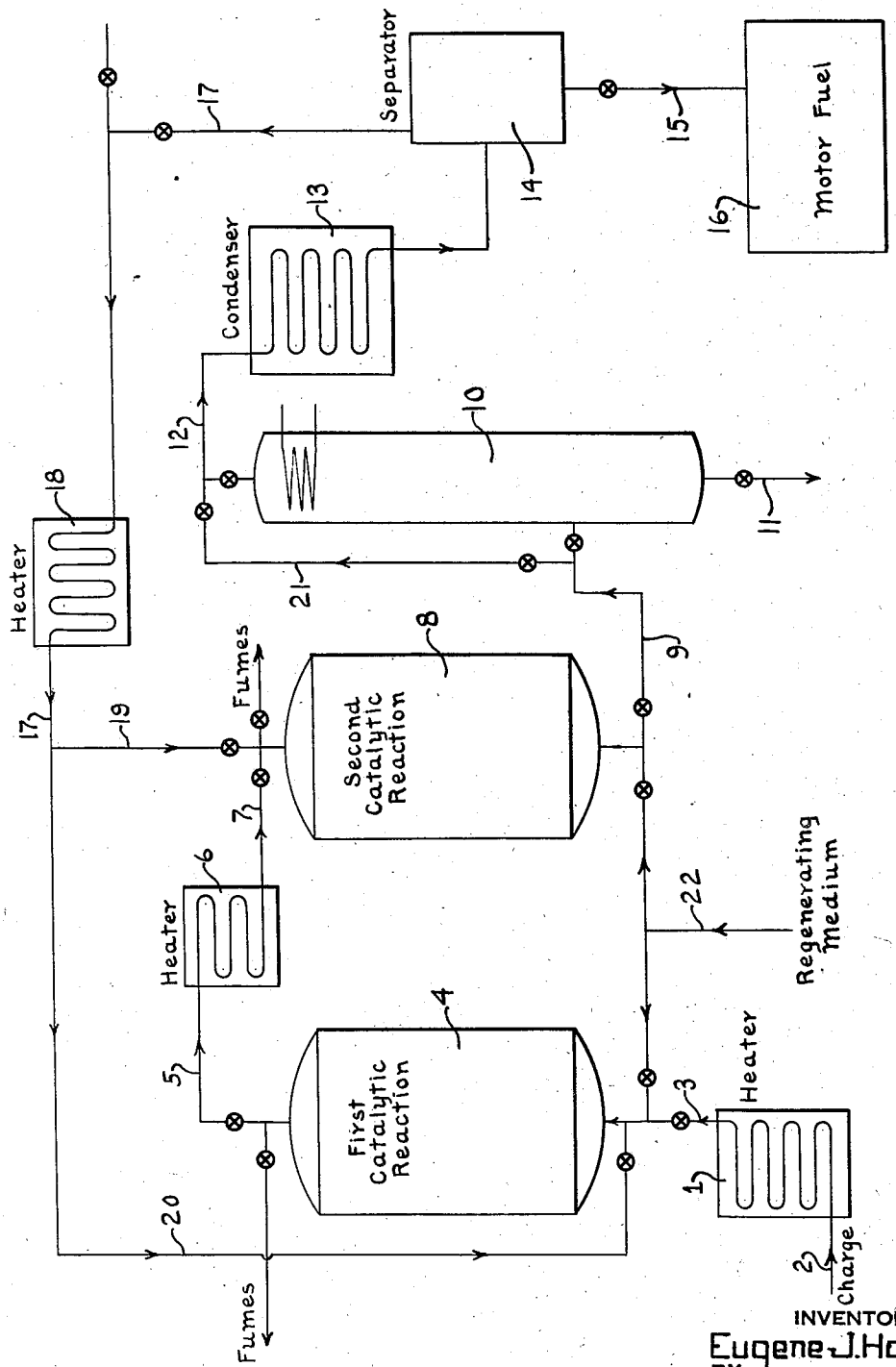
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HIGH GRADE MOTOR FUEL FROM STRAIGHT RUN AND SIMILAR HYDROCARBONS

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HIGH GRADE MOTOR FUEL FROM STRAIGHT RUN AND SIMILAR HYDROCARBONS

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Internal combustion engines of the present day demand a high grade of motor fuel, the principal requirements being high anti-knock value, good road performance, volatility, and low sulphur content.

