

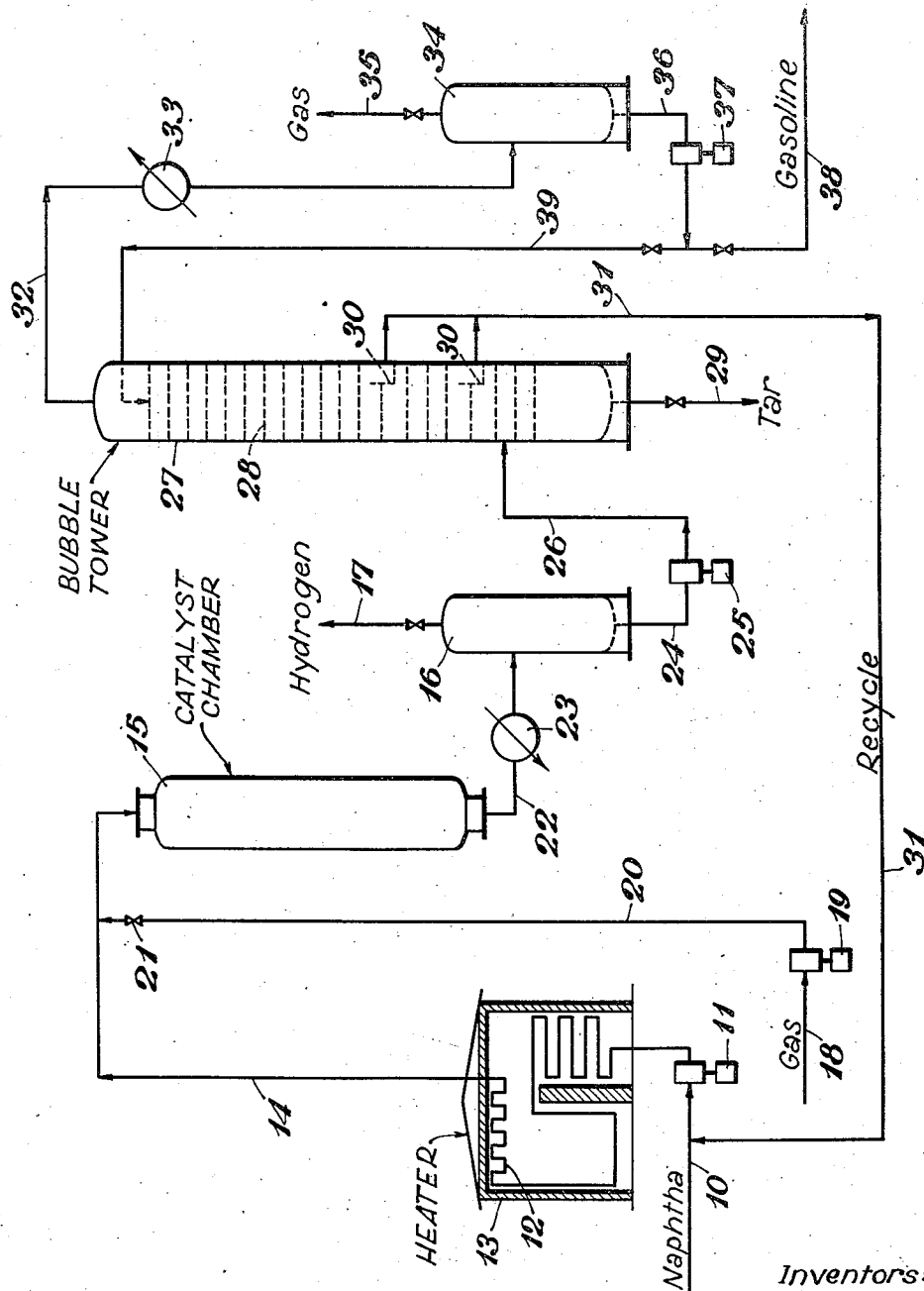
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MOTOR FUEL

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MOTOR FUEL

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This invention relates to the process of treating normally liquid hydrocarbons or mixtures thereof to increase their anti-knock properties, and more particularly to the catalytic dehydrogenation of normally liquid hydrocarbons for use in motor fuels.

