

Aug. 18, 1959

P. S. VILES

2,900,427

PRODUCTION OF AROMATICS FROM PARAFFIN HYDROCARBONS

Filed Sept. 28, 1956

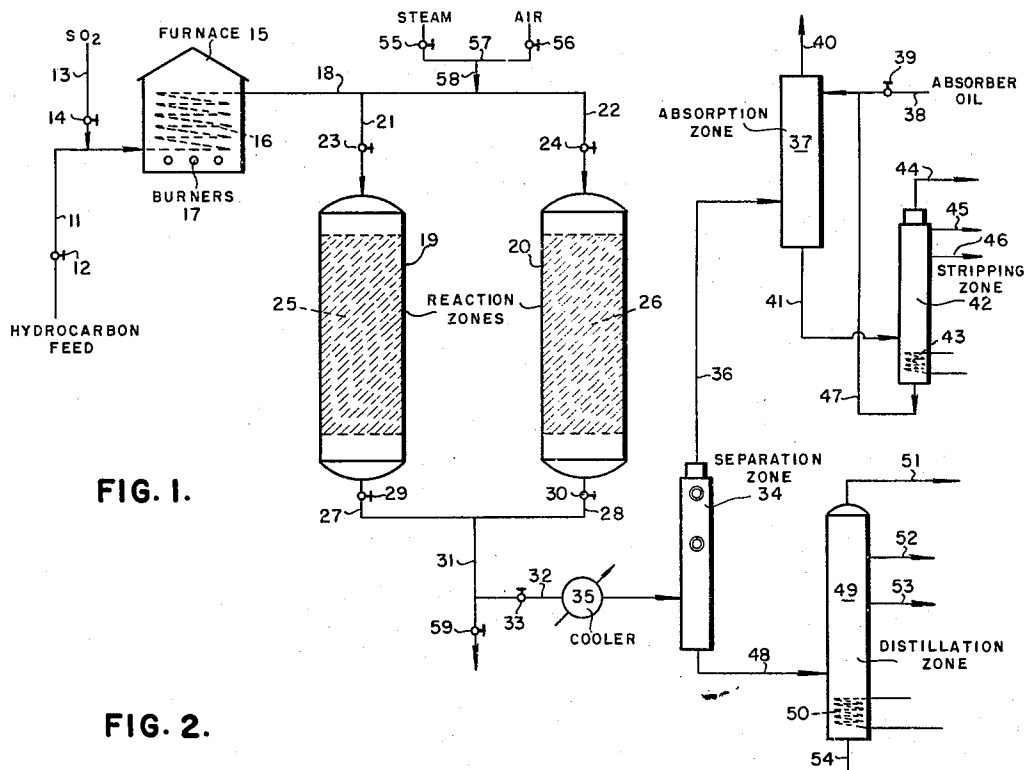
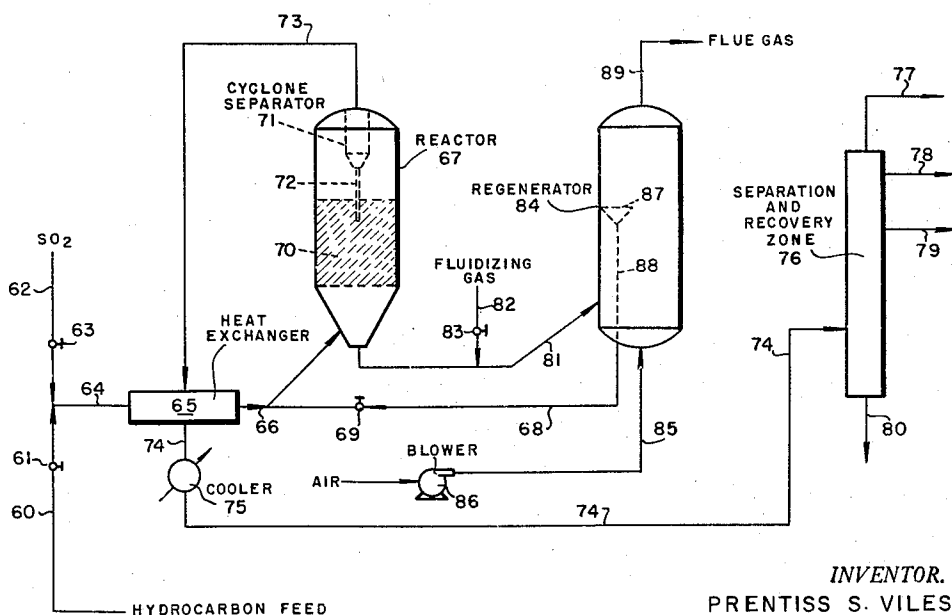


FIG. 1.

