

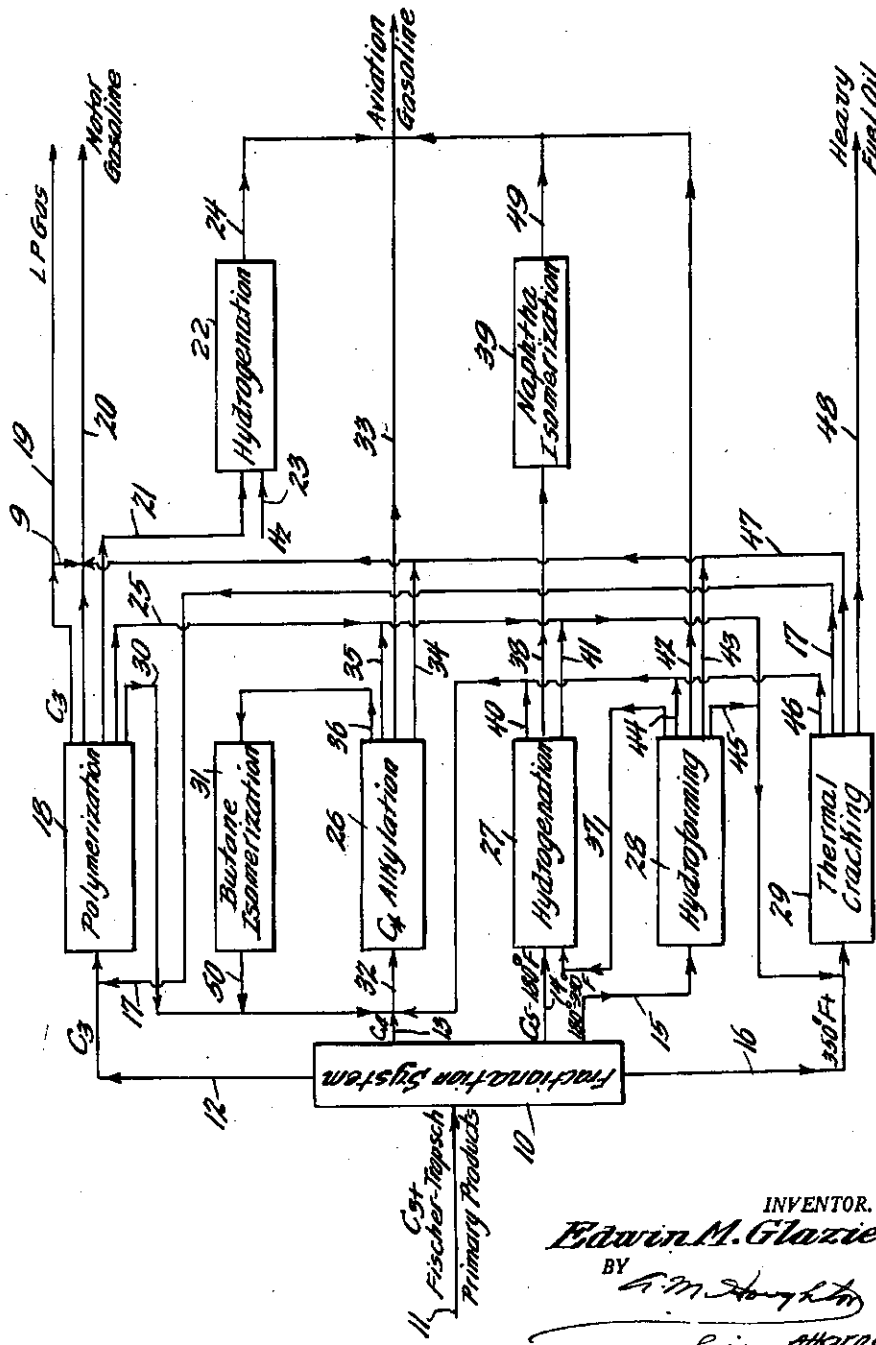
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PRODUCTION OF AVIATION GASOLINE

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PRODUCTION OF AVIATION GASOLINE

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This invention relates to a process for the production of increased quantities of aviation gasoline from the primary products of a Fischer-Tropsch synthesis process.

The primary products of a Fischer-Tropsch synthesis process consist predominantly of straight chain paraffinic hydrocarbons and monoolefinic hydrocarbons. The straight chain paraffinic hydrocarbons can be tolerated in aviation gasoline in only small amounts because these hydrocarbons impart low octane characteristics to gasoline. While the olefins do not impair the octane rating of gasoline, appreciable amounts of olefins cannot be tolerated in aviation gasoline because of their gum-forming tendencies. Accordingly, the primary products of a Fischer-Tropsch synthesis process require extensive treatment to produce appreciable quantities of aviation gasoline.

Numerous processes have heretofore been proposed for upgrading Synthine gasoline, but these processes have been directed to the production of high antiknock motor fuels in good yields, with the result that relatively small amounts of aviation fuels have been obtained. In accordance with the process of the present invention, however, aviation gasoline is produced in amounts corresponding to at least about two and one-half times the amount of motor gasoline.

In accordance with the present invention, the primary hydrocarbon products of a Fischer-Tropsch synthesis process are fractionated into a C₃ fraction containing a small amount of C₄'s, a C₄ fraction, a light naphtha fraction from C₅ up to about 180° F. end point, a heavy naphtha fraction boiling between about 180° and about 350° F., and a fuel oil fraction boiling from about 350° F. up to and including wax-like materials.