One of the objects of this invention is to provide new and improved methods which can be used to convert normally liquid hydrocarbons, such as those generally found in petroleum naphthas, into motor fuels or motor fuel products of higher anti-knock rating than the original stock. Another object of our invention is to provide new and improved methods by which the life of the catalyst used in these reactions may be greatly increased.

In the catalytic dehydrogenation of normally liquid hydrocarbons, such as petroleum naphthas and certain naphtha cuts, the catalyst loses a substantial portion of its activity in relatively short periods of operation and, consequently, it is necessary to revivify the catalyst after short runs in order to accomplish the desired amount of dehydrogenation. This loss in activity by the catalyst may be due to several reasons, such as carbon or coke deposition on the surface of the catalyst, change in the physical structure of the surface of the catalyst or a chemical change of a portion of the catalyst. We have found however, that dehydrogenation catalysts may be revivified in situ or during the dehydrogenating process by introducing into the catalyst zone, along with the hydrocarbons undergoing treatment, a small amount of certain normally gaseous nitrogen-containing compounds, such as nitric oxide, nitrogen peroxide, mixtures thereof, or mixtures of either or both of these oxides with ammonia. These normally gaseous nitrogen-containing compounds not only prolong the life of the catalyst and maintain a cleaner catalyst surface, but they also assist in the conversion of the low knock rating hydrocarbons or naphtha into products of higher knock rating than the original stock.

Our process may be used in the dehydrogenation of many normally liquid hydrocarbons and hydrocarbon mixtures, such as straight-run petroleum naphthas, low knock rating hydrocarbon mixtures boiling slightly above the gasoline range, and normally liquid hydrocarbon fractions containing substantial amounts of paraffins with six or more carbon atoms per molecule. Straight-run naphthas and hydrocarbons, boiling within the range of 200 to 550° F., which generally have very poor anti-knock properties, are particularly

suitable charging stocks. Also, selected cuts from low knock-rating naphthas may be used as the charging stock, for example an 8-carbon-atom cut from a commercial straight-run Mid-Continent naphtha containing about 48% paraffin, 17% aromatics and 35% naphthenes, may be treated according to our process in order to improve its anti-knock properties. Likewise a 7-carbon-atom cut from the same or similar naphthas, containing varying amounts of paraffins, aromatics and naphthenes, may be used as the feed stock. It should be understood that our process is not limited to the treatment of the above types of feed stocks. The charging stocks are preferably sweetened before treating by our process, although hydrocarbon fractions which are sour to doctor solution may be used. When sour fractions are treated according to our invention, the catalysts have been found to have a substantial sweetening and desulfurizing, as well as dehydrogenating action.

Our process is carried out at elevated temperatures, for example at temperatures within the range of 650 to 1200° F., depending upon the charging stock, feed rate, form of catalyst used, etc. In general, temperatures in the upper portion of this range, for example 850 to 1100° F., are most suitable for the dehydrogenation of normally liquid hydrocarbons, such as petroleum naphthas and cuts of hydrocarbons boiling between 200 and 550° F. The pressure employed in our process may vary from substantially atmospheric to superatmospheric pressures. When pressures within the range of 100 to 400 pounds per square inch are used, the temperature employed should be slightly higher than the optimum temperature for a particular catalyst and charging stock at atmospheric pressure or pressures ranging substantially between atmospheric pressure and 50 pounds per square inch. When ammonia is employed with the nitric oxide or nitrogen peroxide, we may operate within the above range of pressures, as well as higher pressures, for example, 400 to 2000 pounds per square inch. Any of the above mentioned temperatures may be used with these higher pressures but we prefer to use temperatures ranging from 300 to 1200° F. The feed rate of the normally liquid hydrocarbon is preferably such that the hydrocarbon vapors pass over the catalyst with a contact time of 1 to 5 seconds. For the same catalyst and charging stock, a somewhat greater feed rate may be used if the temperature is raised slightly.

