as NaCl	U.O.P. 22		18.2	
Reid Vapor Pressure	ASTM D-323		7.0	
Distillation, Vol. Percent Rec. at 760 mm. Hg:				
I.B.P.	ASTM D-86		115	
5	ASTM D-86		181	
10	ASTM D-86		227	
15	ASTM D-86		270	
20	ASTM D-86		310	
25	ASTM D-86		350	
30	ASTM D-86		393	
35	ASTM D-86		433	
40	ASTM D-86		473	
45	ASTM D-86		514	
50	ASTM D-86		554	
55	ASTM D-86		592	
60	ASTM D-86		630	
65	ASTM D-86		666	
70	ASTM D-86		708	

A tubular glass reactor of 10 mm. inside diameter and 70 mm. length was packed to a height of 38 mm. with six grams of aluminosilicate catalyst having a particle size of from 8 to 14 mesh. The particulate catalyst employed was a treated synthetic zeolite of the type marketed by the Union Carbide Co. under the trademark Linde Molecular Sieve, type Y, number SK110. The zeolite contained 5.2 weight percent manganese which had been incorporated therein by cation exchange resulting in replacement of alkali metal cations from a substantial number of the total available cation sites in the crystalline structure. The catalyst was further loaded with 0.5 weight percent palladium ions. The crystalline material had a pore size of 10 A. and a silicon to aluminum ratio of 2.5.

Prior to passing the crude oil through the fixed bed of catalyst in the reactor, the palladium-carrying catalyst was pre-conditioned by passing hydrogen gas through the bed at a flow rate of 20 ml. per minute for 4 hours while maintaining the hydrogen gas at a temperature of 1,000° F.

The Libyan crude oil was next passed through the catalyst bed in the reactor at a rate of 0.5 ml. per minute (equivalent to a space velocity of 5 pounds of crude per pound of catalyst per hour). The system was maintained at atmospheric pressure during the run and the temperature employed was 630° F. The liquid product from the catalytic conversion was collected, as was the gas generated by the catalysis. The pour point of the liquid product was measured and compared with the pour point of the original crude prior to treatment. The amount of gas generated as the crude oil was passed through the catalyst bed was also measured and recorded. After completing the first pass of 170 ml. of the crude oil through the catalyst bed, a second pass of a substantial portion of the liquid product yielded in the first run was carried out. A third pass in which 60 ml. of the liquid product from the second pass was contacted with the catalyst was also completed.

The results of the catalytic conversion runs using crude oil of the type described are set forth in Table I.

TABLE I.—POUR POINT REDUCTION

Original Crude	35
Processed Crude (First Pass)	10
Processed Crude (Second Pass)	10
Processed Crude (Third Pass)	10

Ml. of crude throughput	Gas Generation: Total Gas Evolved, ml.	Average Gas ml./ml. crude
First Pass:		
0-10	1,350	135
10-30	210	10.5
35-50	58	2.9
50-70	62	3.0
70-90	38	1.9
90-110	37	1.9
110-130	35	1.7
130-150	32	1.6
150-170	32	1.6
Second Pass:		
0-20	60	3.0
20-50	36	1.8
50-70	28	1.4
70-90	24	1.2
90-110	24	1.2
Third Pass:		
0-20	28	1.4
20-50	27	1.4
50-60	15	1.5

The data in Table I indicate that one pass through the catalyst bed is sufficient to achieve substantially all of the pour point reduction which can be effected by contact with the catalyst. Thus, a pour point reduction of 25° F. was obtained in the first pass, and the pour point was not significantly further lowered by the second and third passes of the material through the catalyst bed. While the above conditions have been disclosed as having utility with a fixed catalyst bed, it should be pointed out that they are equally applicable to a fluidized bed

operation, except that the space velocity parameter will require slight modification.

