Jan. 3, 1967 L. C. DOELP ETAL 3,296,120

TWO STAGE DRIPOLENE HYDROGENATION

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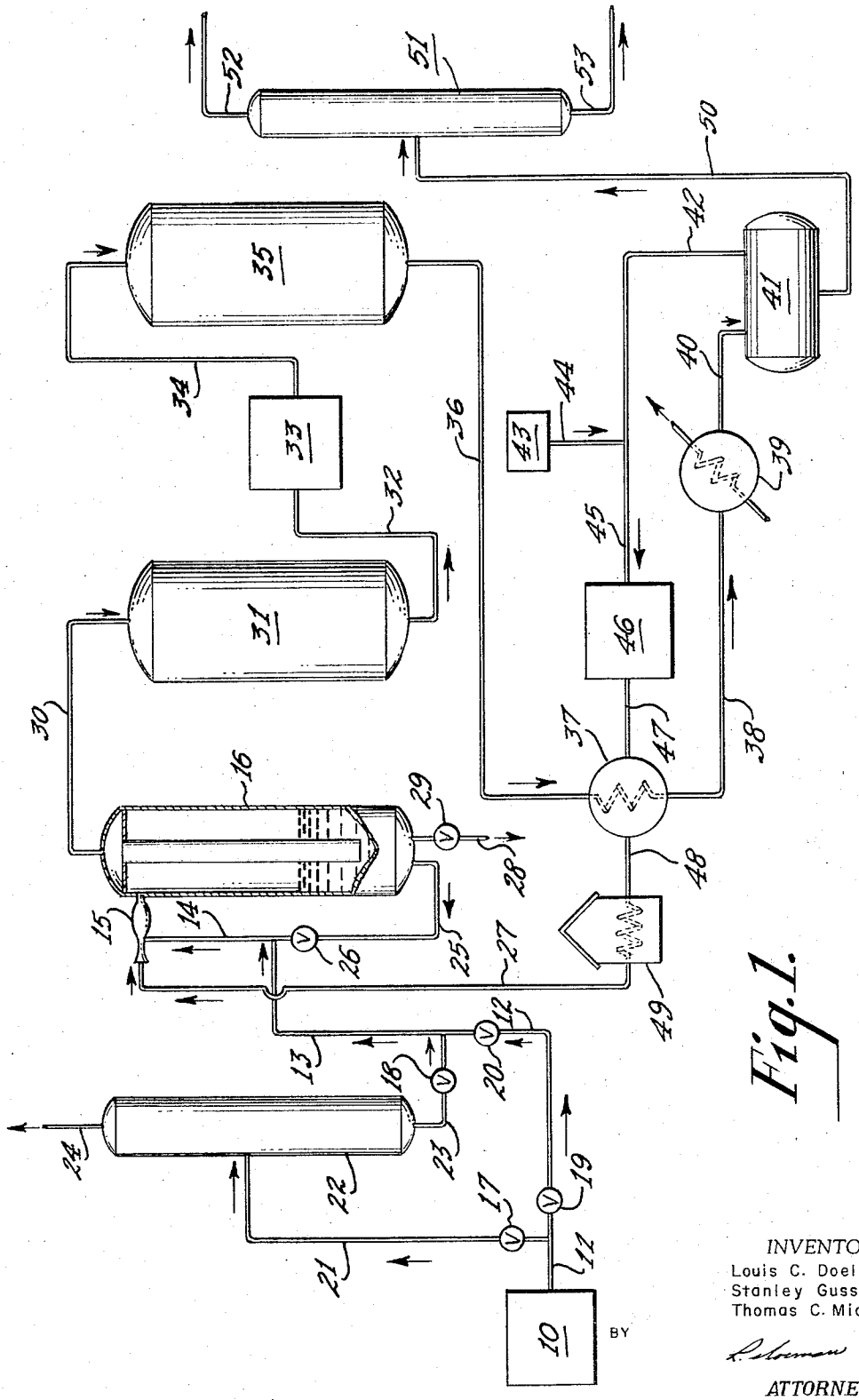


Fig. 1.


