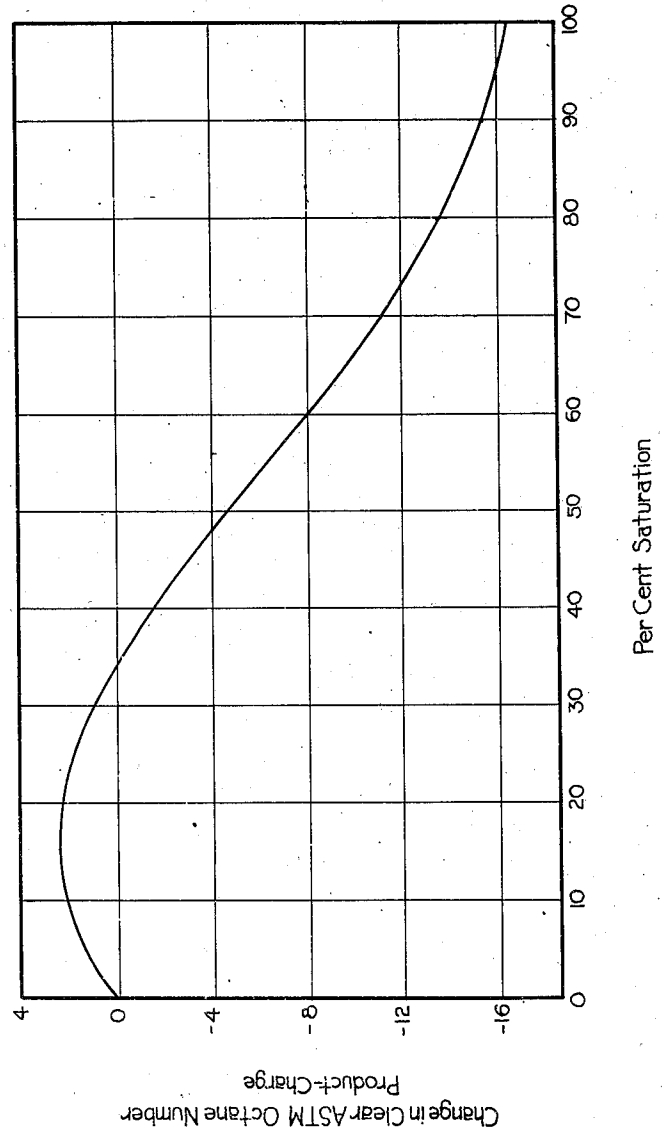
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PRODUCTION OF GASOLINE

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PRODUCTION OF GASOLINE

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2 Claims. (Cl. 196—50)

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This invention relates to the production of high-octane leaded gasolines from thermal gasoline stocks.

Notwithstanding the publicity and importance of catalytic methods the most important means of producing high-octane gasolines is by thermal methods; that is, by the thermal cracking of higher boiling oils (Dubbs, De Florez, Cross, Holmes Manley, T. V. P. processes) and/or the thermal reforming of low octane gasoline stocks. These processes give highly olefinic gasolines having octane numbers generally between about 65 and 74. These octane ratings are not sufficiently high to produce the maximum quantities of finished gasoline meeting the present requirements. (The octane number requirements for most automobile motors has gradually increased and is now about 75.) Thermal stocks of higher octane number could be produced by these thermal methods. However, production costs are greatly increased and the yields of gasoline per barrel of crude oil sharply decline with each additional octane number increase beyond the present range of octane numbers of these stocks. Consequently, it is the practice to obtain the required octane rating of these stocks by the addition of tetra ethyl lead (T. E. L.). In general, the desired octane number of the leaded product is appreciably above the octane rating of the marketed gasoline in order to compensate for a certain amount of blended low-octane components, such in particular as straight run gasoline. The amount and quality of the low-octane components to be blended therefore largely control the octane number required of the leaded thermal gasoline in order to meet the prevailing octane number specifications.

These thermal gasoline stocks are quite highly unsaturated and require considerable refining before they can be leaded and blended. They may be refined by any one of a number of refining treatments such as the conventional treatments with sulfuric acid or clay, but these treatments incur large refining losses. A preferred method for refining such thermal stocks is by hydrogenation. A hydrogenation treatment destroys the small amounts of diolefins and other gum-forming constituents with substantially no treating losses. While very mild treatment has been quite successful in some cases it has been frequently reported that refining by hydrogenation results in an excessive depreciation of the octane number of the stock. This has been postulated to be due to the hydrogenation of olefins. In order to counteract this depreciation of the octane number it is usually recommended to effect the hydrogenation at a relatively high temperature to obtain a certain amount of catalytic reforming simultaneously with the hydrogenation. However, hydrogenation at reforming temperatures is coupled with short catalyst life and greater expense and is not entirely satisfactory.

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It has been found that in the refining of thermal gasoline stocks (i. e. olefinic gasoline stocks produced by thermal methods such in particular as thermal cracking and thermal reforming) by hydrogenation the octane number of the product goes through a maximum as the percentage of saturation (i. e. the percent decrease in bromine number due to hydrogenation) is increased and then declines at a relatively rapid rate. This point of maximum octane number occurs at a relatively low percentage of saturation. The hydrogenation can be carried out to this point of maximum octane number and the octane number of the refined product increased to the desired level by the addition of T. E. L. It has now been found, however, that this method of operation is not the most advantageous. It has been found that the optimum saturation to be effected by the hydrogenation treatment is a function of the desired octane number of the finished product and does not correspond to this maximum octane number.