EXAMPLE II

A straight-run distillate from the Libyan crude utilized in Example I was prepared and had the following properties:

Property	Test Method	Value
Gravity, ° A.P.I.	ASTM D-287	36.8
Flash Point, P.M., ° F	ASTM-D-93	235
Pour Point, ° F	ASTM D-97	20
Viscosity at 100° F., Cs	ASTM D-445	3.873
Refractive Index, $N_{D20°}$ C	ASTM D-1218	1.4676
Sulfur, Total, wt. percent	ASTM D-1552	0.21
Distillation, ° F., I.B.P	ASTM D-86	464
5% Vol	ASTM D-86	482
10% Vol	ASTM D-86	491
20% Vol	ASTM D-86	504
30% Vol	ASTM D-86	516
40% Vol	ASTM D-86	530
50% Vol	ASTM D-86	545
60% Vol	ASTM D-86	562
70% Vol	ASTM D-86	581
80% Vol	ASTM D-86	601
90% Vol	ASTM D-86	614
95% Vol	ASTM D-86	639
E.P	ASTM D-86	651

The distillate was subjected to catalytic conversion by contact with a fixed catalytic bed of the type described in Example I. The catalyst employed was identical to that used in Example I, and the pre-treatment of the catalyst bed by passing hydrogen gas therethrough, as well as the temperature, pressure and space velocity conditions used during the process, were the same as in Example I.

The results obtained from the catalytic conversion are portrayed by the graphs shown in FIGURES 1 and 4. In FIGURE 4, the ml. of gas generated by the catalyst per ml. of distillate feed to the catalyst bed is represented by the lowermost curve in this graph and the values are plotted on the ordinate axis to the left of the graph.

The rate of feed of the distillate in ml./minute is plotted as the central curve on FIGURE 4 and the values for this parameter are located on the ordinate axis to the right of the graph. The liquid product which was collected per ml. of distillate feed (in ml. per ml.) is plotted as the uppermost curve and the values for this curve also appear on the ordinate axis to the right. The abscissa of both FIGURES 1 and 4 shows the total distillate feed passed through the catalyst bed in milliliters.

In FIGURE 1, the pour points of the distillate feed and the liquid product are represented by the upper and lower curves, respectively. The pour point of the liquid product was measured for several different values of total distillate feed.

In referring to FIGURES 1 and 4, it will be noted that the pour point of the distillate was depressed 10° F. by passage through the catalyst bed. It will further be noted that, except for the initial liquid throughput, substantially all of the liquid distillate was recovered, after catalytic conversion, as a liquid product and relatively little of the total product was in gaseous form. The total percentage of the liquid feed recovered as liquid product, after the first 20 ml. of throughput, averaged 99.9 weight percent. Thus, no significant loss by change of state or holdup in the catalyst bed occurs in the process of the invention.

EXAMPLE III

A Libyan crude oil having a pour point of 50° F. was passed through a six gram bed of catalyst extending to a height of 38 mm. in a glass reactor tube of the size described in Example I. The catalyst was a synthetic zeolite similar to that used in the process described in Example I except that the zeolite had been decationized to the extent of removing all cations from about 70 percent of the available cation sites, the remaining sites remaining occupied by sodium ions. No loading of the catalyst with one of the Group VIII metal ions was employed. The catalyst was not subjected to contact with hydrogen gas prior to or during the process. The temperature, pressure and space velocity conditions used during the run were those used in the Example I procedure.

The results of pour point, liquid product and gas product measurements are portrayed in the graphs shown in FIGURES 2 and 5 which are laid out similarly to the FIGURE 1 and FIGURE 4 graphs hereinbefore described. It should be pointed out, however, that the pour point measurements on the liquid product as graphed in FIGURE 2 were made on composite blends which were made by combining several of the liquid product cuts collected at the intervals indicated on the uppermost curve in FIGURE 5. It is of interest to note that the greatest pour point reduction, an amount of 85° F. (from 50° F. to −35° F.), occurred in the case of the first blend collected. The blend was a composite of cuts taken during the initial throughput period when gas formation was relatively high. After leveling off later in the process, the pour point reduction became an amount of about 35° F. It was again noted that very little gas was generated following the initial throughput of 20 or 30 ml. of the crude oil. Also there was negligible holdup of liquid in the catalyst bed.

EXAMPLE IV

The graphs of FIGURES 3 and 6 depict, in similar fashion to the FIGURE 2 and FIGURE 5 graphs, the results obtained when the process described in Example III was carried out, using the same crude oil and an identical decationized catalyst system except that the catalyst contained 0.6 weight percent palladium ions. It will be noted that the initial reduction in pour point is less pronounced in the case of palladium loaded catalyst, but that the average overall pour point reduction of about 50° F. is greater than in the case of the decationized catalyst without the inclusion of the palladium ions.