The C₃ fraction containing a small amount of C₄ hydrocarbons is subjected to catalytic non-selective polymerization to produce gasoline boiling range hydrocarbons. The amount of C₄ hydrocarbons in the charge to the polymerization unit is fixed by the desirability of providing the optimum ratio of saturated to unsaturated C₄'s in the feed to the alkylation unit. I have found that the C₄ hydrocarbons charged to the polymerization unit usually constitute about 12 to about 15 per cent of the C₄ hydrocarbons present in the overall process. A small amount of the gasoline boiling range hydrocarbons produced in the polymerization unit is withdrawn for blending into a motor gasoline, the remaining gasoline boiling range hydrocarbons being hydrogenated to produce aviation gasoline blending stock.

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The C₄ fraction is subjected to alkylation to produce motor and aviation gasoline alkylates. Unalkylated butane consisting predominantly of normal butane is isomerized to isobutane, the isobutane then being returned to the alkylation unit.

The light naphtha fraction from C₅ up to about 180° F. end point is subjected to hydrogenation followed by isomerization to produce a highly isoparaffinic aviation gasoline blending stock.

The heavy naphtha fraction boiling between about 180° and about 350° F. is subjected to hydroforming to produce an aviation gasoline base stock containing about 90 per cent aromatics and 10 per cent paraffins. In the hydroforming step there is a net production of hydrogen which is approximately equal to the hydrogen consumption in the hydrogenation of the C₅ to 180° F. fraction.

The fuel oil fraction is subjected to thermal cracking to produce C₃ hydrocarbons and C₄ hydrocarbons, a light naphtha suitable for blending into a motor gasoline and heavy fuel oil. The C₃ hydrocarbons from the thermal cracking step are separated and returned to the catalytic non-selective polymerization step. The C₄ hydrocarbons from the thermal cracking step are separated and returned to the alkylation step.

An important phase of the integrated process of the invention is the interrelation of the hydrogenation and the hydroforming operations performed, respectively, on the primary C₅-180° F. and 180°-350° F. fractions in order to prevent the formation of benzene from the C₆ hydrocarbons. Inclusion of excessive quantities of benzene in aviation fuel is undesirable because of the adverse effect that it has on the freezing point of the fuel. Accordingly, by the process of the present invention, the fraction containing hydrocarbons of the type which if subjected to hydroforming reaction conditions would be converted to benzene, i. e., the C₅-180° F. fraction, is subjected to hydrogenating reaction conditions. Hydrogenation of this fraction saturates the olefins contained therein without converting any of the hydrocarbons to aromatics. Subsequent isomerization of the paraffinic hydrogenate thus formed produces an excellent aviation gasoline blending stock. Hydroforming of the 180°-350° F. fraction converts essentially all of the olefins and a portion of the paraffins in this fraction to a highly aromatic aviation gasoline base stock. There is a net production of hydrogen in the hydroforming operation which is approximately equal to the hydrogen consumption in the hydrogenation operation making it unnecessary to supply outside

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hydrogen for treating the C₅ to 180° F. hydrocarbons.

The only outside hydrogen required in carrying out the integrated process of the invention is that needed for polymer hydrogenation. Hydrogen may or may not be used as a cracking inhibitor during the isomerization of the hydrogenate. When hydrogen is needed it can be obtained from a portion of the relatively hydrogen-rich absorber off-gas from the product recovery system of the Fischer-Tropsch process.

The process of the invention will be more fully understood from the following detailed discussion. A preferred embodiment of the invention is illustrated in the attached drawing which is a schematic flow diagram of the finely integrated process of the invention. It should be understood that a simplified drawing is given for purposes of ready comprehension of the invention and that in reality each block on the drawing represents a complete process in itself. Obviously many modifications of the processes set forth hereinafter may be made without departing from the spirit and the scope of the invention.

Now referring to the drawing, the Fischer-Tropsch primary products consisting of C₃ hydrocarbons up to and including wax-like materials enter a fractionation system 10 by line 11. It is understood, of course, that fractionation system 10 may comprise several fractionating units. For instance, a preferred procedure in accordance with commercial practice comprises separating the Fischer-Tropsch primary hydrocarbon products into a C₃-C₄ fraction and a C₅+ fraction. The C₃-C₄ fraction is then fractionated into a C₃ overhead fraction containing a small amount of C₄'s which is removed by line 12 and a C₄ bottoms fraction which is removed by line 13. The C₄ bottoms fraction contains a substantial amount of butylenes so that when this fraction is added to the butylenes from the hydroforming and thermal cracking units described hereinbelow the molar ratio of saturated to unsaturated C₄'s entering the alkylation unit will be optimum. The C₅+ fraction is separated into a C₅-180° F. overhead fraction which is removed by line 14 and a 180° F.+ bottoms fraction. The 180° F.+ bottoms fraction is then separated into a 180° F.-350° F. overhead fraction which is removed by line 15 and a 350° F.+ bottoms fraction which is removed by line 16.