INVENTORS.
Louis C. Doelp,
Stanley Gussow &
Thomas C. Michael

ATTORNEY.

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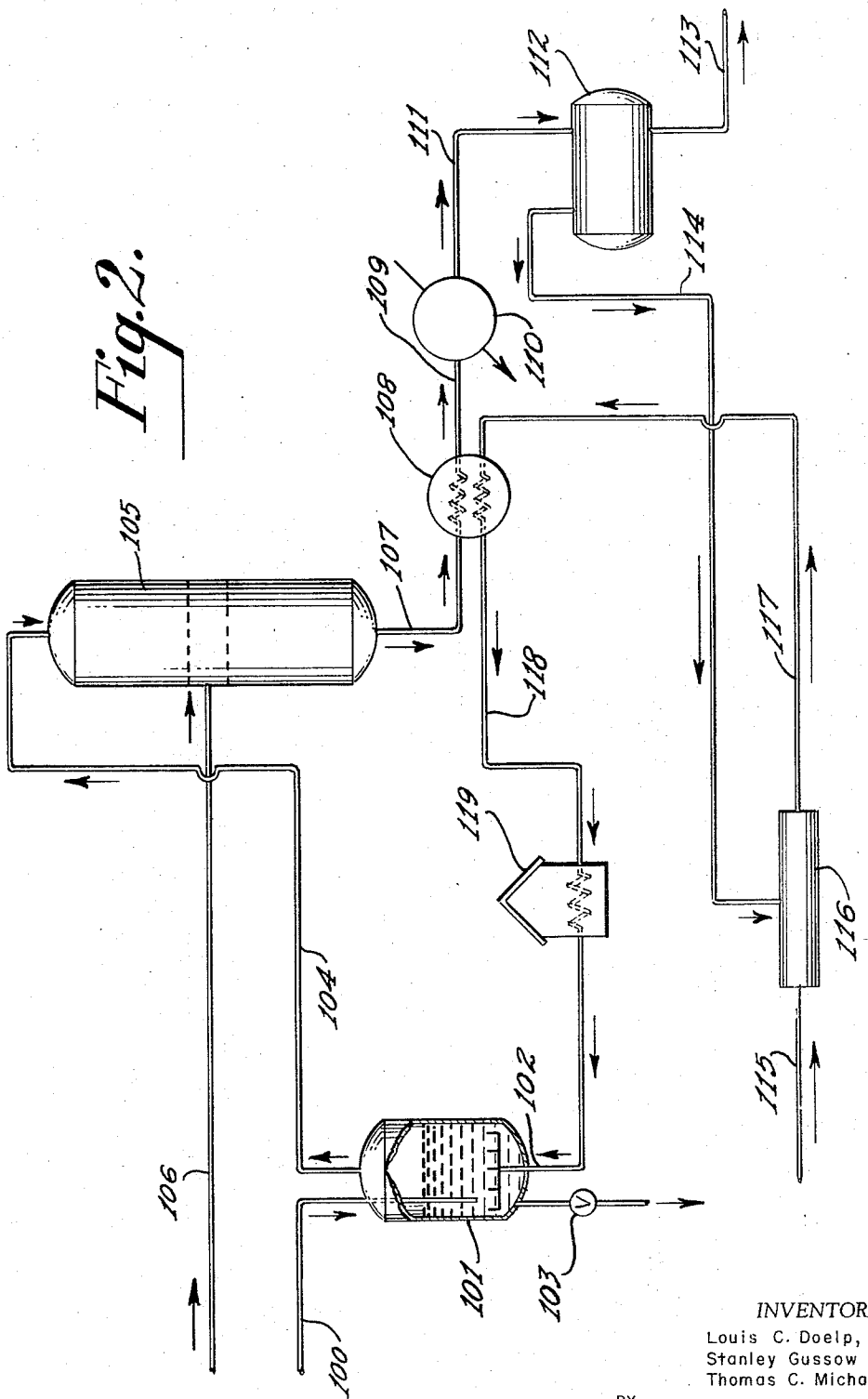
Fig. 2.





