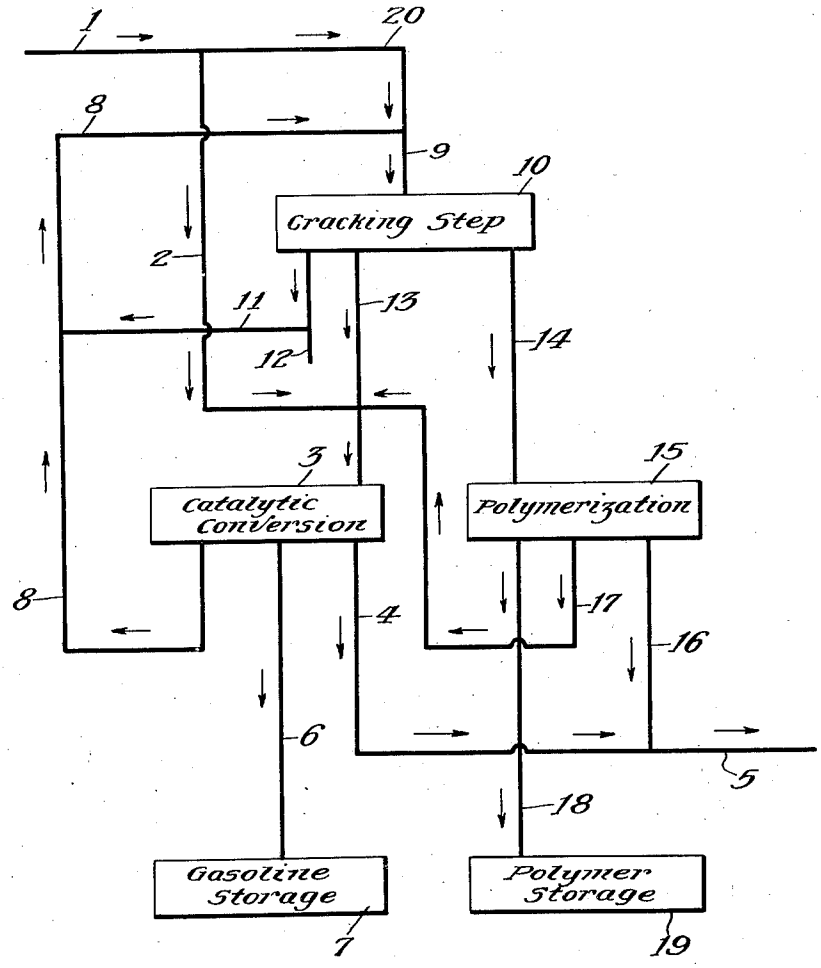
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CATALYTIC CONVERSION OF HYDROCARBONS

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CATALYTIC CONVERSION OF HYDROCARBONS

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1 Claim. (Cl. 196—10)

This invention relates to a process for converting hydrocarbon oils into substantially saturated motor fuels. More particularly, the process relates to the catalytic conversion of hydrocarbon oils of boiling range higher than gasoline. Although the source of hydrocarbon oil converted according to the present process is usually crude petroleum oil, similar oils from other suitable sources such as shale oil, coal tar, etc., may be used.

The motor fuels produced according to the present invention may be used in any internal combustion engine, but they are particularly suitable for use in airplane motors because of their good antiknock properties, particularly in regard to improvement in octane number upon the addition of tetraethyl lead, and because they are substantially olefin-free and meet the strict specifications applied to this type of fuel by the aviation industry.

A number of processes have been developed to increase the yields of gasoline obtainable from petroleum oils among which is the non-catalytic cracking process, wherein oils of greater than gasoline boiling range are subjected to decomposition under suitable conditions of temperature and pressure to convert them to substantial yields of gasoline. In a similar fashion, naphthas and gasolines produced by the straight-run distillation of petroleum oils may be reformed to improve their octane number and thus their value as motor fuel. These reactions are carried out in various non-catalytic cracking operations.

More recently processes have been developed wherein hydrocarbon oils are contacted with suitable catalytic masses and converted into increased yields of motor fuels having better antiknock properties than is usually economically obtainable by the non-catalytic thermal process. Various other types of processes, including polymerization of olefins, alkylation of paraffins or aromatics with olefins, etc., have been developed for use in conjunction with these methods to improve the properties of the finished gasoline and increase the yields of motor fuel obtainable.

It is with improvements in the method of catalytically converting hydrocarbon oils into premium grade motor fuels particularly suitable for use as aviation base fuels that the present invention is concerned.