The C₃ fraction in line 12, together with a fraction consisting essentially of C₃ hydrocarbons in line 17, is passed to a catalytic polymerization unit 18. In the polymerization unit the propylenes and butylenes are non-selectively polymerized in the presence of a polymerization catalyst such as sulfuric acid, phosphoric acid, or copper pyrophosphate at a temperature in the range of 150° to 600° F. In accordance with a preferred form of the invention the C₃ fraction containing about 14 per cent of C₄'s is contacted with 70 to 75 per cent sulfuric acid in a reaction chamber for a period of 10 to 20 minutes at a temperature of about 170° to 180° F. under a pressure of about 600 p. s. i. g. The effluent from the reaction chamber flows to a settling chamber where the acid catalyst settles out. Hydrocarbons withdrawn from the settling chamber are passed to a debutanizer where C₃ and C₄ hydrocarbons are separated from the heavier hydrocarbons. The C₃ and C₄ hydrocarbons are then fractionated, the C₃ hydrocarbons being withdrawn through line 19 as liquefied

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petroleum gas. The C₄ hydrocarbons (chiefly paraffins) are withdrawn through line 20 to serve as a part of the charge to an alkylation unit 26. The heavy hydrocarbons from the debutanizer are separated into a heavy polymer gasoline fraction withdrawn through line 20, a light polymer gasoline fraction withdrawn through line 21 and a polymer naphtha fraction boiling above about 420° F. withdrawn through line 25. The heavy polymer gasoline fraction is blended with thermally cracked naphtha, heavy hydroformate, and heavy alkylate to form motor gasoline. The motor gasoline thus formed may be further blended with a portion of the liquefied petroleum gas introduced through line 9, the optimum amount of liquefied petroleum gas depending, of course, upon the particular Reid vapor pressure (RVP) desired. By employing liquefied petroleum gas instead of butane for adjusting the vapor pressure of gasoline I can obtain greater yields of aviation gasoline.

The light polymer gasoline fraction obtained from polymerization unit 18 is introduced into a hydrogenation unit 22 by line 21. This unit characteristically produces high yields of high octane aviation gasoline blending stock. In the hydrogenation unit the unsaturated hydrocarbons are converted almost completely to saturated hydrocarbons. Substantially complete saturation of the olefins is necessary because of the stringent accelerated gum specification for aviation fuels. Hydrogenation can be carried out in the presence of a conventional hydrogenation catalyst such as compounds, i. e., oxides and sulfides, of molybdenum, tungsten, chromium, vanadium, tin, zinc, iron, cobalt, and nickel. The catalysts may be used alone or in combination with promoters and carriers, such as clay, silica gel, alumina and the like. Depending, of course, upon the particular catalyst chosen the hydrogenation may be carried out at a temperature within the range of 300° to 700° F. and at pressures up to 4500 p. s. i. g. When a nickel catalyst supported on porcelain is used, hydrogenation can be carried out at mild conditions of temperature and pressure of the order of about 360° F. and 50 p. s. i. g. The hydrogenation unit may comprise a series of six reaction chambers, the first two of which may contain partially spent catalyst obtained from the subsequent reaction chambers. In a unit of this type the feed is vaporized and then combined with a stream of preheated hydrogen. The mixture thus formed passes through the first two reaction chambers wherein the feed is freed of any catalyst poisons that may be present. The treated feed then passes through the remaining reaction chambers. The effluent from the reaction system is passed through a condenser wherein the octanes are liquefied and withdrawn through line 24. Typical aviation gasoline volumetric yields from a unit of this type are above 100 per cent, usually of the order of about 104 to 105 per cent, based on the light polymer gasoline charge. The product obtained from a hydrogenation unit of this type generally has a clear ASTM octane number averaging between about 95 and about 100.

The C₄ fraction containing about 60 per cent of butylenes obtained from fractionation system 10 is passed, together with C₄ hydrocarbons obtained from polymerization unit 18, a butane isomerization unit 31, hydrogenation unit 27, hydroforming unit 28, and a thermal cracking unit 29 into

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alkylation unit 26 to produce isooctanes. The alkylation reaction is advantageously carried out in the presence of an alkylation catalyst such as sulfuric acid, phosphoric acid, hydrogen fluoride, boron trifluoride-water complexes, aluminum chloride, aluminum chloride-hydrocarbon complexes, and the like. A high ratio of isoparaffin to olefin, advantageously 4 to 15 parts of isoparaffin per part of olefin, is preferred in that lower ratios encourage polymerization to occur. In general, temperatures between 0° and 150° F. and pressures sufficient to maintain the reactants in liquid phase are preferred. In continuous operation, contact times of 0.5 to 30 minutes may be used. According to a preferred embodiment of the invention, the isoparaffin and olefin in a ratio of 5:1 are intimately contacted in a reaction chamber maintained at a temperature of about 50° F. and a pressure of about 75 p. s. i. g. and in the presence of 90 per cent sulfuric acid. The alkylate obtained from the reaction chamber is freed from acid and then fractionally distilled whereupon C₄ hydrocarbons are separated and withdrawn through line 36. Fighting grade aviation alkylate having an end point of about 330° F. is withdrawn through line 33. This alkylate typically has a clear ASTM octane number above about 95. Heavy alkylate having an end point of about 420° F. suitable for blending into motor gasoline is withdrawn through line 34. A small amount of polymer boiling above about 420° F. is withdrawn through line 35. The material boiling above about 420° F. serves as part of the charge stock for thermal cracking unit 29.