INVENTORS.
Louis C. Doelp,
Stanley Gussow &
Thomas C. Michael

BY

ATTORNEY.

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# TWO STAGE DRIPOLENE HYDROGENATION

Louis C. Doelp, Glen Mills, Stanley Gussow, Broomall, and Thomas C. Michael, Glenolden, Pa., assignors to Air Products and Chemicals, Inc., Philadelphia, Pa., a corporation of Delaware

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This invention relates to the catalytic hydrogenation of olefinic hydrocarbons and, more specifically, to the catalytic hydrogenation of pyrolysis condensates such as dripolene for motor gasoline or aromatics production.

Dripolene is the normally liquid mixture of hydrocarbons obtained as a byproduct in the production of ethylene during the high temperature pyrolysis of gaseous and/or liquid hydrocarbons. A material which condenses out of the hydrocarbons when the pyrolysis products are rapidly cooled, e.g., by quenching, is a liquid known as dripolene, which generally boils between 75 to 500° F.

While suggestions have been made to send dripolene to aromatic extraction units for recovery of pure aromatics such as benzene, the material is unsuitable without further treatment for use in aromatics production due to its high olefin content. Even the potential of dripolene as a blending stock for gasolines has not been realizable. Since dripolene contains materials such as olefins and diolefins which tend to form gum-like polymers, especially when heated, the quantity of dripolene blended into motor fuels has been relatively small.

Various suggestions directed to the selective hydrogenation of mono-olefins and/or diolefins, without simultaneously hydrogenating the aromatic compounds present in dripolene, have not been commercially satisfactory due to such problems as comparatively low conversion rates, excessive coke make and catalyst deactivation.

It is therefore, an object of the present invention to provide an improved method for the selective catalytic hydrogenation of olefinic hydrocarbons present in dripolene charge stocks.

It is another object of the present invention to provide a process for the selective catalytic hydrogenation of olefinic hydrocarbons present in dripolene without simultaneously hydrogenating aromatic compounds.

It is a further object of the invention to provide a method for the selective hydrogenation of dripolene to provide a blending stock for motor gasolines.

It is still another object of the present invention to provide a process for the catalytic hydrogenation of dripolene which may be conducted for periods substantially in excess of those heretofore obtained.

In accordance with the present invention, the catalytic hydrogenation of dripolene charge stock is effected in at least one reaction zone by contacting a commingled stream of vaporized dripolene and a hydrogen-containing gas with sulfided cobalt molybdate under a carefully regulated set of conditions such as temperature, pressure, hydrogen to oil ratio and space rate. The hydrogenation is highly selective in two important aspects: (1) aromatics hydrogenation does not occure at any level of olefin hydrogenation and (2) appreciable hydrogenation of monoolefins occurs only after diolefins have been completely hydrogenated to mono-olefins. Another desirable feature of the present invention, especially with respect to the preparation of a blending stock for motor gasolines, is the fact that hydrogenation of the charge stock results in a slight gain in the leaded octane rating and only a slight lowering of the clear octane number.



The catalyst employed in the practice of the present invention is an alumina-supported cobalt molybdate which is in a sulfided state during it use. The catalyst may either be presulfided or, depending on the nature of the charge stock, permitted to attain its sulfided state during the initial startup of the operation. The catalyst contains a total of about 8 to 18% by weight of the oxides of the molybdenum and cobalt in the approximate weight ratio of about 4/1 to 5/1 ($MoO_3$/CoO). The preferred catalysts are those containing at all times during use at least one atom of sulfur for each atom of cobalt and for each atom of molybdenum. Thus, for a cobalt molybdate catalyst which, prior to sulfidation, contains 15% $MoO_3$ and 3% CoO, the minimum sulfur content of the freshly sulfided catalyst will be about 7.9% by weight. In the described operation, this catalyst is not subject to deactiviation by sulfur or nitrogen in the feed or hydrogen stream and, in fact, contributes to the removal of such contaminants by converting them into readily separable materials.