The oil refiner has been faced with the problem that a large part of the hydrocarbon stock in the gasoline boiling range available to him is not directly useable for motor fuel. In practically all crude oils today, all the straight run gasoline, as well as the naphtha, is below the octane rating of most of the gasoline sold. Hence, to meet the increased demand for motor fuels of good quality, the refiner has been forced to give more and more attention to means to bring his low grade naphthas and gasolines to meet market specifications. Reforming in general is an expensive operation, usually involving heavy losses, especially when effected in a single pass operation. Attempts to reduce losses have led to complications in process and greater expense in equipment. To the refiner, the problem is rendered still more complex from an economical standpoint, since he must consider the various stocks which may be available to him in the light of various ways in which improvement can be obtained. He must first consider the possibility of securing better octane rating by the addition of anti-knock agents, such, for example, as tetraethyl lead. When the desired octane rating can be so obtained, the motor fuel seldom has the other desired qualities of volatility and good road performance required or desired in today's motor fuel. There is, however, the possibility of reaching market requirements partly by reforming and partly by the use of addition agents. But here again, when the product is tested, it is usually discovered that there is little or no spread between the octane ratings by research method and by C. F. R. motor method, for the wider the spread the better the road performance. Hence it may well be that duplication of high grade gasolines soon to be on the market will not be possible by the addition of anti-knock agents and that it will be advantageous for the refiner to invest money in reforming plants and to market a product which is not leaded.

Intensive work has been performed by applicant over a long period, for the purpose of improving low grade hydrocarbons and naphthas in the temperature range of approximately 200° to 420° F. in an economical manner, i. e. with the smallest possible loss in liquid and with a minimum amount of equipment. Much of his work is disclosed in his U. S. Patent No. 2,141,185, which issued December 27, 1938. The present application represents, in certain respects, a further development of and improvement on the operations disclosed and claimed in said patent. In fact the present invention is a more complete solution of the problem of improving low grade naphthas in volatility, in octane rating, in reducing their sulphur content, and has been found to be applicable to all naphthas.

The invention contemplates the improvement of the naphtha to desired extent in a once through operation with a minimum loss of liquid yield. For most charging stocks it involves two steps or stages which follow each other, usually without any intermediate fractionation or condensation. In the first stage, both the volatility and the octane of the naphtha are improved and this is accomplished in a splitting operation, with very small gas make and little or no loss of liquid yield. Usually the liquid yield of this stage is equal to that of the charge, but often it is slightly more, as 100 to 103%. The second stage completes the desired increase in octane rating, as up to 75 or 80 octane (C. F. R. motor method) by a dehydrogenating reaction which is conducted so as to make little or no change in the boiling range of the hydrocarbons charged thereto. By preference, both reactions are promoted by catalysts, since catalytic operations give the greatest flexibility and the best liquid yields. Moreover, reaction temperatures can be kept low, as not over 925° F. Two catalysts are preferably used in series at different temperatures and producing different effects on the charge, but the character and extent of the reactions are individually controlled, and the effects are cumulative. Both reactions give octane increase, and, in most instances, it is preferable to so conduct the operation that much the same increase in octane is produced in each. The first reaction takes place at relatively low temperature, as of the order of 700° to 750° F., or in the range of 650° to 800° F. At such temperatures and at suitable feed rates, very little gas is produced, there is a very small coke deposit, and practically no loss of liquid. Usually, the liquid yield is about equal to or somewhat above that of the charge, as between 99% and 103%, due to the splitting reaction, which produces a large percentage, as of the order of 20 to 30%, of material lower boiling than the charge, thereby improving the volatility; for example, if the charge boils between 280° and 410° F., the product obtained from the splitting operation contains 20 to 30% of gasoline boiling below 280° F. The raising of the A. P. I. gravity effected during this reaction accounts for the liquid re-