The C₄ hydrocarbons in line 36 are passed to butane isomerization unit 31. The isomerization of the C₄ hydrocarbons can be carried out in the presence of any of the active butane isomerization catalysts such as the chlorides or bromides of aluminum, zinc, iron, zirconium, tin, barium, columbium, tantalum, and boron. These catalysts may be used in granular, solid, or lump form, or supported on a solid adsorbent, such as synthetic and natural clays, silica gel, pumice, brick, coke, activated alumina, and active carbon. If desired, a metallic halide can be suspended or dissolved in an inert liquid or can be reacted with unsaturated hydrocarbons to form active metallic halide-hydrocarbon complexes. Isomerization can be carried out in liquid or gas phase. When a metallic halide catalyst is used, isomerization is advantageously carried out in the presence of a hydrogen halide promoter such as anhydrous hydrogen chloride, in an amount corresponding to between about 0.1 and about 10 per cent by weight based on the weight of the C₄ hydrocarbons present. The isomerization of the C₄ hydrocarbons can be carried out at temperatures ranging from room temperature to 300° F. and at pressures up to 1500 p. s. i. g., the particular pressure depending upon the type of operation employed. According to one embodiment, a stream of C₄ hydrocarbons in admixture with 1 to 3 per cent by weight of anhydrous hydrogen chloride may be divided, one portion passing through a first isomerization zone containing a solid aluminum chloride catalyst, the remaining portion together with effluent from the first isomerizing zone passing through a second isomerization zone containing an aluminum chloride-hydrocarbon complex catalyst. Each of the isomerization zones is maintained at a temperature within the range of 200° to 260° F. and a space velocity between about 2 and about 8 is employed. Under optimum conditions normal butane is isomerized to isobutane in an amount

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corresponding to an ultimate yield of isobutane between about 90 and 97 per cent. After being stripped of hydrogen chloride, the isomerized product may be fractionated into a normal butane recycle stream and an isobutane product stream withdrawn through line 50.

The primary C₅-180° F. fraction in line 14 is passed to a hydrogenation unit 27. In this unit the C₅-180° F. fraction is subjected to hydrogenating conditions in the presence of a typical hydrogenating catalyst such as an oxide or sulfide of molybdenum, tungsten, chromium, vanadium, tin, zinc, iron, cobalt, and nickel. The catalysts may be used alone or in combination with promoters and carriers, such as clay, silica gel, alumina and the like. The conditions employed in this unit comprise a temperature between 800° and about 950° F., a pressure of about 200 p. s. i. g., and a space velocity of about 1.0 to about 5.0 volumes of charge per volume of catalyst per hour. Optimum conditions in this unit are a temperature of about 900° F., and a space velocity of about 2. Under these conditions substantially all of the olefin hydrocarbons are converted to paraffinic hydrocarbons and substantially no aromatic hydrocarbons are formed. Some aromatic hydrocarbons are desirable in aviation gasoline. However, the inclusion of substantial amounts of benzene in aviation gasoline is undesirable because of its tendency to raise the freezing point of the fuel above the maximum of -76° F. as specified in U. S. Fighting Grade Aviation Fuel Specification AN-F-48a. In carrying out the reaction in hydrogenation unit 27, a high hydrogen partial pressure is maintained by recycling hydrogen-rich gas at a rate of about 2,000 to 5,000 cubic feet of gas per barrel of charge. The hydrogen consumed in this unit is approximately equal to the hydrogen produced in hydroforming unit 28. Accordingly, the hydrogen produced in hydroforming unit 28 passes through line 37. Hydrogenation unit 27 may comprise four or more reaction chambers. When four chambers are employed, two of them are "on stream" while the other two are in different stages of regeneration. The length of the on-stream period depends upon the activity of the catalyst which in turn depends upon the carbon "lay-down" on the catalyst. The products from hydrogenation unit 27 are fractionated into a hydrogen-containing gas substantially free of hydrocarbons heavier than propane which is recycled to the unit; a C₄ hydrocarbon fraction withdrawn through line 40 to serve as part of the charge to alkylation unit 26; a light hydrogenate fraction having an end point of about 300° F. withdrawn through line 38 to serve as the charge to a naphtha isomerization unit 39; and a heavy hydrogenate boiling above about 300° F. which is withdrawn through line 41 to serve as a part of the charge to thermal cracking unit 29.

In naphtha isomerization unit 39, low octane number pentanes and hexanes obtained from hydrogenation unit 27 are converted to isomers of higher octane number suitable for blending into aviation gasoline. The isomerization of the light hydrogenate fraction in naphtha isomerization unit 39 can be carried out in the presence of any of the active isomerization catalysts such as the chlorides or bromides of aluminum, zinc, iron, zirconium, tin, barium, columbium, tantalum, and boron. These catalysts may be used in granular, solid, or lump form, or supported on a solid adsorbent, such as synthetic and natural clays, silica gel, pumice, brick, coke, activated

alumina, and active carbon. If desired, a metallic halide can be suspended or dissolved in an inert liquid or can be reacted with unsaturated hydrocarbons to form active metallic halide-hydrocarbon complexes. The reaction is also advantageously carried out in the presence of a hydrogen halide promoter in an amount corresponding to between about 0.1 and about 10 per cent by weight based on the weight of the hydrocarbons present in the reaction zone.

The isomerization of the light hydrogenate can be carried out at temperatures ranging from room temperature to 800° F. However, isomerization at the higher temperatures is accompanied by undesirable cracking and other decomposition reactions. To inhibit the undesirable reactions, various cracking inhibitors may be used, such as hydrogen, propane, butanes and pentanes. The pressure employed will depend upon the type of operation, i. e., liquid or gas phase. For liquid phase operation at temperatures between 150° and 350° F., pressures between 200 and 1500 p. s. i. g. should be employed. Space velocities between 0.1 and 5 volumes of liquid feed per volume of catalyst per hour can be used. In accordance with one embodiment of the invention the light hydrogenate fraction from hydrogenation unit 27 is fractionated into a C₅ fraction and a C₆+ fraction. The C₅ fraction, together with hydrogen and hydrogen chloride, is passed through a reaction zone containing an aluminum chloride-hydrocarbon complex catalyst at a temperature of 212° F., a pressure of 300 p. s. i. g., and a space velocity of 1. The C₆+ fraction is passed, together with hydrogen and hydrogen chloride, through a second reaction zone containing an aluminum chloride-hydrocarbon complex catalyst at a temperature of 250° F., a pressure of 850 p. s. i. g., and a space velocity of 2. The effluents from the two reaction zones are then combined and passed to strippers where the hydrogen and hydrogen chloride are separately removed. The stripped product is then caustic washed and withdrawn through line 49. Obtained from the naphtha isomerization unit are high yields, in the order of about 100 volume per cent based on the charge, of aviation gasoline blending stock generally having a clear ASTM octane number of 90 to 95.