Our process may be applied to a variety of de-

hydrogenation catalysts, but we prefer to use it with chromium-containing catalysts since they seem to be highly responsive to the action of the normally gaseous nitrogen-containing compounds. Examples of the catalysts which may be used will be described hereinafter, but for the purpose of further illustrating our process with the aid of the attached drawing—a schematic illustration of an apparatus suitable for practicing our invention—magnesium chromite will be used as the catalyst.

The hydrocarbon oil or naphtha to be dehydrogenated is passed by conduit 10 to the pump 11 where sufficient pressure is applied to force it through the heating coils 12 of the furnace 13, transfer line 14, catalyst chamber 15, and to the separator 16. If the reaction is to be carried out at about atmospheric pressure, the pressure applied by the pump 11 should be sufficient to overcome the pressure drop through the heating coils 12 and catalyst chamber 15—generally this will range from 10 to 30 pounds per square inch. When the process is carried out at about atmospheric pressure or relatively low pressures, we prefer to use a pressure from 5 to 50 pounds above that needed to overcome the pressure drop through the system so that the hydrogen and other inert gases can be removed from the top of separator 16, through valved conduit 17, and eliminated from the system. Also, the higher pressures hereinbefore described may be obtained with the pump 11.

The nitrogen-containing gas, for example, nitrogen peroxide or an admixture of nitrogen peroxide and ammonia, is passed through conduit 18 to the pump or compressor 19 and thence through valved conduit 20 to the stream of hydrocarbon products entering the catalyst chamber 15. A throttle valve 21 may be used in conduit 20 to regulate the flow of nitrogen-containing gas entering the system. The amount of nitrogen-containing gas used may vary from 1 to 6 mols per 100 mols of feed stock but generally from $\frac{1}{2}$ to 3 mols of nitrogen-containing gas per 100 mols of feed stock is sufficient to sustain the activity of the catalyst for relatively long periods of time and materially retard the deposition of coke and coke-like materials on the surface thereof. When ammonia is used along with nitric oxide and nitrogen peroxide, the amount of ammonia in the mixture may vary from 5 to 80%. As pointed out hereinbefore, these oxides of nitrogen or mixtures of ammonia and the oxides of nitrogen not only serve to prolong the activity of the catalyst but they assist in raising the anti-knock value of the hydrocarbon fraction subjected to dehydrogenation.

The temperature of the heated feed stock leaving the heater 13 is preferably above the temperature maintained in the catalyst chamber 15 in order to compensate for heat losses and the endothermic dehydrogenation reaction. By placing thermocouples in the catalyst mass within the catalyst chamber 15, this temperature can be easily controlled.

The catalyst may be positioned in chamber 15 in any suitable manner, for example, the tower may be packed with small pellets or pieces of the catalyst, or perforated trays may be disposed in the tower to support the catalyst. The catalyst may be in the form of small pellets or crystals or adsorbed on various finely divided materials, such as Fuller's earth, activated clay or bauxite, silica gel and the like. The various forms in which

the catalyst may be employed will be illustrated hereinafter.

The reaction products are removed from the bottom of the catalyst tower through conduit 22 and passed to the cooler or condenser 23 wherein substantially all of the normally liquid products are condensed. The products from the condenser are then introduced into the separator 16 where hydrogen and unreacted gases are vented from the system through valved conduit 17. The reaction products are removed from the bottom of the separator through conduit 24 and forced by the pump 25 through conduit 26 to a conventional type of bubble tower 27.