The conditions of temperature, pressure, liquid hourly space velocity and hydrogen-containing gas rate are interrelated. The temperature in the reaction zones is maintained between 300 to 900° F. and preferably between 400 and 800° F. Pressures from about 100 up to 1,000 p.s.i.g. can be utilized with pressures from 400 to 800 p.s.i.g. being preferred. A liquid hourly space velocity (LHSV) of 0.1 to 20 may be employed with a preferred LHSV in the range of 1 to 5. The hydrogen-containing gas may be derived from a naphtha reforming operation, but, in any respect, is composed of at least 25% by volume hydrogen. The hydrogen is employed in a proportion of 500 to 10,000 standard cubic feet per barrel of dripolene charge stock and preferably in the amount of 1,000 to 7,000 standard cubic feet per barrel of charge stock.

The temperature of the charge stock in passing through each reaction zone rises because of the exothermic nature of the reaction to an outlet temperature above that of the inlet temperature but is not allowed to rise in excess of an outlet temperature of 900° F. The total vapor effluent from the first and each intermediate reaction zone is immediately cooled to an appropriate lower temperature before being admitted to the next succeeding reaction zone wherein the reactants again contact catalyst. Within the operating temperature range, the catalyst cycle life has been projected to be greater than 6 months.

Since the catalyst is deactivated when excessive temperatures are encountered, the inlet temperature of the charge to each reactor in the system is selected to be as low as reasonably possible so as to approach, but not to exceed, during the ensuing reaction the predetermined maximum temperature desired at the reactor outlet, considering the expected exothermic temperature elevation produced in the reaction. Ordinarily, under the

preferred range of operating conditions, the inlet temperature will be above about 300° F. and preferably in the range of 400 to 600° F. In the reaction, it is desirable that the ΔT due to the exothermic nature of the reaction be contained within the range of 50 to 150° F. for efficient operation and satisfactory results.

With continued operation over comparatively long periods, it may be desirable to raise the operating temperature to some extent. Periodic increases in temperature will primarily be dictated by the required properties of the unit liquid product.

In addition, the size of the several reaction zones or reactors of the series and the quantity of catalyst therein need not be equal. Accordingly, the temperature to which the products from a preceding reaction zone are cooled before admission to the next reaction zone will be governed by the extent of the expected temperature rise therein and consistent with achieving the desired product.

Under these conditions, the catalyst is maintained at a high catalytic activity level which is important not only from the standpoint of the immediate benefits in the yield of recovered valuable liquid product but also, and more importantly, from the standpoint of enhanced uninterrupted on-stream periods of operation.

The invention is clarified by reference to the following description read in connection with the drawings. FIGURES 1 and 2 are highly schematic illustrations of specific embodiments for dripolene hydrogenation.

In FIGURE 1, dripolene is passed to a vaporizer either directly or indirectly. When the full dripolene charge stock is employed, valves **17** and **18** are closed and dripolene from storage area **10** is passed through lines **11** to **14** directly to venturi device **15**, which is attached to vaporizer **16**.

As an alternative embodiment, a particular fraction may be separated from the dripolene charge stock in a feed-splitter and sent to the vaporizer. In this second embodiment, valves **19** and **20** are closed and dripolene from storage area **10** is conveyed by lines **11** and **21** to feed-splitter **22**. In the feed-splitter, a particular fraction, such as the 115° F. to bottoms or 150° F. to bottoms fraction, is separated from the charge stock and then transmitted to venturi device **15** through lines **23**, **13**, and **14**. The lower boiling fraction from the feed-splitter is composed mainly of $C_5$ hydrocarbons and is removed by line **24** for further separation and/or recovery.

In either embodiment, the dripolene from storage area **10** is preferably raised to the desired operating pressure and may be heated to between 200 to 400° F. (by means not shown) prior to its introduction into vaporizer **16**.

The dripolene charge stock supplied by line **13** may be blended with liquid from line **25**, which has not vaporized in vaporizer **16**. Generally, however, valve **26** is closed and charge stock from line **13** is passed through line **14** to venturi device **15**, where it is mixed with hot (700 to 1100° F.) hydrogen-containing recycle gas from line **27**. The commingled mixture of dripolene charge stock and hydrogen-containing gas is flashed in vaporizer **16** where about 0.2 to 5% and generally 1 to 2% of the liquid remains unvaporized. The excess accumulation of unvaporized charge is drawn off through line **28** which is regulated by valve **29**.