The 180°-350° F. fraction in line 15 is practically free of C₈ hydrocarbons and therefore can be subjected to typical hydroforming without the formation of benzene. Accordingly, the 180°-350° F. fraction is passed through a bed of hydroforming catalyst such as molybdena-on-alumina, chromia-on-alumina, or vanadia-on-alumina at a temperature between about 350° and about 1000° F., a pressure of about 200 p. s. i. g. and a liquid space velocity of about 0.2 to about 1.0 volumes of charge per volume of catalyst per hour.

Hydroforming unit 28 may be constructed similarly to hydrogenation unit 27. These units differ essentially in their optimum operating conditions. In carrying out the hydroforming reaction, hydrogen-rich gas is recycled at the rate of about 2,000 to 5,000 cubic feet of gas per barrel of charge. In accordance with a preferred form of my invention I have found that in hydroforming unit 28 a temperature of 950° F. and a space velocity of 0.5 converts essentially all of the olefins and a portion of the paraffins in the 180°-350° F. fraction to a highly aromatic aviation gasoline base stock. The aviation gasoline base stock thus obtained consists of about 85 to about 95 per cent by weight of aromatic hydrocarbons and has an end point of about 300° F.

The highly aromatic aviation gasoline base stock is withdrawn through line 42. Also produced in this unit is a heavy hydroformate having an end point of about 400° F. The heavy hydroformate suitable for blending into motor gasoline is withdrawn through line 43. A C₄ fraction suitable for charging to alkylation unit 26 is separately withdrawn through line 44.

In hydroforming unit 28 there is a net production of hydrogen sufficient to offset the consumption of hydrogen in hydrogenation unit 27. Accordingly, a stream of gas containing hydrogen in an amount sufficient to make up for the hydrogen consumed in hydrogenation unit 27 is withdrawn through line 37. A hydroformate bottoms fraction boiling above about 400° F. and suitable for thermal cracking is withdrawn through line 45.

The primary fraction boiling above about 350° F. and the heavy residue produced in the several processes described above are combined to produce a combined charge stock which is subjected to cracking in thermal cracking unit 29. This unit produces C₃ and C₄ hydrocarbons, a light naphtha suitable for blending into a motor gasoline, and a heavy fuel oil. The C₃ hydrocarbons are removed through line 17 to polymerization unit 18. The C₄ hydrocarbons are removed through line 46 to alkylation unit 26. The light naphtha fraction is removed through line 47 and is blended with heavy hydroformate obtained from hydroforming unit 28, heavy alkylate obtained from alkylation unit 26, a heavy polymer gasoline fraction and liquefied petroleum gas obtained from polymerization unit 18 to form motor gasoline. Heavy fuel oil is withdrawn through line 48. In accordance with a preferred embodiment of the invention, the combined cracking charge stock may be passed through a furnace cracking coil at a temperature within the range of about 850° to about 950° F. and a pressure between about 350 and about 750 p. s. i. g. On leaving the heating coil, the cracked products are discharged into a quench chamber where rapid cooling is effected by mixture with the cooler fresh feed. Cracked fuel oil is separated and withdrawn from the bottom of the quench drum through line 48, and the effluent vapor is then fractionated into a pressure distillate having an end point of about 420° F. withdrawn through line 47, C₄ hydrocarbons withdrawn through line 46, C₃ hydrocarbons withdrawn through line 17, and gas oils (not shown) for recycling to the thermal cracking unit.

It should be understood that in commercial practice much of the equipment including heat exchangers, pumps, fractionation equipment, catalyst regeneration facilities, and the like employed in the various units hereinabove defined would be common to one or more of the units.

The following example is given to illustrate the approximate yields of the various products obtained on a continuous basis in accordance with a preferred embodiment of the invention. In the following example where "parts" is mentioned it should be understood that I am referring to parts by volume.

When 1000 parts by volume of hydrocarbons from C₃ up to and including wax-like materials obtained from the Fischer-Tropsch process are fractionally distilled, there are obtained 265 parts of a C₃-C₄ hydrocarbon fraction about 80 per cent of which is C₃ hydrocarbons, 95 parts of a C₄ hydrocarbon fraction consisting of about 60 per cent of unsaturates, 155 parts of a light naph-

tha fraction from about C₃ up to 180° F. end point, and 285 parts of a heavy naphtha fraction boiling between 180° and 350° F. After these materials are separated there remains 200 parts of a bottoms fraction boiling above about 350° F.

When the 265 parts of C₃-C₄ hydrocarbons are contacted with 70 to 75 per cent sulfuric acid for a period of 10 to 20 minutes at 175° F. and at 600 p. s. i. g., there are obtained 106 parts of C₃ hydrocarbons, 25 parts of C₄ hydrocarbons (chiefly butanes), 29 parts of a heavy polymer gasoline having a 420° F. end point and a clear ASTM octane of about 80, 86 parts of a light polymer gasoline having a 240° F. end and 2 parts of polymer naphtha.