FIG. 2.



INVENTOR.
PRENTISS S. VILES,

BY

James B. McCallum
ATTORNEY

1

2,900,427

PRODUCTION OF AROMATICS FROM PARAFFIN HYDROCARBONS

Prentiss S. Viles, Baytown, Tex., assignor, by mesne assignments, to Esso Research and Engineering Company, Elizabeth, N.J., a corporation of Delaware

Application September 28, 1956, Serial No. 612,607

12 Claims. (Cl. 260—673)

The present invention is concerned with the production of unsaturated hydrocarbons. More particularly, the invention relates to the conversion of hydrocarbons in the presence of sulfur dioxide. In its more specific aspects, the invention is concerned with the production of unsaturated hydrocarbons from saturated hydrocarbons in admixture with sulfur dioxide.

The present invention may be briefly described as a method for forming unsaturated hydrocarbons, such as olefins and aromatics, by forming a mixture of a saturated hydrocarbon, such as a paraffin, having a molecular weight of at least 30 with sulfur dioxide and then contacting the mixture with a cobalt molybdate catalyst at a temperature in excess of about 800° F. to form a product containing unsaturated hydrocarbons and recovering the product.

The feed hydrocarbon employed in the present invention may suitably range from about the boiling point of ethane up to about 750° F. The feed hydrocarbon may be a normally gaseous hydrocarbon, such as one having a molecular weight of no less than about 30, and homologues thereof and may comprise a normally liquid hydrocarbon. A preferred feed stock will include ethane and higher boiling materials, natural gas components, normally liquid hydrocarbons, such as those boiling in the kerosene and gasoline boiling range as well as gas oil hydrocarbons. It will be desirable and possible to form olefins from the paraffinic hydrocarbons including ethane, propane, butane, pentane, and the like while the higher boiling members, such as heptanes, hexanes, octanes, and the higher members of the homologous series will tend to form unsaturated ring compounds, such as aromatics.

The catalyst employed in the present invention is cobalt molybdate preferably on a support. By cobalt molybdate it is to be understood that, within the purview of the present invention, cobalt molybdate is a mixture of cobaltous oxide (CoO) and molybdic trioxide (MoO₃). The cobaltous oxide and molybdic trioxide may be employed in a preferred ratio of mol per mol as the catalyst but the ratio of cobaltous oxide to molybdic trioxide may range from 0.1:1 to 1:0.1 mol of cobaltous oxide per mol of molybdic trioxide.

The amount of cobalt molybdate on the support may range from about 1.0 to 25.0 weight percent with a preferred amount of approximately 15.0% by weight of the total catalyst.

The supports for the cobalt molybdate may suitably be alumina, zirconia, magnesia, silica, silica-alumina, Filtrol, kieselguhr, Floridan, and the like. Preferred supports are pure alpha and gamma alumina.

The temperatures employed in the practice of the present invention may suitably fall within the range of about 800° to about 1600° F. with a preferred temperature range of 1100° to about 1400° F. Quite satisfactory re-

2

sults have been obtained at about 1300° F. The pressures may range from about 0 pounds absolute to about 1000 pounds per square inch gauge.

The feed stock may be contacted with the catalyst at a suitable feed rate which may be in the range from about 1 to about 500 volumes of feed per volume of catalyst per hour with a preferred v./v./hour from about 50 to about 100. The reaction may be conducted in either the vapor or liquid phase but vapor phase is to be preferred for the low boiling hydrocarbons.

The invention may be practiced in various types of equipment. For example, the reaction zone may have a catalyst bed arranged therein as a fixed bed or the reaction may be conducted in the so-called fluidized powder technique wherein the cobalt molybdate is suspended in vaporized hydrocarbons. Furthermore, the reaction may be conducted in a suspension or in a slurry.

The reaction zone employed in the present invention may be constructed of material which provides a non-reactive surface with the product or which forms with the product a surface which does not react further with the product. Thus, with steel or ferrous metal reaction walls and conduits of such nature, the product may react therewith initially to form a non-reactive coating thereon. Preferably, the reaction zone walls and the interior of conduits employed for transporting the product are suitably constructed of non-reactive material such as glass, ceramic ware, and the like or ferrous metal equipment may be lined with such non-reactive material.