covery of 100% or more. The reaction also gives an increase of octane of some 10 to 25 points by the production of such lighter material, which is mostly of the iso paraffin type, the average of the lighter material so produced being 60 to 80% iso paraffins. The products of the first reaction are then sent, at higher temperature, to a dehydrogenating catalyst which has little or no effect on the boiling range. The operating conditions of this reaction are adjusted to complete the increase in the octane number to the desired rating, and the octane rise here may range from 10 up to about 50 points. In this reaction there is a loss, which varies with the severity of the selected operating conditions, due to gas and coke formation and to the lowering of the A. P. I. gravity of the fuel by dehydrogenation. The reaction is conducted between 850° and 925° F., as around 875° F. for example. The gas produced is 70 to 80% hydrogen and is directly useable when added to the charge to reduce coke formation on the catalyst, as taught in the aforesaid U. S. Patent No. 2,141,185, and is further useful to assist in the regeneration of the catalyst. Both operations reduce the sulphur content of the charge. Hence, by combining the two operations, a solution of the problem of reforming naphthas, with high liquid recovery and without the expense and disadvantages of the use of addition agents, becomes a commercial reality.

It must be kept in mind that the charging material which is to be improved is already in the gasoline boiling range, and that it is, as a rule, highly resistant to chemical transformation giving an increase of from 30 to 80 points of octane. Therefore, for greatest success, catalysts of extremely high activity are required. Also, for an economical operation, the catalysts must be kept at high activity through frequent regenerations, which should take place while the catalysts remain in place. These two requirements of high sustained activity and stability to frequent alternating reactions of reforming and regeneration impose a severe test upon catalytic materials to be used. Hence it is not merely sufficient to find a catalyst or a combination of catalysts which together will improve the octane as well as other qualities of naphtha, or to establish the best conditions of operation for the use of the catalysts. The activity and strength of the catalysts become of primary importance, because they must be capable of regeneration in situ, before the process can be of any value, and they must be practically stable in yield and quality of products for a period of at least six months, if the process is to be economical. For proper operation, the catalyst must be in the form of bits, fragments, or molded pieces. It must not lose its shape, change its size, or crumble into powder. Many catalysts have been prepared with an original strength which was apparently suitable, but which gradually lost their strength, when used under the severe conditions of operation, some after a few hours, others after a few days, a few weeks, or a few months.

The catalyst for the first reaction zone should be a catalyst of as high activity as possible. Silica alumina blends or compounds of a high degree of purity, with or without the addition or inclusion of small quantities of other active materials, including metal oxides such as listed below, are suitable. The most active catalysts for this reaction so far developed have been synthetic materials produced in the hydrous state, for example, by interreaction or coprecipitation of suitable substances, such as sodium silicate and an aluminum compound, as sodium aluminate or an aluminum salt, under controlled pH conditions and followed by suitable treatment to reduce the content of alkali metal to a minimum, as disclosed, for example, in the copending applications of John R. Bates, Serial Nos. 170,648 and 174,966, filed October 23, 1937 and November 17, 1937, respectively, now U. S. Patents 2,283,172 and 2,283,173.

The catalysts for the second or dehydrogenating reaction may comprise any suitable materials for promoting such a reaction. Among the best materials for this purpose are vanadium, molybdenum, chromium and tungsten, although others, such as iron, lead, copper, nickel and manganese, may also be utilized, or combinations of any of the above. The catalysts normally contain from 5 to 30% of such metals or metal compounds, and they may be prepared in any known or suitable manner, as under hydrous reaction conditions including the methods referred to above for the catalysts for the first zone. They may also be prepared by depositing the metals in and on previously prepared carriers which have the necessary strength and which may be either active or inert.

As indicated previously, the catalysts for both the reaction zones must have sufficient strength to maintain their size and shape during continued and prolonged use. When preformed carriers are utilized on which catalytic material is deposited, it is important to see that they have the proper strength and stability. When the carrier is inert or of low activity, the required strength is readily obtained through the use of heat. When the catalyst is formed synthetically by interreaction or coprecipitation from solutions, difficulties are often encountered in preparing the contact material with suitable strength and stability. In such cases, strength can be obtained without using a degree of heat which would injure the adsorptive properties of the catalyst material, by mixing and molding the gels or precipitates, as disclosed in U. S. Patent No. 2,146,718, issued to G. R. Bond, Jr., on February 14, 1939, or by making dried gels fluid and casting the same in pellets, as disclosed in the copending application of H. A. Shabaker, Serial No. 209,070, filed May 20, 1938, now U. S. Patent 2,299,768, or, in some instances, by adding to the mix a small amount of high swelling bentonite, as disclosed in the copending application of J. R. Bates and G. R. Bond, Jr., Serial No. 270,202, filed April 26, 1939, now U. S. Patent 2,283,174. Strength of at least 1800 grams applied to a 4 millimeter pellet through a knife edge is required, and the pellets must maintain such strength throughout the entire period of use.