Vapor mixture passes from the vaporizer through line **30** and after any required adjustment in temperature enters the first reactor **31** where the mixture contacts sufided cobalt molybdate catalyst. The effluent from the first reactor is then passed through line **32** into a cooling device **33** and thereafter transmitted by line **34** to the second reactor **35**. The second reactor is operated in a manner essentially identical with that of the first reactor.

Reactor effluent from the second reactor is heat exchanged with recycle gas in heat exchanger **37** and then cooled to about 80° F. in a second heat exchanger **39**, after passing through lines **36** and **38**, respectively. The cold reactor effluent is passed through line **40** to a gas-liquid separator **41**. Gas escapes from the separator through line **42** and together with added makeup hydrogen from source **43** (and line **44**) moves through line **45** to recycle pump **46**. The recycled hydrogen-containing gas, after passing through line **47** and heat exchanger **37**, is then passed through line **48** and heater **49** to attain the required temperature before being sent back to venturi device **15** by line **27**.

Liquid from the gas-liquid separator **41** is sent by line **50** to stabilizer **51**. The overhead from the stabilizer ordinarily would pass through line **52** to a gas plant (not shown), while liquid is conveyed from the bottom of the stabilizer through line **53** to a rerun column and/or to gasoline storage (not shown). If a rerun column is employed the bottoms fraction may be recycled to the vaporizer by suitable means (not shown).

In the alternative procedure shown by FIGURE 2, dripolene charge stock from line **100** after any desired adjustment with respect to pressure and temperature is sent directly to feed vaporizer **101**. Hot hydrogen-containing gas from line **102** is employed to vaporize the dripolene charge stock. A desired amount of unvaporized charge material is maintained in the vaporizer while excess amounts (less than about 5% of the charge) are withdrawn through valved line **103**.

The vapors from vaporizer **101** are then passed through line **104** and after any required adjustment in temperature enter a two-stage hydrogenation reactor **105**, where the vapors contact sulfided cobalt molybdate catalyst.

In the production of a blending stock for motor gasolines, a liquid gasoline component, preferably free of diolefins, from line **106**, is employed for a direct interstage quench to cool the vapors from the first stage of the reactor to about 50 to 150° F. below the outlet temperature before they enter the second stage. The reaction conditions in the second stage are similar to those employed in the first stage.

In the production of aromatics, other quenching agents may be employed such as the product itself.

The effluent from the two-stage hydrogenation reactor **105** is conveyed by lines **107** and **109** through a heat exchanger **108** and high-pressure condenser **110**. The partially condensed material is then transmitted by line **111** to a high-pressure liquid gas separator **112**, from which the liquid is sent by line **113** to a stabilizer (not shown) and all or part of the gas is recycled through line **114** to the hydrogen stream.

Makeup hydrogen from a reformer or another convenient source is supplied from line **115** to multistage compressor **116**, wherein a mixture of makeup hydrogen and recycle gas is pressurized for use in vaporizer **101**. The hydrogen-containing gas from compressor **116** is transmitted through line **117** to heat exchanger **108**, where it is initially heated by the effluent from reactor **105**. The gas thus heated is sent through line **118** for any further heating, if required, in heater **119** prior to introduction into vaporizer **101**.

*Example I*

A dripolene charge stock was analyzed by conventional techniques and found to have the following characteristics and composition:

TABLE 1

| ASTM distillation range ° F.: | Charge stock A |
|---|---|
| Int. | 127 |
| 5% | 150 |
| 10% | 154 |
| 20% | 162 |
| 30% | 170 |
| 40% | 180 |

TABLE 1—Continued

| ASTM distillation range ° F.: | Charge stock A |
|---|---|
| 50% | 190 |
| 60% | 201 |
| 70% | 213 |
| 80% | 231 |
| 90% | 257 |
| 95% | 272 |
| E.P. (end point) | 293 |
| D.P. (dry point) | 289 |
| ° API gravity | 44.6 |
| Total nitrogen, p.p.m. | 5 |
| Bromine number | 64.5 |
| Bromine number (after maleic anhydride treat) | 39.4 |
| Molecular weight | 85 |