The amount of sulfur dioxide employed in the practice of the present invention may suitably range from about 0.5% to about 50% by weight of the mixture with the hydrocarbon. When employing vapor phase operations, the amount of sulfur dioxide may suitably range from about 10% to about 50% by weight of the mixture with a preferred range from about 15% to about 45% by weight of the mixture, whereas with liquid phase reaction conditions, the amount of sulfur dioxide in the mixture may range from about 0.5% to about 10% by weight of the mixture with a preferred range from about 2.5% to about 7.5% by weight of the mixture.

The present invention will be further described by reference to the drawing in which:

Fig. 1 is in the form of a flow diagram illustrating one mode of the invention; and

Fig. 2 is in the form of a flow diagram illustrating a preferred mode.

Referring now to the drawing and first to Fig. 1, numeral 11 designates a charge line by way of which a feed hydrocarbon is introduced into the system. Line 11 is controlled by a valve, such as 12. Leading into line 11 is line 13 controlled by valve 14 by way of which a suitable amount of sulfur dioxide is admixed with the hydrocarbon in line 11. The mixture of hydrocarbon and sulfur dioxide is discharged into a furnace 15 provided with a coil 16 and with gas burners 17 by way of which the temperature is raised to a temperature in the range given supra. The heated gaseous or vaporous mixture discharges from furnace 15 by way of line 18 and may be routed into reaction zones 19 and 20 by way of lines 21 and 22 controlled, respectively, by valves 23 and 24. Beds 25 and 26 comprising a supported cobalt molybdate catalyst are arranged in reaction zones 19 and 20. The gaseous reactant mixture contacts the beds 25 and 26 under the conditions stated hereinbefore to produce a product containing a substantial amount of unsaturated materials. The unsaturated product discharges from zones 19 and 20 by way of lines 27 and

28 controlled, respectively, by valves 29 and 30 into line 31 and by way of branch line 32 containing a valve 33 into a separation zone 34. Line 32 suitably contains a temperature quenching means, such as cooler 35, by way of which the temperature of the product is reduced rapidly from a temperature within the range of 800° to 1600° F. to about 150° F. within a time no greater than about 1 second to stop the reaction. Instead of employing a cooler as a quench zone, a suitable quench liquid may be employed. Suitable quench liquids may include steam and non-reactive hydrocarbons, such as gas oil and the like.

The quenched and cooled product in separation zone 34 is separated into a gas phase and a liquid phase. The gas phase is withdrawn by way of line 36 and discharged into an absorption zone, such as 37, where the gaseous product is contacted with a suitable absorption medium, such as a hydrocarbon introduced by line 38 controlled by valve 39. Fixed gases are removed from absorption zone 37 by way of line 40, whereas the enriched absorption oil is discharged by way of line 41 into a stripping zone 42 which is provided with a suitable temperature adjusting means, such as a heating coil 43. The absorbed hydrocarbons are removed from the absorption medium in zone 42 and are discharged from zone 42 by way of lines 44, 45 and 46 as may be desired. The stripped absorption medium is then recycled by way of line 47 and by way of line 38 for reuse in the process.

The liquid phase in zone 34 is discharged therefrom by way of line 48 into a distillation zone such as 49. Distillation zone 49 is shown as a single fractional distillation tower but it is understood to include, if desired, a plurality of fractional distillation towers, each provided with all auxiliary equipment usually found associated with the modern distillation tower. Such equipment will include means for inducing reflux, condensing and cooling means and suitable internal vapor-liquid contacting means, such as bell cap trays, plates, and the like. Distillation zone 49 is shown as being provided with a temperature adjusting means as illustrated by heating coil 50 and is provided with lines 51, 52 and 53 as well as a draw-off line 54 for separation and withdrawal of products.

From time to time the beds 25 and 26 may become fouled with carbonaceous deposits resulting from the reaction. When that occurs, the valves 12 and 14 will be closed and valves 55 and 56 in manifold 57 will be opened allowing a mixture of steam and air to be discharged by way of line 58 into line 18 and thence into lines 21 and 22 to cause and support a combustion operation in the beds 25 and 26 to burn off the carbonaceous deposits from the catalyst. Since the valve 33 would be closed, valve 59 in line 31 would be open allowing discharge of the flue gas.