When the 86 parts of light polymer gasoline are hydrogenated in the presence of a nickel catalyst supported on porcelain at 360° F. and 50 p. s. i. g., 87 parts of aviation gasoline blending stock having a 250° F. end point and a clear ASTM octane of about 98 are obtained.

The 95 parts by weight of C₄ hydrocarbons rich in butylenes obtained from the initial separation step of the process, together with the 25 parts of C₄ hydrocarbons (chiefly butanes) obtained from the above polymerization step, 152 parts of C₄ hydrocarbons, predominantly isobutane, obtained from the isomerization of normal butane, 8 parts of C₄ hydrocarbons obtained from the hydrogenation step, 21 parts of C₄ hydrocarbons obtained from the hydroforming step, and 32 parts of C₄ hydrocarbons obtained from the thermal cracking of the heavier hydrocarbons are alkylated at 50° F. at a pressure of 75 p. s. i. g. in the presence of 90 per cent sulfuric acid catalyst. The ratio of isobutane to butylene is 4:1. Upon fractionation of the alkylated products there are obtained 156 parts of unalkylated C₄ hydrocarbons consisting predominantly of normal butane, 146 parts of aviation alkylate having a 330° F. end point and a clear ASTM octane of about 96, 3 parts of heavy alkylate having an end point of about 420° F., and 3 parts of polymer boiling above about 420° F.

The 156 parts of butanes separated out of the alkylation products are isomerized with an aluminum chloride catalyst in the presence of 2 per cent by weight of hydrogen chloride at 250° F. and 200 p. s. i. g. to give 152 parts of C₄ hydrocarbons consisting predominantly of isobutane.

The 155 parts of light naphtha from about C₅ to 180° F. end point obtained in the initial separation step of the process are hydrogenated over a molybdena-on-alumina catalyst at 900° F., 200 p. s. i. g., and a space velocity of 2, in the presence of about 3000 cubic feet of a hydrogen-rich gas per barrel of charge, said gas containing about 75 per cent of hydrogen whereby there are obtained 8 parts of C₄ hydrocarbons, 132 parts of light hydrogenate, and 3 parts of heavy hydrogenate boiling above about 300° F.

The 132 parts of light hydrogenate obtained from the preceding hydrogenation step are isomerized over an aluminum chloride-hydrocarbon complex catalyst in the presence of anhydrous hydrogen chloride at 250° F., 850 p. s. i. g., and a space velocity of 2, whereby there are obtained 121 parts of aviation gasoline having a 300° F. end point and a clear ASTM octane of about 97.

The 285 parts of 180° to 350° F. hydrocarbons obtained from the initial separation step of the process are hydroformed over a molybdena-on-alumina catalyst at 950° F., 200 p. s. i. g., and a space velocity of 0.5, in the presence of about 3000 cubic feet of a hydrogen-rich gas per bar-

rel of charge whereby there are obtained 21 parts of C₄ hydrocarbons, 121 parts of aviation gasoline base stock having a 300° F. end point and a clear ASTM octane of about 98, 32 parts of heavy hydroformate suitable for blending into a motor gasoline, and 6 parts of hydroformate bottoms boiling above about 400° F. suitable as charge stock for thermal cracking. This unit produces about 1000 cubic feet of hydrogen-rich gas per barrel of charge. The hydrogen constitutes about 75 percent of the gas.

214 parts of hydrocarbons boiling above about 350° F. and consisting of 200 parts from the initial separation step, 3 parts of heavy hydrogenate, 6 parts of hydroformate, 3 parts of heavy alkylate, and 2 parts of polymer naphtha are thermally cracked at 900° F. and 700 p. s. i. g. Obtained from this cracking operation are 30 parts of C₃ hydrocarbons, 32 parts of C₄ hydrocarbons, 116 parts of motor gasoline having a 420° F. end point and a clear ASTM octane of about 77, and 36 parts of heavy fuel oil. A quantity of fixed gases amounting to about 300 cubic feet per barrel of charge is also produced.

When the 29 parts of heavy polymer gasoline, 3 parts of heavy alkylate, 32 parts of heavy hydroformate, and 116 parts of cracked gasoline are blended with 5 parts of propane, there are obtained 185 parts of motor gasoline having an RVP of about 10 p. s. i. a. and a clear CFRM octane of about 75. When the 87 parts of aviation gasoline blending stock from the hydrogenation step are combined with the 146 parts of aviation alkylate, 121 parts of aviation gasoline from the isomerization step, and 121 parts of aviation base stock from the hydroforming step, there are obtained 475 parts of aviation gasoline having an RVP of about 6 p. s. i. a. and a lean mixture octane number of about 100 and a rich mixture performance number of about 130 with 4.6 cc. of tetraethyl lead per gallon. The aviation gasoline blend thus obtained contains about 25 per cent aromatics, the remainder consisting of iso- and normal paraffins.

While the invention has been described herein with particular reference to certain specific embodiments thereof by way of illustration, it is to be understood that the invention is not limited to such embodiments except as hereinafter defined in the appended claims.