TABLE 2

| Chemical composition vol. percent of fraction | Charge stock A |
|---|---|
| Paraffins | 10.2 |
| Olefins | 30.6 |
| Naphthenes | 8.2 |
| Aromatics | 51.0 |
| | 100.0 |

To produce a stable motor gasoline, a mixture of hydrogen-containing gas and dripolene, having the characteristics and composition set forth for Charge Stock A, was contacted with sulfided cobalt molybdate catalyst, containing prior to sulfidation 15% $MoO_3$ and 3% CoO, in a reactor at the following conditions:

TABLE 3

| | Run (a) | Run (b) |
|---|---|---|
| Temperature, ° F | 550 | 450 |
| Pressure, p.s.i.g. | 600 | 600 |
| Space rate, LHSV | 3 | 3 |
| Hydrogen to Oil Ratio, mol/mol | 4 | 2 |

Under the aforementioned operating conditions, the initial charge stock was hydrogenated to a bromine number of 35 for product (*a*) and 47 for product (*b*). The products of this partial hydrogenation of the charge stock after distillation to an approximate 95 volume percent overhead had the characteristics shown in the following table.

TABLE 4

| | Charge Stock A | Product (a) | Product (b) |
|---|---|---|---|
| API Gravity | 44.6 | 46.5 | 46.5 |
| ASTM Distillation, ° F: | | | |
| IBP | 127 | 128 | 130 |
| 50% | 190 | 192 | 194 |
| 90% | 257 | 260 | 262 |
| Molecular Wt. | 85 | 85 | 85 |
| Bromine No. | 64.5 | 35 | 47 |
| Bromine No. (After M.A. Treat) | 39.4 | 35 | 47 |
| F-1 Clear Octane Number | 97.2 | 96.5 | 96.9 |
| F-1 +3 cc. TEL (Tetraethyllead) | 100.4 | 102.5 | 101.2 |
| Existent Gum, mg./100 ml. *n-Hexane Washed | 68.4 | *0.1 | *0.6 |
| 5 Hr. Potential Gum, mg./100 ml. | 1,800 | 0.4 | 5.7 |
| 16 Hr. Potential Gum, mg./100 ml. | 3,000 | 6.8 | 7.8 |
| Cu Dish Gum, mg./100 ml. | 95 | 1.0 | |
| Induction ($O_2$ stab.) Hrs. | 1/4 | 16+ | 16+ |
| Sulfur, Wt. percent | .090 | .022 | .040 |
| Nitrogen, p.p.m. | 5 | | |
| Hydrogen Consumed, s.c.f./bbl. | | 197 | 117 |
| N,N'-di-sec-butyl-p-phenylenediamine Inhibitor, #1, /000 bbls. | 0 | 5 | 10 |



Typical material balances of Product (*a*) and Product (*b*) are set forth in Table 5.

TABLE 5

| | Charge Stock A | | Product (a) | Product (b) |
|---|---|---|---|---|
| Bromine No. | | 64.5 | 35.0 | 47.0 |
| Bromine No. after M.A. Treat | | 39.4 | 35.0 | 47.0 |
| Wt. Basis of Feed to Vaporizer: | Prod. (a) | Prod. (b) | | |
| $C_5^+$ | 100.0 | 100.0 | | |
| Hydrogen | 0.4 | 0.2 | | |
| Total | 100.4 | 100.2 | | |
| $C_3$ | | | 0.1 | 0.1 |
| $C_4$ | | | 0.5 | 0.4 |
| $C_5^+$ Product | | | 97.8 | 97.7 |
| Btms | | | 2.0 | 2.0 |
| Total | | | 100.4 | 100.2 |
| Volume Basis: | | | | |
| $C_5^+$ | | 100.0 | 99.9 | 99.9 |
| Btms | | | 1.0 | 1.0 |
| Total | | 100.0 | 100.9 | 100.9 |
| Vol. percent Composition of total $C_5^+$: | | | | |
| Paraffins | | 10.2 | 16.8 | 12.8 |
| Olefins | | 30.6 | 16.6 | 25.6 |
| Mono-olefins | | 11.3 | 9.4 | 14.5 |
| Diolefins | | 5.3 | | 0.0 |
| Cyclo-olefins | | 14.0 | 7.2 | 11.1 |
| Naphthenes | | 8.2 | 15.6 | 10.6 |
| Aromatics | | 51.0 | 51.0 | 51.0 |
| Benzene | | 27.0 | 27.0 | 27.0 |
| Toluene | | 16.3 | 16.3 | 16.3 |
| Xylenes | | 7.7 | 7.7 | 7.7 |
| Hydrogen Consumed, S.c.f./bbl. | | | 197 | 117 |
| Sulfur, wt. percent Chg | | 0.090 | 0.022 | 0.040 |
| Percent Desulfurization | | | 76 | 56 |