The bubble tower is provided with bubble trays 28 and this tower is operated in the conventional manner. Heavy products of the character of gas oil or tar are removed from the bottom of the tower through valved conduit 29. Side cuts may be taken from the side of the tower at one or more places with the aid of trap-out plates 30 and recycled through conduit 31 for further treatment. Preferably the side streams are taken at a lower part of the tower to avoid the recycling of any appreciable amount of those hydrocarbons boiling within the gasoline range. If the initial feed stock to the system has an end boiling point within the gasoline range, say between 350 and 400° F., the product recycled through line 31 should preferably have an initial boiling point that is equal to or slightly above the end boiling point of the initial feed stock. If a fraction of low-knock naphtha containing mostly C₈ hydrocarbons is used as the initial charging stock, the material recycled through line 31 should preferably consist mostly of hydrocarbons containing 9 or more carbon atoms per molecule. Obviously, our process may be carried out without recycling any of the products from the bubble tower 27.

The overhead from the tower, which may have a boiling range similar to that of the feed stock, or an end boiling point lower than or above the feed stock, is passed through conduit 32 to the condenser 33 and thence to the separator 34 where any uncondensed gas is permitted to escape from the system through valved conduit 35. The high anti-knock motor fuel product is withdrawn from the bottom of the separator 34 through conduit 36 and forced by the pump 37 through valved conduit 38 to a suitable storage tank. If desired, a part of the product in line 36 may be passed through valved conduit 39 to the top of the tower 27 and used as reflux therein. Instead of using a portion of the product in line 36 as the reflux, suitable cooling coils may be used in the top of the bubble tower to knock back a portion of the vapors for use as reflux condensate in the tower.

The temperature maintained in the bottom and top of the tower 27 as well as the pressure employed in this tower will vary with the composition of the material entering the tower and the type of fractionation desired. For example, if the product entering the bubble tower through line 26 has an initial boiling point of about 200° F. and an end boiling point of about 400° F., the bottom and top temperatures, respectively, should be maintained at about 440° F. and 230° F. when the tower is operated at a pressure of about 35 pounds per square inch. In this specific illustration, overhead from the bubble tower will have an end boiling point of approximately 375° F. and the product recycled through line 31 will have an initial boiling point of approxi-

mately 350° F. It will be apparent to those skilled in the art that a wide range of temperatures and pressures may be used in the operation of the bubble tower.

The data and examples set forth hereinafter illustrate the improved results obtained by our process when magnesium chromite is used as the dehydrogenating catalyst. In both of the examples set forth in Table I, the charging stock was a naphtha fraction containing predominantly C₈ hydrocarbons and it had a knock rating of 45.5. The data set forth in Example 2, as contrasted with the data set forth in Example 1, show the improved results obtained by including a small amount of nitric oxide in the feed stock.

Table I

	Example 1	Example 2
Volume of catalyst.....cc.	50	50
Feed rate of naphtha fraction...cc/hr.	56	81
Dehydrogenation temperature.....degrees	910	900
Pressure.....	Atmospheric	Atmospheric
Hydrogen content of gas evolved.....percent	55.00	85.0
Mol percent of nitric oxide added.....	0.00	1.1
Refractive index of feed stock.....	1.4194	1.4194
Increase in refractive index of products—samples taken at hourly intervals:		
1st hour.....	.0073	.0042
2nd hour.....	.0047	.0046
3rd hour.....	.0036	.0046
4th hour.....	.0029	.0057
5th hour.....	.0022	.0044

It will be noted that the refractive index of the dehydrogenated product obtained in Example 2 remained practically constant during the run whereas the refractive index of the dehydrogenated product obtained in Example 1 decreased progressively throughout the entire run. These data concerning the refractive index clearly show that the nitric oxide revivifies the catalyst in situ and, consequently, greatly increases the efficiency and utility of the catalyst. Since an increase in the index of refraction represents an increase in the unsaturated nature of the product or antiknock value, it is apparent that our new process gives a fairly uniform type of product of enhanced antiknock value.

In both of the examples set forth in Table II, the charging stock was a naphtha fraction containing predominantly C₈ hydrocarbons and it had a knock rating of 38. In Example 2, a small amount of nitrogen peroxide was passed over the magnesium chromite catalyst along with the feed stock.