I claim:

1. In the production of aviation gasoline from the primary hydrocarbon products of a Fischer-Tropsch synthesis process the steps comprising separating the hydrocarbons from C₅ up to about 350° F. end point into a C₅-180° F. fraction and a 180°-350° F. fraction; subjecting the C₅-180° F. fraction in the presence of a normally gaseous hydrogen-rich fraction obtained as defined hereinbelow to hydrogenating conditions of reaction such that substantially all of the olefinic hydrocarbons are converted to paraffinic hydrocarbons; separately recovering from said hydrogenation a light hydrogenate boiling between about 100° and about 300° F. and containing a mixture of normal and isoparaffins; catalytically isomerizing said light hydrogenate under conditions to effect substantial conversion of the normal paraffins to isoparaffins; separately recovering from said isomerization a highly isoparaffinic aviation gasoline blending stock; subjecting said 180°-350° F. fraction to hydroforming conditions of reaction such that substantial cyclization of the hydrocarbons occurs and a normally gaseous hydrogen-rich fraction in an

amount sufficient to offset the hydrogen consumed in the hydrogenation of the aforesaid C₅-180° F. fraction is produced; separately recovering from said hydroforming a highly aromatic aviation gasoline base stock and said normally gaseous hydrogen-rich fraction; and combining the aviation gasoline blending stock with the aviation gasoline base stock.

2. In the production of aviation gasoline from the primary hydrocarbon products of a Fischer-Tropsch synthesis process the steps comprising separating the hydrocarbons from C₅ up to about 350° F. end point into a C₅-180° F. fraction and a 180°-350° F. fraction; subjecting the C₅-180° F. fraction in the presence of a normally gaseous hydrogen-rich fraction obtained as defined hereinbelow to hydrogenation in the presence of a hydrogenation catalyst at a temperature between about 800° and about 950° F., a pressure of about 200 pounds per square inch gauge, and a space velocity between about 1.0 and about 5.0 volumes of charge per volume of catalyst per hour to convert substantially all of the olefinic hydrocarbons to paraffinic hydrocarbons; separately recovering from said hydrogenation a light hydrogenate boiling between about 100° and about 300° F. and containing a mixture of normal and isoparaffins; catalytically isomerizing said light hydrogenate at a temperature between about room temperature and about 350° F., a pressure between about 200 and about 1500 pounds per square inch gauge, and a space velocity between about 0.1 and 5 volumes of liquid feed per volume of catalyst per hour; separately recovering from said isomerization a highly isoparaffinic aviation gasoline blending stock; subjecting said 180°-350° F. fraction to hydroforming in the presence of a hydroforming catalyst at a temperature between about 850° and about 1000° F., a pressure of about 200 pounds per square inch gauge, and a space velocity between about 0.2 and about 1.0 volume of charge per volume of catalyst per hour to convert substantially all of the olefins and a portion of the paraffins to a highly aromatic aviation gasoline base stock and to produce a normally gaseous hydrogen-rich fraction in an amount sufficient to offset the hydrogen consumed in the hydrogenation of the aforesaid C₅-180° F. fraction; separately recovering from said hydroforming said highly aromatic aviation gasoline base stock and said normally gaseous hydrogen-rich fraction; and combining the aviation gasoline blending stock with the aviation gasoline base stock.

3. In the production of aviation gasoline from the primary hydrocarbon products of a Fischer-Tropsch synthesis process the steps comprising separating the hydrocarbons from C₅ up to about 350° F. end point into a C₅-180° F. fraction and a 180°-350° F. fraction; subjecting the C₅-180° F. fraction in the presence of a normally gaseous hydrogen-rich fraction obtained as defined hereinbelow to hydrogenation in the presence of a molybdena-on-alumina hydrogenation catalyst at a temperature of about 900° F., a pressure of about 200 pounds per square inch gauge and a space velocity of about 2; separately recovering from said hydrogenation a light hydrogenate boiling between about 100° and about 300° F. and containing a mixture of normal and isoparaffins; catalytically isomerizing said light hydrogenate over an aluminum chloride-hydrocarbon complex catalyst in the presence of anhydrous hydrogen chloride at 250° F., 850 pounds per square inch gauge, and a space velocity of 2

to effect substantial conversion of the normal paraffins to isoparaffins; separately recovering from said isomerization a highly isoparaffinic aviation gasoline blending stock; subjecting said 180°-350° F. fraction to hydroforming in the presence of a molybdena-on-alumina hydroforming catalyst at a temperature of about 950° F., a pressure of about 200 pounds per square inch gauge and a space velocity of about 0.5 to convert substantially all of the olefins and a portion of the paraffins to a highly aromatic aviation gasoline base stock and to produce a normally gaseous hydrogen-rich fraction in an amount sufficient to offset the hydrogen consumed in the hydrogenation of the aforesaid C₅-180° F. fraction; separately recovering from said hydroforming said highly aromatic aviation gasoline base stock and said normally gaseous hydrogen-rich fraction; and combining the aviation gasoline blending stock with the aviation gasoline base stock.