Referring now to Fig. 2, numeral 60 designates a charge line controlled by valve 61 by way of which a hydrocarbon of the type illustrated is introduced into the system and is admixed with sulfur dioxide introduced by way of line 62, controlled by valve 63, the mixture passing through line 64 into a heating means or heat exchanger 65. The heated gaseous mixture discharges by way of line 66 into a reaction zone 67 of the fluidized type in admixture with finely divided or powdered cobalt molybdate catalyst introduced by line 68, controlled by valve 69.

The cobalt molybdate catalyst, when a fluidized system is used, may have particle diameters suitable for fluidization, for example, particle diameters in the range from about 1 to about 120 microns with a substantial or major amount of the catalyst particles being in the range of about 20 to about 120 microns to insure proper fluidization.

The mixture of SO₂, hydrocarbon, and catalyst in the reaction zone 67 forms a dense bed 70 of catalyst, hydrocarbon, and SO₂ under the temperature conditions stated and a reaction takes place whereby the hydrocarbons are

converted in substantial amounts to unsaturated material. The reacted mixture passes into a separation zone such as a cyclone 71 provided with a dip leg 72 in the upper part of zone 70 which effects a separation between the product and the catalyst, the product being discharged from zone 67 by way of line 73 in heat exchange with the feed in heat exchanger 65, the feed being introduced by line 64. The partially cooled product then discharges by line 74 into a cooler 75 and is then introduced by line 74 into a separation and recovery zone 76. Separation and recovery zone 76 may include absorption and distillation zones and/or solvent extraction zones and the like by way of which recovery and separation and/or purification is made among the several hydrocarbons which will be found in the product.

The several products may be separated as desired and withdrawn by way of lines 77, 78, 79 and 80 for further use and/or purification.

The catalyst is withdrawn from reaction zone 67 by way of line 81 and may be admixed with a fluidizing gas, such as steam, introduced by line 82, controlled by valve 83 and the mixture of steam and catalyst is discharged into a regenerator 84 wherein a combustion operation is maintained by air introduced by line 85 containing a blower 86. The combustion operation in regenerator zone or vessel 84 effectively removes the carbonaceous deposits from the catalyst, the regenerated catalyst being withdrawn from zone 84 by way of funnel member 87 and conduit 88 which connects to line 63.

Products of combustion are withdrawn and discharged from regenerator 84 by way of line 89.

It is preferred to employ the fluidized operation although both modes are suitable.

It is understood that any one of the several separated fractions may be further treated such as with a selective solvent for olefins or with a selective solvent for aromatics to purify and concentrate such compounds. For example, where a product, such as a C₄ fraction including olefins, is withdrawn, such fraction may suitably be treated with sulfuric acid of a sufficient strength to absorb the olefins and to allow the concentration and recovery thereof. Where the selected fraction includes aromatics, it may suitably be treated with a solvent which is selective for concentration of aromatics, such as sulfur dioxide, phenol, and the like.

The present invention will be further illustrated by runs in which ethane was contacted with an alumina supported cobalt molybdate catalyst arranged as a bed in a reaction zone. In one run, the ethane was charged as is and in another run the ethane was admixed with sulfur dioxide.

Reaction conditions and analysis of the product recovered from the reaction under the conditions given are shown in Table I:

Table I

	Charge	Product	Charge	Product
Temp., ° F.		1,300		1,300
Pressure		Atmospheric		Atmospheric
Charge Rate, v./v./Hr.		195		195
Mol. percent:				
Sulfur Dioxide		41.5		
Carbon Dioxide		0.03	0.1	0.55
Hydrogen Sulfide		0.04	0.2	0.02
Carbon Monoxide	0.75	0.24	1.6	46.62
Nitrogen		0.30		
Hydrogen	1.2	97.91	0.6	10.90
Methane	0.2	0.30		9.86
Ethylene	2.51	0.05	1.8	3.28
Ethane	94.75	0.65	53.9	6.14
Propylene	0.37		0.2	9.04
Propane	0.16	0.15	0.1	4.24
Isobutane				3.23
n-butane	0.01	0.07		1.16
Butylenes	0.01			7.04
Isopentane		0.04		0.44
n-pentane	0.03	0.03		0.18
Pentylenes	0.02	0.01		0.79
Cyclopentane and Heavier		0.06		0.47

5

Comparing the first two columns of data, it will be seen that, where sulfur dioxide was absent from the ethane, the ethane was substantially completely converted to hydrogen with the formation of minor amounts of other hydrocarbons. However, comparing the data in columns 3 and 4, where a substantial amount of sulfur dioxide was present, it will be seen that the ethane was largely converted to hydrocarbons of a higher molecular weight and in an unsaturated condition. It is to be noted that substantial quantities of carbon monoxide were formed. The hydrogen sulfide formed during the reaction reacted with the steel walls of the conduits used to transport the reaction product from the reaction vessel.