Table II

	Example 1	Example 2
Volume of catalyst.....cc.	60	50
Feed rate of naphtha fraction...cc/hr.	60	60
Dehydrogenation temperature.....°F.	910	900
Average anti-knock value of dehydrogenated product.....	49	51
Mol percent of nitrogen peroxide added.....	0.0	2.9
Refractive index of feed stock.....	1.4188	1.4188
Increase in refractive index of product—samples taken at hourly intervals:		
1st hour.....	.0027	.0024
2d hour.....	.0020	.0024
3d hour.....	.0018	.0027
4th hour.....	.0017	.0025
5th hour.....		.0028

The data concerning the refractive index of the dehydrogenated product clearly demonstrate that the nitrogen peroxide materially retards the deactivation of the catalyst during use, and con-

sequently certain catalysts may be used in the process for relatively long periods without resorting to other means of revivifying the same. When ammonia is used in combination with the oxides of nitrogen, similar improved results are obtained with respect to the dehydrogenated product and longevity of the catalyst.

While our process may be used with a variety of dehydrogenation catalysts it is particularly adapted for use with chromium-containing dehydrogenating catalysts, such as the metallic chromites.

The metallic chromites which are particularly adapted for use in our process are metal chromites having as the metallic constituents such metals as copper, silver, gold, cadmium, magnesium, beryllium, calcium, strontium, zinc, boron, cobalt or nickel, or a mixture of one or more of these chromites, prepared by the thermal decomposition of a complex metal chromate in crystal form. These complex metal chromates may be in the form of hydrated metal ammonium chromate, or an ammonio metal ammonium chromate, or an ammonio metal chromate. The metal chromite catalyst may be prepared from the hydrated metal ammonium chromate crystals by heating the same to a red heat. The cobalt and nickel chromites prepared in this way are finely divided gray powders whereas the magnesium and calcium chromites are black rigid solids. The metal chromite catalysts may be prepared from the ammonio metal ammonium chromate crystals by heating the same to a temperature not substantially above 425° F. in order to avoid the "glow" phenomenon. The metal chromite catalyst is prepared from the ammonio metal chromate crystals by heating the same to a red heat. These metallic chromites may be used in the form which results from the crystal decomposition, or they may be formed into pellets or mounted on suitable supports.

One method of preparing these hydrated metal ammonium chromate crystals, from which the metal chromite is prepared, consists in mixing aqueous solutions of a suitable salt, such as the chloride or nitrate, of one or more of the above metals with ammonium chromate, and allowing the solution to stand until the crystals have formed. The metal salt and ammonium chromate should be used in approximately stoichiometric proportions. The ammonio metal ammonium chromate may be obtained by mixing aqueous solutions of a suitable metal salt and ammonium chromate or chromic acid anhydride, preferably in approximately stoichiometric proportions. Concentrated ammonium hydroxide is added until the resulting precipitate of metal ammonium chromate is redissolved and a clear solution formed. Upon standing the desired chromate will precipitate in crystalline form. One method of preparing the ammonio metal chromate crystals consists in mixing concentrated aqueous solutions containing substantially equimolecular quantities of a suitable salt of a bivalent metal, such as nickelous sulfate, and potassium or sodium dichromate, and adding an excess of an organic base. A crystalline compound separates out, which, if nickelous sulfate, potassium di-chromate and pyridine are used, is believed to have the formula $\text{NiCr}_2\text{O}_7 \cdot 4\text{C}_5\text{H}_5\text{N}$. Sufficient concentrated ammonium hydroxide is then added to redissolve the crystals and produce a clear solution. The pyridine or other nitrogen base separates as an upper layer and is removed by decantation. The clear solution is allowed to stand for a few hours, and a complex ammonio metal chromate crystal-

lizes out in well defined crystals which are filtered off and dried.

It should be understood that the above mentioned chromite catalysts, as well as other chromite catalysts, may be prepared by different methods.

