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TREATMENT OF NAPHTHA CONTAINING
OXYGENATED COMPOUNDSDu Bois Eastman, Montebello, Calif., assignor to
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The present invention relates to a process for the improvement in respect to anti-knock properties, gum and color stability and corrosion properties of hydrocarbon mixtures or naphtha of the type which includes oxygen-containing organic compounds, particularly those produced by the catalytic reduction of carbon monoxide with hydrogen.

Typical synthetic naphthas in question result from passage of hydrogen and carbon monoxide in contact with a suitable synthesis catalyst usually selected from metals of the iron group, e. g. iron, cobalt, nickel or ruthenium, under conventional and respectively established conditions of temperature, pressure and the like. Objections to many processes of this class usually include relatively low anti-knock ratings of the naphtha fractions and while more recent improvements in operating technique have resulted in a greatly improved product, the current demands for motor fuels of high octane value render it desirable to improve the octane numbers of the products by economical methods. Moreover poor gum and color stability as well as undesirable corrosion properties, due possibly to the inevitable presence of oxygenated hydrocarbon compounds in the product, require correction.

The raw products obtained from the synthesis of hydrocarbons from carbon monoxide and hydrogen are markedly different from those usually encountered in the conventional oil refinery. The most characteristic differences between naturally occurring oils and the synthetic Hydrocol oils result from the presence of relatively large amounts of oxygenated compounds and olefinic hydrocarbons in the synthetic product.

From about 70 to about 80 per cent of the synthesis product obtained from an efficient synthesis operation for the production of motor fuel hydrocarbons boils within the motor fuel range. The synthesis operation is more or less standardized. In general, carbon monoxide and hydrogen in molar ratio of about 1:2 is passed over an iron catalyst. The temperature is generally within the range of 500 to 700° F. and the pressure within the range of 150 to 550 pounds per square inch gauge. A powdered iron catalyst in fluidized condition is generally used. Various activators and promoters may be used with the catalyst to improve its efficiency and selectivity.

The naphtha fraction, e. g., 100 to 400° F., is suitable for production of motor gasoline. About 65 to about 75 weight per cent of the hydrocarbon product falls in this category. A higher boiling fraction, e. g., a 400 to 625° F. fraction, may suitably be used for production of Diesel fuels and comprises roughly 10 to 20 weight per cent of the hydrocarbon product. Small quantities of higher and lower boiling hydrocarbons are produced. The hydrocarbon product referred to

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herein is the hydrocarbon fraction, as distinguished from the water fraction, of the effluent and includes hydrocarbon-soluble oxygenated compounds.

Since the naphtha fraction is the most economically desirable from the standpoint of motor fuel production, it is important that this fraction be upgraded as much as possible for use in production of finished fuels. Octane number, a measure of the anti-detonation quality of a fuel, is especially important. The present invention provides a process for greatly improving this property of the all important naphtha fraction of the synthesis products.

The present invention has for its main objective the provision of a treatment process specifically applicable to synthetic liquid products of the foregoing class, by which a substantial improvement in the anti-knock properties together with gum and color stability and corrosion properties may be effected at a relatively low cost. A more particular object is to provide a process which by comparison with other methods of refining, effects the foregoing improvement with a relatively restricted loss of naphtha, under conditions of rapid treatment, with a minimum of catalyst utilization and capable of being carried out in apparatus of familiar and existing type. Other objects will be apparent from consideration of the following disclosure.

More particularly it has been discovered in accordance with the present invention that a quite substantial improvement in octane value, amounting usually to about 12 octane numbers is available by treatment of the foregoing synthetic hydrocarbon product, at temperatures within the range of about 700–900° F. by contact with a catalyst of the class consisting of bauxite, activated alumina and fuller's earth. Thus, in accordance with the present invention the synthetic naphtha fraction or any other liquid fraction containing hydrocarbons and oxygenated compounds in the gasoline boiling range is caused to pass in contact with such a catalyst at the aforementioned temperature range but preferably within the range of about 800–850° F., advantageously at pressures near atmospheric.