According to the process of the present invention, thermal gasoline stocks from petroleum are hydrogenated to an optimum saturation which is a function of and dependent upon the desired octane number of the leaded product. Stated in another way, the hydrogenation is carried out to a specific degree of saturation which allows a refined product of any given desired octane number to be obtained with the minimum amount of T. E. L. The relationship between the optimum percentage of saturation (S) and the desired octane number is given approximately by the following formula:

$$S=11+4.7(N'-N)\pm5$$

wherein S is the percent saturation as hereinbefore defined, N' is the desired ASTM octane number of the leaded product, N is the ASTM octane number of the thermal stock treated, and ±5 is a small allowable variation to allow for slight differences between different feed stocks.

In order that the invention may be better understood, reference is had to the attached drawing wherein there is shown by means of a graph the change in ASTM octane number of a 400 end point cracked gasoline from Dubbs cracking

of West Texas oil (bromine number 75) at various degrees of saturation (unleaded). The hydrogenation in this particular case was carried out with a tungsten sulfide catalyst promoted by a small amount of nickel sulfide at a temperature of 800° F. and a pressure of about 750 p. s. i. The percentage saturation was controlled by controlling the liquid hourly space velocity and the partial pressure of hydrogen. Referring to the graph, it will be seen that the octane number rises relatively sharply to a maximum and then drops sharply with increasing saturation so that at complete saturation the octane number has fallen over 18 points. Similar curves can be determined for leaded gasolines produced from such cracked gasoline stocks. However, the maximum points of the curves for various particular maximum octane numbers, corresponding to minimum T. E. L. requirements, shift to the right with increasing octane number requirements. The path of this shift is expressed by the above-given formula.

The process of the invention is generally applicable for the production of leaded gasoline from thermal gasoline stocks such as described above. Such stocks have bromine numbers of at least 50.

The hydrogenation of the thermal gasoline stocks may be carried out with any of the hydrogenation catalysts commonly used for the hydrogenation of petroleum fractions. Particularly suitable catalysts are tungsten sulfide, nickel sulfide, molybdenum sulfide, tungsten sulfide promoted with a sulfide of iron, cobalt or nickel, and cobalt molybdate. Various other suitable catalysts are discussed in U. S. Patent No. 1,890,434 and British Patent 335,511.

The hydrogenation may be carried out with the gasoline stock in the vapor phase, in the liquid phase, or in mixed phase, and under various conditions of temperature, pressure and space velocity commonly used for hydrogenation of gasoline stocks. The temperature, for example, may be advantageously between 400 and 850° F. and the pressure may be advantageously between 100 and 1000 p. s. i. The degree of saturation may be controlled by control of any one or combination of the operating variables such as the catalyst activity, space velocity, temperature and pressure. A preferred variable for control is the liquid hourly space velocity either alone or in combination with hydrogen pressure. The conditions, in any case, are so controlled for the individual catalyst, feed stock and desired octane number that the bromine number is decreased by an amount satisfying the above equation.

Example I

A California pressure distillate fraction boiling essentially between 110° F. and 210° F. and having a bromine number of 92 was hydrogenated with a nickel sulfide-tungsten sulfide catalyst in which the nickel sulfide was the predominant constituent. The temperature was 700° F.; the pressure was 700 p. s. i., and the molal ratio of recycled gas (largely hydrogen) to hydrocarbon feed was about 7:1. The liquid hourly space velocity was varied between 10 and 55 to obtain

the desired percent saturation. The original ASTM octane number was 73.8. The maximum clear ASTM octane number occurred when the saturation was carried to about 8%. However, for a gasoline of ASTM octane number of 77 the optimum saturation was found to be about 27%. For a gasoline of ASTM octane number of 75 the optimum saturation was found to be about 14%.

Example II

A thermally cracked gasoline boiling essentially between 200° F. and 300° F. and having a bromine number of 87.2 and an ASTM octane number of 70.4 was hydrogenated at temperatures between 700 and 800° F., pressure between 426 and 625 p. s. i., molal ratio of recycled gas (largely hydrogen) to hydrocarbon feed of about 7:1 and liquid hourly space velocities between 2.0 and 27.4 to control the percent saturation. It was found that the maximum clear ASTM octane number occurred at about 9% saturation. However, when a gasoline of 75 ASTM octane number was desired it was found that the optimum saturation was about 32%. When a gasoline of 73 ASTM octane number was desired the optimum saturation was found to be about 21%.

I claim as my invention:

1. In a process for the production of a leaded gasoline having an improved ASTM octane number from a thermal gasoline stock having an ASTM octane number N by hydrogenation of said thermal gasoline stock and addition of tetraethyl-lead, the improvement which comprises carrying out the hydrogenation of the thermal gasoline stock under conditions to effect such a percentage saturation of the stock S that

$$S=11+4.7(N'-N)\pm5$$

wherein N' is the desired ASTM octane number of the hydrogenated and leaded product.

2. Process according to claim 1 in which the hydrogenation is carried out at a temperature between about 400° F. and 850° F. and the percentage saturation is controlled by varying the space velocity.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,202,401	Rosen	May 28, 1940
2,367,527	Ridgway	Jan. 16, 1945
2,371,355	Ross et al.	Mar. 13, 1945
2,382,910	Pinkston	Aug. 14, 1945

FOREIGN PATENTS

Number	Country	Date
423,001	Great Britain	Jan. 23, 1935

OTHER REFERENCES

II me Congr. mond. Petrole, vol. 2, pages 271–275 (1937) (article by Kudo et al., "On the Hydrogenation of Cracked Gasoline").