Moderate pressures promote both reactions, as up to about 300 pounds per square inch. Since practical operation passes the products of the first reaction directly to the second reaction zone, the same pressure is usually employed for the entire operation, a satisfactory pressure being of the order of 150 pounds per square inch. Losses are reduced by mingling gaseous material with the charge to either or both of the zones, in the form of steam or refractory gases, such as methane, ethane, propane, butane, hydrogen or mixtures of any of these, as taught in my previous Patent No. 2,141,185, issued December 27, 1938, since such gases tend to inhibit secondary reactions and to keep down the deposit of contami-

nants upon the catalyst. The fixed gases from the dehydrogenating operation are entirely suitable for this purpose, and they may be tapped back into the feed lines in any suitable or desired ratio producing a desirable and advantageous partial pressure effect in either or both zones. The recycling of sufficient gas to give approximately a mol to mol ratio of hydrogen to hydrocarbons, in the dehydrogenating zone, gives a good operation.

Rates of feed will depend upon the character of the charging stock and the degree of activity of the catalyst used, especially in the first or splitting zone. Since this zone is utilized to lighten the gravity of the charge and to increase the volatility of the same, with minimum production of gas or loss of liquid yield, the feed rates will be high, as of the order of 3 to 1 (three volumes of charge, measured as liquid, per hour per volume of catalyst) to 10 to 1. The conditions in the second or dehydrogenating zone will, in most instances, be more severe, because here the refiner must impose operating conditions which will bring the products from the first zone up to the desired octane rating. Hence the feed rates will be lower, as from about 1 to 1 to about 2 to 1.

Any suitable or desired form and arrangement of apparatus can be utilized in practising the invention. As indicated in the diagrammatic disclosure in the single figure of the accompanying drawing, the essential features of apparatus are a heater 1, to which the naphtha is charged by line 2, preferably in partially preheated condition. In the heater, the naphtha is vaporized and raised to desired temperature of from 600° to 800° F. and passed, by line 3, to converter 4 containing the catalyst for effecting the first or splitting reaction. The products leave converter 4 by line 5, pass preferably through heater or heat exchanger 6, where the temperature is raised to from 850° to 950° F. (care being taken to avoid thermal reforming), and then sent, by line 7, into converter 8, which is filled with a suitable dehydrogenating catalyst for effecting the second or dehydrogenating reaction. The products leave converter 8 by valved line 9, which leads to a fractionating column 10 from which any products boiling outside the desired range may be withdrawn through bottom line 11, while the desired products pass overhead by line 12 to condenser 13 and thence into separator 14, from which the liquid products pass, by line 15, to storage in tank 16 or to other treatment or use. Fixed gases from separator 14 leave by line 17, and any desired or required quantity of such gases may be sent through heater 18 and thence by branched lines 19 and 20 to be added to the products entering dehydrogenating zone 8 or to the charge entering the first splitting zone 4. When the products of the operation do not produce heavier hydrocarbons, or when their removal is not required, fractionator 10 may be by-passed by means of valved line 21.

Each of the reaction zones may contain one or several converters, so that the operation may be intermittent or continuous as desired. When it is continuous, one or more of the converters in each reaction zone will be in regeneration while at least one converter in each zone is on stream. The regenerating medium, usually air or an oxygen containing gas, may be supplied by line 22, from which valved branches lead to each of the converters. Fumes of regeneration will leave from the opposite end of the converter by suitable lines, as indicated. For the dehydrogenating catalyst at least, the regeneration may include a reducing step and the gases from separator 14 may be utilized for this purpose. If necessary or desirable, a purifier (not shown) may be provided in line 17 before or after heater 18, to render the gases suitable for use both to furnish an atmosphere of fixed gas during on stream operation and for reduction during regeneration.