EXAMPLE II

A dripolene charge stock was analyzed by conventional techniques and found to have the following characteristics and composition:

TABLE 6

| ASTM distillation range ° F.: | Charge stock B |
|---|---|
| Int. | 117 |
| 5% | 142 |
| 10% | 150 |
| 20% | 159 |
| 30% | 170 |
| 40% | 181 |
| 50% | 192 |
| 60% | 204 |
| 70% | 218 |
| 80% | 240 |
| 90% | 272 |
| 95% | 288 |
| E.P. | 312 |
| D.P. | 309 |
| ° API gravity | 45.4 |
| Total nitrogen, p.p.m. | 4.5 |
| Bromine number | 67 |
| Bromine number (after maleic anhydride [M.A.] treatment) | 48 |
| Molecular weight | 85 |

TABLE 7

| Chemical composition vol. percent of fraction: | Charge stock B |
|---|---|
| Paraffins | 14.2 |
| Olefins | 26.4 |
| Naphthenes | 8.1 |
| Aromatics | 51.3 |
| | 100.0 |

For aromatics production, a mixture of hydrogen-containing gas and dripolene, having the characteristics and

composition of Charge Stock B, was contacted with sulfided cobalt molybdate catalyst in a reactor of the following conditions:

TABLE 8

| | Run (c) |
|---|---|
| Temperature, ° F. | 600 |
| Pressure, p.s.i.g. | 600 |
| Space Rate, LHSV | 2 |
| Hydrogen to oil ratio, mol./mol. | 4 |

Under the aforementioned operating conditions, the initial charge stock was completely hydrogenated as shown by Table 9.

TABLE 9

| | Charge Stock B | Product (c) |
|---|---|---|
| Bromine No. | 67.0 | 0.8 |
| Bromine No. after M.A. Treat. | 48.0 | 0.8 |
| Wt. Basis of Feed to Vaporizer: | | |
| $C_5^+$ | 100.0 | |
| Hydrogen | 0.8 | |
| Total | 100.8 | |
| $C_3$ | | 0.2 |
| $C_4$ | | 0.6 |
| $C_5^+$ Product | | 99.0 |
| Btms | | 1.0 |
| Total | | 100.8 |
| Volume Basis: | | |
| $C_5^+$ | 100.0 | 101.1 |
| Btms | | |
| Total | 100.0 | 101.1 |
| Vol. percent Composition of total $C_5^+$: | | |
| Paraffins | 14.2 | 28.7 |
| Olefins | 26.4 | 0.3 |
| Mono-olefins | 9.8 | 0.3 |
| Diolefins | 5.6 | |
| Cyclo-olefins | 11.0 | |
| Naphthenes | 8.1 | 20.2 |
| Aromatics | 51.3 | 50.7 |
| Benzene | 26.0 | 25.7 |
| Toluene | 15.1 | 14.9 |
| Xylenes | 6.8 | 8.7 |
| $C_9$ Benzene | 1.0 | 1.3 |
| $C_{10}$ Benzene | 0.1 | 0.1 |
| $C_{11}$ Benzene | 0.3 | |
| Styrene | 2.0 | |
| Hydrogen Consumed, s.c.f./bbl. | | 446 |
| Sulfur, Wt. percent Chg. | 0.082 | 0.0015 |
| Percent Desulfurization | | 98 |
| Existent Gum mg./100 ml. | 83.8 | 1.4 |
| 5 Hr. Potential Gum, mg./100 ml. | $2.197\times10^3$ | 1.9 |
| 16 Hr. Potential Gum, mg./100 ml. | $3.177\times10^3$ | 3.0 |