Runs were then made employing propane as the feed. In one run the propane was charged to a bed of alumina supported cobalt molybdate in a reaction vessel in the absence of sulfur dioxide. In another operation, sulfur dioxide was admixed with the propane and charged to the reaction vessel in contact with the bed of cobalt molybdate. Operations with admixtures of sulfur dioxide were conducted under various charge rates as set out in the following table:

Table II

	Charge	Product	Charge	Product		Charge	Product
Temp., ° F.				1300	1300		1300
Pressure		Atmospheric		Atmospheric	Atmospheric		Atmospheric
Charge rate, v./v./hr.		195		100	180		300
Mol. percent:							
Sulfur dioxide			14.8			43.1	
Carbon dioxide	0.1		0.3		1.14	0.3	4.77
Hydrogen sulfide			0.1		0.5		0.03
Carbon monoxide	0.2	3.40		0.4	0.8		27.64
Nitrogen				16.13	12.31		0.71
Hydrogen	0.1	42.06		0.70	0.18		30.30
Methane	0.1	47.28		37.75	35.19	0.1	21.92
Ethylene	0.1	2.62		32.83	28.17	0.2	6.26
Ethane	2.2	1.63	2.0	4.71	4.94		2.51
Propylene		0.83		0.59	3.41	1.3	4.43
Propane	96.1	1.91	81.1	3.57	6.62		0.34
Iso-butane	0.9			2.83	6.29	53.7	
n-butane	0.1	0.04	0.5	0.39	0.49	0.1	0.35
Butylenes		0.03					
Iso-pentane			0.2				
n-pentane				0.07	0.2		0.05
Pentylenes					0.20		
Cyclopentane and heavier				0.05	0.80		0.70

From the data in Table II, it will be clear that where sulfur dioxide was not present in the propane, the propane was substantially completely converted to hydrogen and methane with small amounts of other hydrocarbons and carbon monoxide being formed. However, observing column 4 where the feed stock set out in column 3 was employed which contain 14.8 mol percent of sulfur dioxide, substantial amounts of heavier hydrocarbons and olefins were produced. Again comparing the fifth column where a 43.1 mol percent of sulfur dioxide was present with the sixth and seventh columns, again it will be seen that substantial quantities of heavier hydrocarbons and olefins were formed.

It will be noted that in the several runs the charge rate in v./v./hour was increased from 100 to 300 v./v./hour with most desirable results being obtained at the short contact times which favor the production of heavier hydrocarbons and olefins as shown by the data.

Other operations were conducted with a raffinate obtained by solvent extraction with sulfur dioxide of a xylenes fraction. This raffinate was substantially completely octane and boiled in the range from about 250° to about 320° F. The raffinate fraction was then contacted with a bed of alumina supported cobalt molybdate and a product obtained which was then analyzed. The results from these runs are shown in Table III:

6

Table III

Charge Stock	Xylene Raffinate	Xylene Raffinate	Xylene Raffinate
Charge Rate, cc./Hr.		400	400
Temperature, ° F.		1000	1000
Pressure, p.s.i.g.		200	200
Liquid Product:			
Yield, cc./Hr.		265	260
Gas Yields, Cu. Ft./Hr.		4.6	4.4
	Xylene Raffinate	Liquid Product	Liquid Product
Liquid Sample Analysis, Mol. Percent:			
Benzene		2.15	3.14
Toluene		8.10	10.91
Xylenes		17.65	23.93
Total C ₉ Aromatics		7.88	9.30
Total C ₁₀ Aromatics		0.41	0.53
Total Aromatics	2.4	36.19	47.80
Total Naphthenes plus Olefins	28.1	16.45	16.02
Total Paraffins	69.5	47.36	36.17

In the data in the second column shown in Table III the raffinate had been washed with caustic to remove all sulfur dioxide whereas in the third column of data the

raffinate contained approximately 6% to 7% by weight of sulfur dioxide.