The converters 4 and 8 may be of any suitable or desired type, either arranged for straight through flow of reactants or uniform distribution of charge in and throughout the catalytic mass and uniform removal of products from all parts of the mass. For best operation, efficient temperature control of the catalytic mass is important, in order that it shall not fall below reaction temperature during on stream operation, or rise so high as to impair the catalyst during regeneration. Suitable forms of converters are disclosed, for example, in U. S. Patents Nos. 2,078,947, 2,078,948, 2,078,949 and 2,078,950, all issued on May 4, 1937. It is also possible to combine both reactions in a single converter structure, after the manner disclosed, for example, in my copending applications Serial No. 171,700, filed October 29, 1937 (Patent No. 2,193,816 issued March 19, 1940), and Serial No. 202,689 now U. S. Patent 2,276,307, filed April 18, 1938.

The following examples are given to indicate the use of the invention with various charging stocks. In all instances stable, highly active, synthetically made silica-alumina catalysts of high purity with a silica to alumina ratio of about 12:1 were used in the first reaction zone, and molybdenum catalysts comprising at least 7% molybdenum incorporated in a stable carrier in the second or dehydrogenating zone. All the catalysts had the required degree of hardness. The operations were conducted under a pressure of 150 pounds per square inch, with hydrogen added to the charge to the second zone in substantially mol to mol ratio. Distillation data given in the examples are Engler according to the ASTM method.

First example

A naphtha from East Texas crude with a boiling range of 244–410° F. (10% over at 274° F., 50% at 314° F. and 90% at 377° F.), an A. P. I. gravity of 50° and an octane rating of 40.8 C. F. R. motor method) was charged at reaction temperature and at a rate of about 6:1 (six volumes of charge, liquid measure, to one volume of catalyst) to the first catalytic reaction zone which was maintained at about 750° F., giving a very low formation of gas and of coke. The liquid recovery from this reaction was 100%, and the products had an initial boiling point of 90° F., were 10% over at 184° F., 50% over at 295° F. and 90% over at 379° F.; their A. P. I. gravity was 54.9° and their octane rating 56.7 (C. F. R. motor method). They were charged without intermediate fractionation but with an increase in temperature to the second or dehydrogenating zone maintained at approximately 875° F., at a rate slightly above 3:1. The liquid recovery was 88% and the products had an A. P. I. gravity of 50.6° with an initial boiling point of 85° F., 10% over at 167° F., 50% over at 285° F., and 90% over at 376° F. The octane number of the products was 78.7 (C. F. R. motor method) and 86.2 (C. F. R. research method).

Second example

A naphtha from Coastal (grade B) crude with a boiling range of 198–410° F. (10% over at 238°

F., 50% at 293° F., and 90% at 372° F.), an A. P. I. gravity of 49.2° and an octane rating of 57 (C. F. R. motor method) was subjected to substantially the same two stage operation as in the first example. From the first reaction zone, the liquid recovery was 99.8%, and the products had an initial boiling point of 101° F., were 10% over at 181° F., 50% over at 275° F., and 90% over at 392° F.; their A. P. I. gravity was 54.7° and their octane rating 67.9 (C. F. R. motor method) and 71.3 (C. F. R. research method). From the second or dehydrogenating zone, the liquid recovery was 90.4% and the products had an A. P. I. gravity of 51° with an initial boiling point of 95° F., 10% over at 165° F., 50% over at 264° F., and 90% over at 372° F. The octane number of such final product was 78.6 (C. F. R. motor method) and 85.2 (C. F. R. research method).

Third example

A naphtha from Michigan crude having a boiling range of 188–405° F. (10% over at 214° F., 50% over at 274° F., and 90% over at 354° F.), an A. P. I. gravity of 59.4, and an octane rating of 21 (C. F. R. motor method) was submitted to the two-stage reaction. It was charged to the first zone at a rate of about 6:1, the catalyst being maintained at about 750° F. The liquid recovery from the first reaction was 99.6%. The products had an initial boiling point of 99° F., with 10% over at 172° F., 50% over at 257° F., and 90% over at 353° F; the A. P. I. gravity was 62.5° and the octane was 32.7 (C. F. R. motor method). Without intermediate fractionation, they were charged to the second or dehydrogenating zone maintained at a temperature of about 900° F., the charging rate being slightly in excess of one volume of hydrocarbons, measured as liquid, to one volume of catalyst. The liquid recovery was 85% and the final products had an A. P. I. gravity of 58.5°, with an initial boiling point of 95° F., 10% over at 160° F., 50% over at 240° F., and 90% over at 351° F. The octane number was 74.8 (C. F. R. motor method).