In one specific embodiment the present invention comprises mixing hydrocarbon oil with olefin-containing gasoline such as may be produced by the catalytic or non-catalytic cracking or reforming of hydrocarbon oils, contacting the mixture with a catalytic mass in a primary conversion step at a temperature within the range of approximately 600°–900° F. and a pressure of substantially atmospheric to 1000 pounds per square inch, separating the gasoline and gas, recycling a portion of the insufficiently converted oil to a secondary conversion step wherein it is converted into substantial quantities of olefin-containing gasoline and gas at a temperature within the range of approximately 800°–1200° F. and a pressure of substantially atmospheric to 2000 pounds per square inch, passing the reaction products to a fractionation step, recycling a portion of the insufficiently converted oil, separating olefin-containing gasoline, mixing said gasoline with the original oil charge and passing the mixture to the primary conversion step as previously described, recovering the gases from the secondary conversion step, subjecting them to catalytic polymerization under conditions whereby the olefins are converted to substantially liquid polymer, combining the liquid polymer with the olefin-containing gasoline and the original hydrocarbon oil charge, and passing the mixture to the primary conversion step.

The catalysts which are useful in the present process may include cracking catalysts of various types, such as synthetic precipitated composites consisting essentially of a major portion of precipitated silica having added thereto relatively minor portions of precipitated refractory oxides to form masses consisting of silica-alumina, silica-zirconia, silica-alumina-zirconia, etc., said composites being substantially free of alkali-metal compounds.

In the following specification, the terms "silica-alumina, silica-zirconia, and silica-alumina-zirconia" masses are used in a broad sense. Inasmuch as the chemical knowledge of the solid state has not been developed perfectly, it is not possible to give the structure of all solid substances. All that can be said definitely concerning these masses is that they contain silicon, oxygen, aluminum, and/or zirconium in combination. Generally speaking, however, all these components indicate more or less low catalytic activity, individually, but in the aggregate display high activity. This activity is not an additive function, it being relatively constant for a wide range of proportions of the components, whether in molecular or fractions of molecular proportions. No one component can be determined as the one for which the remaining components may be considered as the promoters according to conventional terminology, nor can any

components be determined as the support and the others the catalyst proper.

According to the description of the preparation of the preferred catalysts given below, precipitated hydrated alumina and/or hydrated zirconia are composited with precipitated hydrated silica gel, otherwise known as silica hydrogel, and then the composite is washed, dried, and calcined, producing a catalytic mass. However, the different catalysts which may be so produced therefrom do not necessarily give exactly equivalent results.

The cracking step whereby the olefin-containing gasoline is produced may consist of any suitable catalytic or non-catalytic process from which gasoline of high anti-knock value and containing substantial quantities of olefin hydrocarbons may be produced. When using a catalytic cracking step, catalysts similar to those described in the foregoing description may be used, although other catalysts are also suitable under certain conditions. These include acid-treated clays, as well as oxides of alumina and/or magnesium having deposited thereon, promoting oxides such as chromia, iron, vanadium, tungsten oxide, molybdenum oxide, etc. The preferred catalysts, however, are generally of the type described as silica-alumina, silica-zirconia, and silica-alumina-zirconia. The operating conditions under which the cracking step is carried out is within the range of approximately 800°–1200° F. and pressures of substantially atmospheric to slightly super atmospheric, say of the order of 50–200 pounds per square inch.

Any suitable type of contactor may be used, including tubes or reaction chambers having catalyst particles disposed therein.

When non-catalytic cracking is the source of olefin-containing gasoline and the gases used in the polymerization step, any suitable conventional type of non-catalytic thermal cracking process may be used. In general, this type of process consists of a tubular heater followed by a reaction chamber, a flashing zone, and a fractionation step for the recovery of the reaction products. The thermal non-catalytic cracking step is generally carried out within the range of approximately 800–1100° F. and a pressure of 100–2000 pounds per square inch. The catalyst employed in the polymerization step for converting normally gaseous olefins into liquid polymer may be the so-called solid phosphoric acid catalyst or sulfuric acid. A solid phosphoric acid catalyst is made by mixing liquid phosphoric acid with kieselguhr or similar suitable silicious material, forming the mixture into shapes, usually by extrusion methods, drying the shapes, and calcining prior to use. The polymerization step is carried out at a temperature of approximately 275–400° F. and a pressure of approximately 200–1000 pounds per square inch.

When using sulfuric acid, a strength of 60% or more is employed. The polymerization is carried out at a temperature of approximately 80–250° F. and a pressure of the order of 200 pounds per square inch.

The catalytic mass employed for treating the raw oil-cracked gasoline-polymer mixture develops an accumulation of carbonaceous deposits which interfere with the catalytic activity and must be removed from time to time. Reactivation is suitably carried out by heating in the presence of oxygen-containing gas at a temperature of 1000° F. or higher. A similar reactivation method may be carried out if catalytic cracking is used as the source of cracked gasoline.