Another type of chromium-containing catalyst which may be used very effectively in our process is an admixture of metallic chromites and activated alumina. The metallic chromite, prepared by any method, is mixed with activated alumina and the mixture ground in a ball mill for three to five hours. A small amount of water is then added to the mixture to form a paste and it is spread in thin layers on a smooth surface, dried and used. We prefer to use about 5 to 15% by weight of the metallic chromite and 95 to 85% of activated alumina, however, as much as 5 to 70% of the catalyst mixture may be the metallic chromite and the rest activated alumina. Examples of the metallic chromites which may be used with activated alumina are sodium chromite, copper chromite, calcium chromite, magnesium chromite, zinc chromite, chromium chromite, manganese chromite and the like. Chromites prepared from the metals in groups I, II, III, IV, VI and VII of Mendelejeff's Periodic Table and chromites of vanadium, iron and cobalt may be used.

Chromium oxide catalyst may also be used in our process. Chromium oxide may be used in the form of pellets or mounted upon some inert material, such as clay, Fuller's earth, pumice and the like. Also, the chromium oxide may be mixed with activated alumina, for example, approximately 10% by weight of chromium oxide (Cr_2O_3) may be mixed with about 90% by weight of activated alumina. This admixture may be used in the form of pellets or suspended on a suitable carrier. The chromium oxide may be prepared by several methods, but we prefer to prepare it by reducing chromium tri-oxide with ethyl alcohol. About eight or ten cc. portions of ethyl alcohol are added at five or six minute intervals to a liter of water containing about 80 grams of chromium tri-oxide. Upon standing for four or five hours, an equal volume of ethyl alcohol is added to the admixture and the solution is then heated, preferably under a reflux, for about fifteen to twenty hours. After this heating step, the reaction mass sets to a dark brown, almost black, jelly. The jelly may be broken up by any suitable means and the excess water removed by filtration. The filtered mass is then further dehydrated by heating to a temperature of approximately 112°C ., whereby the mass is converted into a black vitreous form.

While our process of dehydrogenating normally liquid hydrocarbons and activating the catalyst in situ may be used with any dehydrogenating catalyst, it is particularly suitable for use with chromium-containing catalysts. Molybdenum oxide, molybdenum oxide mixed with activated alumina, magnesium chromite admixed with small amounts (2-10%) of finely divided metallic nickel or platinum, nickel borite, mixtures of aluminum oxide and ferric oxide, and activated alumina are examples of other catalysts that may be used. When using our process with any of these catalysts, the nitrogen-containing gas should be used in amounts ranging from 1 to 6 mols per 100 mols of feed stock, but generally from 1 to 4 mols of nitrogen-containing gas per 100 mols of feed stock is sufficient to sustain the

activity of the catalyst for relatively long periods of time.

While we have described our invention with reference to specific examples and embodiments, it should be understood that our invention is not limited thereto except as specified in the following claims.

We claim:

1. In a catalytic process for producing normally liquid motor fuel products of high anti-knock rating from normally liquid hydrocarbon fractions of low anti-knock rating and simultaneously regenerating the catalyst in situ, the steps comprising passing an admixture containing from 1 to 6 mols of a normally gaseous nitrogen oxide selected from the group consisting of nitric oxide and nitrogen peroxide per 100 mols of a normally liquid hydrocarbon product of low anti-knock rating over a dehydrogenating catalyst at a temperature in excess of about 650°F ., and separating the normally liquid motor fuel product of high anti-knock rating from normally gaseous products.

2. In a catalytic process for producing normally liquid motor fuel products of high anti-knock rating from normally liquid hydrocarbon fractions of low anti-knock rating and simultaneously regenerating the catalyst in situ, the steps comprising passing an admixture containing from 1 to 6 mols of a normally gaseous nitrogen oxide selected from the group consisting of nitric oxide and nitrogen peroxide per 100 mols of a normally liquid hydrocarbon product of low anti-knock rating over a chromium-containing dehydrogenating catalyst at a temperature within the range of 650 to 1200°F ., and separating the normally liquid motor fuel product of high anti-knock rating from normally gaseous products.