Fourth example

Another naphtha from Michigan crude, with a boiling range of 242–408° (10% over at 276° F., 50% over at 325° F., and 90% over at 383° F.), with an A. P. I. gravity of 54.9° and an octane rating of 6 (C. F. R. motor method) was subjected to the two-stage reaction under substantially the operating conditions set forth in the third example. The liquid recovery from the first reaction was 99.2% and the product had an initial boiling point of 90° F., with 10% over at 193° F., 50% over at 304° F., and 90% over at 387° F., with an A. P. I. gravity of 59.7° and an octane rating of 25.5 (C. F. R. motor method). The subsequent dehydrogenating reaction gave a liquid recovery of 80.6%, and the final product had an A. P. I. gravity of 53.9°, with an initial boiling point at 91° F., 10% over at 161° F., 50% over at 283° F., and 90% over at 379° F. The octane number of this final product was 75 (C. F. R. motor method).

Gas made in the dehydrogenating stage from the first example is typical, and its analysis on the mol percent basis is as follows:

H_2	74	C_3	5.2
C_1	8.5	C_4	6
C_2	6.3	C_5	trace

From the above examples it will be apparent that high yields of high octane motor fuel can be prepared from any naphthas in the boiling range of 200° to 420° F., regardless of the octane rating of the original charge, and that the final product has substantially the A. P. I. gravity of the original charge. This accomplishment with relatively small loss is due to the fact that a substantial octane increase and proper adjustment of the volatility of the charge is produced in the first or splitting reaction with practically no loss of liquid, so that actual losses from the recoverable liquid standpoint are confined to the dehydrogenating zone, where operating conditions are adjusted to bring the final product to the octane rating desired. When the required octane increase is small, it will be apparent that only the first or splitting reaction need be used to make the improvement in the naphtha, and, at the same time, the volatility and the road performance of the product will be enhanced. All this is accomplished with little, if any, loss and often with a slight gain in liquid. In fact, this first reaction is most attractive from the operative as well as the economical aspect, because of low temperatures, practical absence of gas make and small deposit left on the catalyst. When the operating conditions of the splitting operation are made severe to effect a greater octane increase, gas and coke formation may be minimized through a partial pressure effect on the charge by adding to the latter a suitable amount of inert gas, such as any of those specified in my aforementioned Patent No. 2,141,185. By combining the dehydrogenating step with the splitting step, it is clear that the two reactions complement each other in bringing any naphtha stock to desired octane rating. In practice, the same overall pressure will be utilized for both reaction stages of the operation, but even this lends itself to independent pressure control of each reaction through the addition of inert gas, such as the gas made in the dehydrogenating reaction, to the charge to the second or to both reaction zones, through modification and adjustment of the partial pressure of the hydrocarbons. The operating conditions for any stock are readily determined by a few test runs in small laboratory apparatus. The primary factor to be established is the rate, whereupon final adjustment in operating conditions to give desired characteristics to the motor fuel may be made in temperature, rate or pressure.

I claim as my invention:

1. Process of making high grade motor fuel from naphthas in the boiling range of 200 to 420° F., which comprises subjecting the naphtha in vapor phase in the temperature range of 650 to 800° F. to a splitting reaction, adjusting the operating conditions to increase volatility and to give an octane increase of at least 10 points substantially without gas make or loss of liquid yield and then subjecting the products without intermediate fractionation and in the temperature range of 850 to 925° F. to a catalytic dehydrogenating reaction to effect further increase in octane rating without any substantial change in the boiling range of said products, the feed rate to each of said reactions being maintained in excess of 1:1 and the rate to the first reaction higher than to the second reaction.