*Example III*

Dripolene, Charge Stock B (Example II), is charged to a vaporizer maintained at 360° F. and 600 p.s.i.g. Hot hydrogen recycle gas of 70 to 80 volume percent purity is employed to vaporize the charged dripolene. Based on an ASTM distillation of the vaporizer bottoms liquid, over 98% of the charge stock is vaporized.

The vaporized material, commingled dripolene and hydrogen-containing gas, is then contacted in a two-stage reactor over sulfided cobalt molybdate catalyst. Interstage cooling is accomplished by liquid quench, using a motor gasoline component free of olefins and amounting to 14% of the charge.

The reactor pressure is maintained at 600 p.s.i.g., space rate is maintained between 2 to 3 vol./hr./vol. and a recycle hydrogen to oil mol ratio is 3. The initial inlet reactor temperature for each stage is 425° F.

Effluent from the reactor after cooling is transmitted to a liquid gas separator. The liquid product from said separator, after stabilization, is blended with gasoline.

The product of this example, on a distilled (95+% overhead) and inhibited basis (5 lbs. N,N'-di-sec-butyl-p-phenylenediamine/1000 bbls.), has the following characteristics:

TABLE 10

| | |
|---|---|
| Bromine No. | 40 |
| Bromine No. after M.A. Treat. | 40 |
| F–1 Clear Octane No. | 96.6 |
| F–1+3 cc. TEL Octane No. | 101.0 |
| Sulfur Content (wt. percent) | 0.05 |

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

The invention claimed is:

**1.** The process for the selective hydrogenation of olefinic hydrocarbons of a dripolene charge stock in two reaction zones which consists essentially of vaporizing the charge stock with 700 to 1100° F. hydrogen containing gas, contacting the resulting vaporized mixture of charge stock and hydrogen containing gas in the first reaction zone with sulfided cobalt molybdate catalyst at a temperature between 300 to 900° F., adjusting the temperature of the effluent from the first reaction zone before said effluent enters a second reaction zone so that the reaction temperature in the second reaction zone is maintained below a maximum of 900° F. and contacting the temperature adjusted effluent from the first reaction zone with sulfided cobalt molybdate catalyst in the second reaction zone.

**2.** The process of claim **1** wherein the inlet temperature of the charge to each reaction zone is between 400–800° F.

**3.** The method for selectively hydrogenating the olefinic hydrocarbons of a dripolene charge stock in two reaction zones wherein substantially none of the aromatic hydrocarbons in the charge stock are hydrogenated which consists essentially of vaporizing the charge stock with 700–1100° F. hydrogen-containing gas, contacting the resulting vaporized mixture of charge stock and hydrogen-containing gas in the first reaction zone at a temperature between 300 to 900° F. with sulfided alumina supported catalyst containing a total of 8 to 18 percent by weight of the oxides of molybdenum and cobalt in the weight ratio of 4:1 to 5:1 molybdenum oxide to cobalt oxide, adjusting the temperature of the effluent from the first reaction zone before said effluent enters a second reaction zone so that the temperature in the second reaction zone is maintained below 900° F. and contacting in a second reaction zone the temperature adjusted effluent from the first reaction zone with a sulfided alumina supported catalyst containing a total of 8 to 18 percent by weight of the oxides of molybdenum and cobalt in the weight ratio of 4:1 to 5:1 molybdenum oxide to cobalt oxide.

**4.** The method of claim **3** wherein the hydrogen-containing gas is composed of at least 25% hydrogen by volume.

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DELBERT E. GANTZ, *Primary Examiner.*

S. P. JONES, *Assistant Examiner.*