The accompanying drawing illustrates one embodiment of the present invention in diagrammatic fashion.

Referring to the drawing, the raw oil charge enters the system through line 1 and passes through line 2 to catalytic conversion step 3, wherein it is contacted with a silica-alumina, silica-zirconia or silica-alumina-zirconia cracking catalyst at a temperature within the range of 600°–900° F. and a pressure of substantially atmospheric to 1000 pounds per square inch. Gaseous products are withdrawn through lines 4 and 5 to gas storage. Gasoline containing substantially no olefins is removed through line 6 to gasoline storage 7. Insufficiently converted oil is passed through lines 8 and 9 to cracking step 10, which, as previously mentioned, may comprise catalytic or non-catalytic cracking. A portion of insufficiently converted oil is withdrawn through line 11, which joins with line 8 and returned to the cracking step. Another portion of insufficiently converted oil may be withdrawn through line 12. The gasoline produced in cracking step 10 is removed through line 13 to catalytic conversion step 3. The gaseous hydrocarbons produced in cracking step 10 are removed through line 14 to polymerization step 15 wherein the olefins are converted to liquid polymer. The residual gases are removed through line 16, which joins with line 5. All or a part of the polymer product may be removed through line 17, which joins with line 13 and is thus passed to catalytic conversion step 3. If so desired, a fraction of the liquid polymer such as isooctene, may be withdrawn through line 18 to polymer storage 19. As an alternative, a part of the original charge may be introduced to cracking step 10 by way of lines 1 and 20.

The following examples are given to illustrate the practicability and usefulness of the process, but should not be construed as limiting it to the exact conditions given therein:

Example 1

A Pennsylvania gas oil of 37.0° A. P. I. gravity was processed as described in the above specification, the low temperature catalytic conversion step being carried out at a temperature of 750° F. and a pressure of 100 pounds per square inch. Mixed with this oil was the catalytically cracked gasoline from the higher temperature cracking step which was operated at 930° F. The charge from which the catalytically cracked gasoline was produced comprised the insufficiently converted oil from the lower temperature step. The gas from the cracking step was polymerized in the presence of solid phosphoric catalyst at a temperature of 410° F. and a pressure of 400 pounds per square inch. The polymer was mixed with the raw oil charge and passed to the low temperature catalytic conversion step. The catalyst employed in both high and low temperature conversion steps was a substantially sodium-free silica-alumina-zirconia mass. The substantially olefin-free gasoline of 400° F. end-point was recovered from the low temperature step. It had an octane number of 79, which was increased to 95 by the addition thereto of 6 cc. of tetraethyl lead per gallon. The total yield of gasoline amounted to 81% of the raw oil charge. The gasoline had a bromine number of 1, an oxygen bomb induction period in excess of 24 hours, 1 milligram of copper-dish gum per 100 cc., and a sulfur content of less than 0.01%.

Example 2

A Mid-Continent topped crude oil was charged to a non-catalytic cracking step as indicated by number 10 in the accompanying drawing. The oil was converted to gasoline and gas at a temperature of approximately 925° F. and a pressure of 300 pounds per square inch. A portion of the recycle oil was returned to the cracking step. An overhead distillate including the cracked gasoline was passed to catalytic conversion step 3, which was operated at a temperature of 750° F. and a pressure of 100 pounds per square inch. The insufficiently converted oil was returned to cracking step 10. The gas formed was removed from the system and a substantially olefin-free gasoline was recovered. The process gases from cracking step 10 were catalytically polymerized using solid phosphoric acid catalyst. The polymer product was passed to catalytic conversion step 3, where it underwent substantial conversion to a saturated gasoline of high octane number. A total yield of 59% of gasoline having an octane number of 74 which was increased to 93 by the addition of 6 cc. of tetra-ethyl lead was obtained. The 300° F. end-point fraction of this gasoline met aviation specifications.

We claim as our invention:

A process for producing substantially saturated gasoline of high anti-knock value which comprises combining olefinic gasoline with hydrocarbon oil heavier than gasoline, subjecting the resultant mixture to the action of a cracking catalyst at a temperature of about 600–900° F., whereby to produce gasoline of low olefin content, separating the low olefin content gasoline from conversion products heavier than gasoline, cracking at least a portion of said heavier products at higher temperature than is maintained in the first-mentioned conversion step, thereby forming olefinic gasoline and gas, separating the gasoline and gas and subjecting thus separated gaseous olefins to polymerization, and supplying resultant polymers and olefinic gasoline formed by the cracking of said heavier products to the first-mentioned conversion step.

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