2. Process of making high grade motor fuel from naphthas in the boiling range of 200–420° F., which comprises subjecting the naphtha charge in vapor phase in the temperature range of 650 to 800° F. to the action of a splitting catalyst of high activity maintained within a reaction zone, withdrawing products from said zone

and directly subjecting them in the temperature range of 850 to 925° F. to the action of a dehydrogenating catalyst in a second reaction zone, maintaining both reaction zones at substantially the same pressure up to 300 pounds per square inch while maintaining the feed rate to each zone in excess of 1:1 and the rate to the first zone higher than to the second zone, whereby a considerable octane increase is obtained in the products from the first zone with substantially no gas or liquid loss and the initial boiling point is lowered substantially while a further increase in octane is obtained in the second zone without any substantial change in the boiling range of the products.

3. Process of making high grade motor fuel from naphthas in the boiling range of 200–420° F. which comprises subjecting the naphtha charge in vapor phase in the temperature range of 650 to 800° F. to the action of a splitting catalyst of high activity maintained within a reaction zone, withdrawing products from said zone and directly subjecting them in the temperature range of 850 to 925° F. to the action of a dehydrogenating catalyst in a second reaction zone, maintaining both reaction zones at substantially the same pressure up to 300 pounds per square inch while maintaining the feed rate to each zone in excess of 1:1, removing fixed gases from said second zone and supplying them at least to the first zone in order to provide a shorter vapor contact time therein than in the second zone whereby an increase in octane of at least 10 points is obtained in the products from the first zone with substantially no gas or liquid loss and the initial boiling point is lowered substantially while a further increase in octane is obtained in the second zone without any substantial change in boiling range of the products.

4. Process of making high grade motor fuel from naphthas in the boiling range of 200 to 420° F. which comprises subjecting the naphtha charge in vapor phase in the temperature range of 650 to 800° F. to the action of a splitting catalyst of high activity maintained within a reaction zone, withdrawing products from said zone and directly subjecting them at reaction temperature to a dehydrogenation catalyst in a second reaction zone, maintaining both reaction zones at substantially the same pressure up to 300 pounds per square inch while maintaining the feed rate to each zone in excess of 1:1 and the rate to the first zone higher than to the second zone, whereby at least 10 points octane increase is obtained in the products from the first zone with substantially no gas or liquid loss and the initial boiling point is lowered substantially while a further increase in octane is obtained in the second zone without any substantial change in the boiling range of the products.

5. Process for making high grade motor fuels which comprises subjecting a naphtha within the boiling range of 200 to 420° F. and with an octane rating of below approximately 50 (C. F. R. Motor Method) in vapor phase at a temperature between 650 and 800° F. to the action of a splitting catalyst maintained within a reaction zone and highly active for cracking higher boiling hydrocarbons to hydrocarbons within the gasoline boiling range, feeding the charge to the zone at a rate between 3:1 and 10:1 and maintaining a pressure within the zone of up to 300 pounds per square inch, correlating the pressure and the rate of feed of the charge to provide a short time of contact of the charge in the reaction zone, whereby the volatility of the products from the reaction is increased by producing of the order of 20 to 30 percent material boiling below the initial boiling point of the charge and an octane increase of at least 10 points is obtained with substantially no gas or liquid loss.

6. Process of making high grade motor fuel from naphthas in the boiling range of 200–420° F. which comprises subjecting the naphtha charge in vapor phase in the temperature range of 650° to 800° F. to the action of a splitting catalyst of high activity maintained within a reaction zone, feeding the charge to the zone at a rate between 3:1 and 10:1 and maintaining a pressure within the zone of up to 300 pounds per square inch, correlating the pressure in accordance with the rate of feed of the charge to provide a short contact time of the charge in the reaction zone, whereby at least 10 points of octane increase is obtained with substantially no gas or liquid loss while the A. P. I. gravity is raised and the volatility of the products is improved, then directly subjecting the products in the temperature range of 850 to 925° F. to the action of a dehydrogenating catalyst in a second reaction zone, correlating the rate of feed of the products and the pressure in the second reaction zone to increase the contact time of the products in that zone over the contact time of the charge in the first mentioned zone whereby a further increase in the octane rating of the products is obtained without any substantial change in the boiling range of said products.

EUGENE J. HOUDRY.