From the foregoing discussion of the invention and the examples of its practice which have been described, it will be perceived that the process provides a technique for quickly, easily and economically reducing the pour point of mixtures of hydrocarbons without the concurrent loss of a significant amount of the treated mixture. Gas generation resulting from the catalysis does not occur to a degree sufficient to constitute any problem of separation, disposal or safety hazard. The conditions of temperature and pressure used in the process are not sufficiently stringent or critical to prevent the successful employment of the process by personnel having relatively little technical training.

In achieving the reduction in the pour point of the hydrocarbon mixtures, the end products which may ultimately be derived upon refinement of the hydrocarbon mixtures can be beneficially altered, and the ease with which the mixtures can be pumped and moved through pipelines at relatively low temperatures is improved.

The foregoing description of the invention is intended to be exemplary of its practice and does not provide a comprehensive statement of all modifications and variations which may be employed in selecting the materials to be used or the conditions to be imposed. Thus, in addition to the natural and synthetic zeolites mentioned as specific examples of the crystalline structure which is to be used as a catalytic material in the process of the invention, other aluminosilicate crystalline materials having the defined structure, such as Faujasite and Modenite, can also be used. The hydrocarbon mixtures to which the process is applied are also subject to considerable variation, and include distillates and gas oils of widely varying properties, as well as various crude oil types. Other variations in process conditions and materials used will readily occur to those skilled in the art and are considered to be encompassed by the spirit and scope of the present invention if the basic principles of the invention are still employed in a catalytic conversion process to obtain pour point depression.

I claim:

1. A process for reducing the pour point of crude petroleum and the like, said pour point reduction being effected without the production of substantial gas due to cracking, and to recover at least 90 weight percent of the charge material as liquid product, said process comprising contacting in the absence of added hydrogen gas said mixture at a temperature in the range of from about 350° F. to about 850° F. with a catalyst comprising an aluminosilicate material of predominantly crystalline structure in which the crystalline structure is a three-dimensional framework containing cation sites and SiO_4 and AlO_4 tetrahedra bonded to each other through oxygen in regular orientation and forming a uniform intracrystalline pore system having a pore size of from about 6 A. to about 14 A., the silicon to aluminum ratio in said aluminosilicate material being from about 1:1 to about 4:1, and said crystalline structure being further characterized by the absence of monovalent cations from some of the available cation sites in said three-dimensional structure and by the absence of Groups VI and VIII metal cations or free metal from all of said available cation sites.

2. The process defined in claim 1 wherein said aluminosilicate material is a zeolite containing polyvalent cations in some of said cation sites.

3. The process defined in claim 1 wherein said aluminosilicate material further comprises, in addition to said crystalline structure, an amorphous aluminosilicate having a silicon to aluminum ratio of from about 3:1 to about 4:1.

4. The process defined in claim 1 wherein said crystalline structure is characterized by a silicon to aluminum ratio exceeding 1.

5. The process defined in claim 1 wherein monovalent cations are absent from at least about 10 percent of the available cation sites in the three-dimensional framework of said crystalline structure.

6. The process defined in claim 1 wherein the pore size of said crystalline structure is from about 8 A. to about 11 A.

7. The process defined in claim 2 wherein said polyvalent cations are divalent.

8. The process defined in claim 4 wherein said silicon to aluminum ratio is about 2.5:1.

9. The process defined in claim 8 wherein the pore size of said crystalline structure is about 9 A. to about 10 A.

10. The process defined in claim 1 wherein at least about 30 percent of the available cation sites in said three-dimensional framework structure are occupied by polyvalent cations.

11. The process defined in claim 1 wherein said hydrocarbon mixture is contacted with said catalyst under atmospheric pressure.

12. The process defined in claim 1 wherein at least 10 percent of the available cation sites are occupied by monovalent alkali metal cations.

13. The process defined in claim 7 wherein said valent cations are selected from the group consisting of calcium, magnesium and barium.

14. The process defined in claim 1 wherein said petroleum, derived hydrocarbon mixture is an untreated crude petroleum, and contact of said crude petroleum with said catalyst is carried out under conditions of temperature and pressure to effect a pour point reduction of at least 10° F. and a conversion of the charge stock crude petroleum to gaseous products of less than 1 percent, based on the weight of the crude petroleum, whereby substantially all of the crude petroleum is converted to a lower pour point liquid material.

15. The process defined in claim 1 wherein said catalyst consists of a crystalline aluminosilicate material of the described crystalline structure, and containing more than 3 weight percent monovalent alkali metal cations disposed in said cation sites.

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