4. A process for the production of aviation gasoline from the primary products of a Fischer-Tropsch synthesis process which comprises separating said primary products into (1) a C₂ hydrocarbon fraction containing about 15 per cent of C₄ hydrocarbons, (2) a C₄ hydrocarbon fraction containing about 70 per cent of butylenes, (3) a light naphtha fraction containing hydrocarbons from C₅ up to about 180° F. end point, (4) a heavy naphtha fraction boiling between about 180° and about 350° F., and (5) a fuel oil fraction boiling from about 350° F. up to and including wax-like hydrocarbons; subjecting fraction (1) together with the C₂ hydrocarbons obtained from the thermal cracking process hereinafter defined to polymerization in the presence of a polymerization catalyst; separating from said polymerization C₃ hydrocarbons, C₄ hydrocarbons, a heavy polymer gasoline fraction, and a light polymer gasoline fraction; subjecting said light polymer gasoline fraction to catalytic hydrogenation; separately recovering aviation gasoline boiling range hydrocarbons from said light polymer hydrogenation; subjecting fraction (2) together with the C₄ hydrocarbons from said polymerization and C₄ hydrocarbons from isomerization, hydrogenation, hydroforming, and thermal cracking processes hereinafter defined to catalytic alkylation; separating from said alkylation a C₄ hydrocarbon fraction consisting predominantly of normal butane, aviation alkylate having an end point of about 330° F., and motor alkylate having an end point of about 420° F.; subjecting said C₄ fraction consisting predominantly of normal butane to catalytic isomerization; separating from said isomerization a C₄ fraction consisting predominantly of isobutane; subjecting fraction (3) in the presence of a normally gaseous hydrogen-rich fraction obtained from the hydro-forming step hereinafter defined to hydrogenating conditions of reaction; separating from said hydrogenation of fraction (3) C₄ hydrocarbons and a light hydrogenate having an end point of about 300° F.; catalytically isomerizing said light hydrogenate; separating from said light hydrogenate isomerization aviation gasoline blending stock; subjecting fraction (4) to hydroforming conditions of reaction; separating from said hydroforming C₄ hydrocarbons, a highly aromatic aviation gasoline base stock, a heavy hydroformate of the motor gasoline boiling range and a normally gaseous hydrogen-rich fraction; subjecting fraction (5) to thermal cracking reaction condi-

tions; separating from said thermal cracking C₃ hydrocarbons, C₄ hydrocarbons, motor gasoline boiling range hydrocarbons, and heavy fuel oil; combining a portion of the C₃ hydrocarbons from said polymerization with the heavy polymer gasoline, motor alkylate, heavy hydroformate and motor gasoline boiling range hydrocarbons from said thermal cracking; and combining the aviation gasoline from said polymer hydrogenation with the aviation alkylate, aviation gasoline blending stock and aromatic aviation gasoline base stock.

5 A process for the production of aviation gasoline from the primary products of a Fischer-Tropsch synthesis process which comprises separating said primary products into (1) a C₃ hydrocarbon fraction containing a small amount of C₄ hydrocarbons, (2) a C₄ hydrocarbon fraction rich in butylenes, (3) a light naphtha fraction containing hydrocarbons from C₅ up to about 180° F. end point, (4) a heavy naphtha fraction boiling between about 180° and about 350° F., and (5) a fuel oil fraction boiling from about 350° F. up to and including wax-like hydrocarbons; subjecting fraction (1) together with the C₃ hydrocarbons obtained from the thermal cracking process hereinafter defined to polymerization in the presence of a polymerization catalyst; separating products of said polymerization into a C₃ hydrocarbon fraction, a C₄ hydrocarbon fraction (chiefly butanes), a heavy polymer gasoline fraction, a light polymer gasoline fraction, and a polymer naphtha fraction; subjecting said light polymer gasoline fraction to catalytic hydrogenation; separately recovering aviation gasoline boiling range hydrocarbons from said polymer hydrogenation; subjecting fraction (2) together with the C₄ hydrocarbons from said polymerization and C₄ hydrocarbons obtained from butane isomerization, hydrogenation, hydroforming, and thermal cracking processes hereinafter defined to alkylation in the presence of an alkylation catalyst; separating products of said alkylation into a C₄ hydrocarbon fraction consisting predominantly of normal butane, aviation alkylate, motor alkylate having an end point of about 420° F., and polymer boiling above about 420° F.; subjecting said C₄ fraction consisting predominantly of normal butane to catalytic isomerization; recovering from said normal butane isomerization a C₄ fraction consisting predominantly of isobutane; subjecting fraction (3) in the presence of a normally gaseous hydrogen-rich fraction obtained from the hydroforming step hereinafter defined

to hydrogenating conditions of reaction such that substantially all of the olefinic hydrocarbons are converted to paraffinic hydrocarbons and substantially no aromatic hydrocarbons are formed; separating products of said hydrogenation into C₄ hydrocarbons, light hydrogenate, and heavy hydrogenate boiling above about 300° F.; isomerizing said light hydrogenate in the presence of an isomerization catalyst; recovering aviation gasoline blending stock from the isomerized light hydrogenate; subjecting fraction (4) to hydroforming conditions of reaction such that substantial cyclization of the hydrocarbons occurs; separating products of said hydroforming into C₄ hydrocarbons, a highly aromatic aviation gasoline base stock, heavy hydroformate of the motor gasoline boiling range, hydroformate bottoms boiling above about 400° F., and a normally gaseous hydrogen-rich fraction; subjecting fraction (5) together with the heavy polymer gasoline fraction from the polymerization step, the polymer boiling above about 420° F. from the alkylation step, the heavy hydrogenate boiling above about 300° F. from the C₆-180° F. hydrogenation step, and the hydroformate bottoms boiling above about 400° F. from the hydroforming step to thermal cracking reaction conditions; separating products of said thermal cracking into C₃ hydrocarbons, C₄ hydrocarbons, motor gasoline boiling range hydrocarbons, and heavy fuel oil; combining a portion of the C₃ hydrocarbons from said polymerization with the heavy polymer gasoline, motor alkylate, heavy hydroformate, and motor gasoline boiling range hydrocarbons from said thermal cracking; and combining the aviation gasoline from said polymer hydrogenation with the aviation alkylate, aviation gasoline blending stock, and aromatic aviation gasoline base stock.

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