3. In a catalytic process for producing normally liquid motor fuel products of high anti-knock rating from normally liquid hydrocarbon fractions of low anti-knock rating and simultaneously regenerating the catalyst in situ, the steps comprising passing an admixture containing from 1 to 6 mols of a normally gaseous nitrogen oxide selected from the group consisting of nitric oxide and nitrogen peroxide per 100 mols of a normally liquid hydrocarbon product of low anti-knock rating over a dehydrogenating catalyst containing a metallic chromite at a temperature within the range of 650 to 1200°F ., and separating the normally liquid motor fuel product of high anti-knock rating from normally gaseous products.

4. In a catalytic process for producing normally liquid motor fuel products of high anti-knock rating from normally liquid hydrocarbon fractions of low anti-knock rating and simultaneously regenerating the catalyst in situ, the steps comprising passing an admixture containing from 1 to 6 mols of a mixture of ammonia and a normally gaseous nitrogen oxide selected from the group consisting of nitric oxide and nitrogen peroxide per 100 mols of a normally liquid hydrocarbon product of low anti-knock rating over a dehydrogenating catalyst at a temperature in excess of about 650°F ., and separating the normally liquid motor fuel product of high anti-knock rating from normally gaseous products.

5. In a catalytic process for producing normally liquid motor fuel products of high anti-knock rating from normally liquid hydrocarbon fractions of low anti-knock rating and simultaneously regenerating the catalyst in situ, the steps comprising passing an admixture containing from 1

to 6 mols of nitrogen peroxide per 100 mols of a normally liquid hydrocarbon product of low anti-knock rating over a dehydrogenating catalyst at a temperature in excess of 650° F., and separating the normally liquid motor fuel product of high anti-knock rating from normally gaseous products.

6. In a catalytic process for producing normally liquid motor fuel products of high anti-knock rating from normally liquid hydrocarbon products of low anti-knock rating and simultaneously regenerating the catalyst in situ, the steps comprising passing an admixture containing from 1 to 6 mols of a normally gaseous nitrogen oxide selected from the group consisting of nitric oxide and nitrogen peroxide per 100 mols of a normally liquid hydrocarbon product of low anti-knock rating over a dehydrogenating metallic-chromite catalyst at a temperature within the range of 650 to 1200° F., and separating the normally liquid motor fuel product of high anti-knock rating from normally gaseous products.

7. In a catalytic process for producing normally liquid motor fuel products of high anti-knock rating from normally liquid hydrocarbon products of low anti-knock rating and simultaneously regenerating the catalyst in situ, the steps comprising passing an admixture containing from 1 to 6 mols of a nitrogen oxide selected from the group consisting of nitric oxide and nitrogen peroxide per 100 mols of normally liquid hydrocarbon products of low anti-knock rating over a dehydrogenating chromium oxide catalyst at a

temperature within the range of 650 to 1200° F., and separating the normally liquid motor fuel product of high anti-knock rating from normally gaseous products.

8. In a catalytic process for producing normally liquid motor fuel products of high anti-knock rating from a normally liquid 8-carbon atom hydrocarbon fraction of low anti-knock rating and simultaneously regenerating the catalyst in situ, the steps comprising passing an admixture containing from 1 to 6 mols of a normally gaseous nitrogen oxide selected from the group consisting of nitric oxide and nitrogen peroxide per 100 mols of normally liquid 8-carbon atom hydrocarbon product over a dehydrogenating catalyst at a temperature in excess of about 650° F., and separating the normally liquid motor fuel product of high anti-knock rating from normally gaseous products.

9. In a catalytic process for producing a normally liquid motor fuel product of high anti-knock rating from a normally liquid hydrocarbon fraction of low anti-knock rating and simultaneously regenerating the catalyst in situ, the steps comprising passing an admixture containing from 1 to 6 mols of nitric oxide per 100 mols of a normally liquid hydrocarbon product of low anti-knock rating over a dehydrogenating catalyst at a temperature in excess of 650° F., and separating the normally liquid motor fuel product of high anti-knock rating from normally gaseous products.

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