Comparing these runs, it will be seen that where sulfur dioxide was present, substantially increased yields of aromatics were obtained as compared to the run where the sulfur dioxide was absent. It is to be noted that the naphthenes and olefins content of the product from the two runs were substantially unchanged indicating that the sulfur dioxide acts to convert paraffins to unsaturated compounds such as aromatics where the chain length is sufficient to form the ring compound.

The present invention is of considerable importance and utility in that paraffinic hydrocarbons and particularly straight chain paraffinic hydrocarbons which are less valuable than olefinic and aromatic hydrocarbons may be converted in substantial yields to the more valuable compounds. The olefins and aromatics are more valuable than the paraffins because the olefins and aromatics have higher octane numbers than the straight chain paraffins and may suitably be used as blending agents in motor and aviation fuels and, furthermore, the olefins and the aromatics are more reactive than the paraffins and may be used in alkylation and other conversion operations.

The nature and objects of the present invention having been completely described and illustrated, what I wish

to claim as new and useful and to secure by Letters Patent is:

1. A method for forming aromatic hydrocarbons from paraffinic hydrocarbons of lower molecular weight which comprises forming a mixture consisting essentially of a normally liquid paraffinic hydrocarbon having a chain length sufficient to form an aromatic ring and having a boiling range up to 750° F. and sulfur dioxide in an amount within the range from about 0.5% to about 50% by weight of the mixture, contacting said mixture with a catalyst consisting of alumina-supported cobalt molybdate at a pressure from about 0 pounds absolute to about 1000 pounds per square inch gauge, at a rate from about 1 to about 500 volumes of mixture per volume of catalyst per hour and at a temperature within the range from about 800° F. to about 1600° F. to form a product containing aromatics and heavier hydrocarbons, and recovering said product.

2. A method in accordance with claim 1 in which the hydrocarbon mixture is contacted in the liquid phase.

3. A method in accordance with claim 1 in which the hydrocarbon mixture is contacted in the vapor phase.

4. A method in accordance with claim 1 in which the mixture is contacted with the catalyst in a fixed bed.

5. A method in accordance with claim 1 in which the mixture is contacted with the catalyst in a fluidized bed.

6. A method in accordance with claim 1 in which the catalyst is cobalt molybdate on alpha alumina.

7. A method in accordance with claim 1 in which the catalyst is cobalt molybdate on gamma alumina.

8. A method for forming aromatic hydrocarbons of higher molecular weight from paraffinic hydrocarbons of lower molecular weight which comprises forming a mixture consisting essentially of a paraffinic hydrocarbon boiling within the range from about the boiling point of hexane to about 750° F. and sulfur dioxide in an amount within the range from about 0.5% to about 10% by

weight of the mixture, contacting said mixture with a catalyst consisting of alumina supported cobalt molybdate at a pressure from about 0 pounds absolute to about 1000 pounds per square inch gauge at a rate from about 1 to about 500 volumes of mixture per volume of catalyst per hour and at a temperature within the range from about 800° F. to about 1600° F. to form a product containing aromatic hydrocarbons heavier than the paraffinic hydrocarbon and recovering said product.

9. A method for forming aromatic hydrocarbons of higher molecular weight from paraffinic hydrocarbons of lower molecular weight which comprises forming a mixture consisting essentially of a normally liquid paraffinic hydrocarbon in the gasoline to gas oil boiling range and sulfur dioxide in an amount within the range from about 0.5% to about 10% by weight of the mixture, contacting said mixture with a catalyst consisting of alumina-supported cobalt molybdate at a temperature within the range from about 800° F. to about 1600° F. to form a product containing aromatic hydrocarbons heavier than the normally liquid paraffinic hydrocarbon, and recovering said product.

10. A method in accordance with claim 1 in which the normally liquid paraffinic hydrocarbon is hexane.

11. A method in accordance with claim 1 in which the normally liquid paraffinic hydrocarbon is heptane.

12. A method in accordance with claim 1 in which the normally liquid paraffinic hydrocarbon is octane.

References Cited in the file of this patent

UNITED STATES PATENTS

2,441,297	Stirton	May 11, 1948
2,604,438	Bannerot	July 22, 1952
2,720,550	Danforth	Oct. 11, 1955
2,772,315	Hadden	Nov. 27, 1956