It has also been found that the capacity of the catalyst to effect maximum improvement in octane value is limited. The effective on-stream time, prior to renewal or regeneration of the catalyst, is determined by the volume of naphtha treated. The on-stream time is the actual or average time any contact mass of catalyst is subjected to contact with the synthetic hydrocarbon product being converted without replacement or regeneration. In short, this period represents, and, depending upon space velocity, is a measure of an overall change or alteration in the character of the catalyst which occurs under the

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influence of the reaction. This change may involve a deposit of some undesired product removable by regeneration, or some other effect arising out of catalyst use, but irrespective of its nature it has been found to bear a definite relationship to the space velocity at which the present reaction is carried out, as well as the total period of use before the catalyst is replaced. For example, results at 5 volumes of liquid hydrocarbon charge per volume of catalyst per hour and 4 hours on-stream time, are identical with those at 20 volumes of liquid hydrocarbon per volume of catalyst per hour where the fresh catalyst is in use for 1 hour.

In accordance with the present invention, the synthetic naphtha, resulting from the reduction of carbon monoxide, is contacted with the catalyst under conditions such that the product of the space velocity, expressed as above, multiplied by the on-stream time, in hours, falls within the range of about 5 to about 30 and is preferably about 10 to 20. In other words, the volumes of naphtha treated per volume of catalyst per cycle (v./v./cycle) is preferably between 10 and 20. Under these conditions, the improvement in octane number reaches or closely approaches maximum.

Moreover, the typically high neutralization number of naphthas of the present class, as for example on the order of about 2.5, is reduced to a value of less than 0.1 and gum and color stability reach practical optimum values. The neutralization number is expressed as milligrams of potassium hydroxide per gram of hydrocarbon required for neutralization. In operations where the naphtha treated, v./v./cycle, exceeds the ranges above mentioned, these important improvements in octane value and neutralization number rapidly vanish. There is no advantage in either octane value improvement or in conversion of oxygenated compounds from operation at less than 10 v./v./cycle. The increased frequency of catalyst regeneration imposes an uneconomic burden. Within the range of conditions disclosed, the present invention provides an improved process for improving octane number of synthetic hydrocarbon fractions, presumably as a result of alteration of the hydrocarbons, and elimination of oxygen from oxygenated hydrocarbon compounds which are more or less inevitably associated with the synthetic naphtha under treatment.

The present invention is not to be confused with prior catalytic cracking and reforming process usually carried out on gas oils or gasoline under different conditions, and with a material alteration in product distribution and yield. For example, thermally cracked naphthas have hitherto been contacted with clays under different conditions for reducing the sulfur content. Also, by the process known as isoforming, higher temperatures are employed to effect an improvement of octane rating in thermally cracked naphthas, whereas in an identical treatment catalytically cracked naphthas have no material response. The present invention provides an improvement in the anti-knock rating of the particular synthetic naphthas of the present class which is superior to the aforementioned treatment of thermally cracked naphthas, with an accompanying elimination of objectionable acidic constituents, all without material loss of naphtha.

The effective simultaneous removal of oxygenated compounds and improvement in octane number accomplished by the present process is

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unexpected. The alcohols and other oxygenated organic compounds present in the raw naphtha in relatively large amounts are substantially completely converted to olefins. The unusually great improvement in octane value of the naphtha cannot be explained as resulting from removal of the oxygen-containing compounds. Caustic washing of the naphtha to remove the oxygenated compounds gives no improvement in octane values. The improvement obtained by treatment with bauxite, fuller's earth, and the like, indicates that the hydrocarbon structure is also changed. It is believed that the primary reaction accompanying deoxygenation is isomerization of the olefins by shifting of the double bond. This is sharply in contrast to processes wherein the primary reaction is cracking. Heavier fractions, e. g., those boiling above 400° F., may be subjected to cracking, e. g., by contact with a silicious cracking catalyst. The catalytic cracking simultaneously deoxygenates oxygenated compounds contained in the higher boiling fraction.

By the process of this invention, a motor fuel of improved octane number is obtained from the product of the hydrocarbon synthesis reaction between carbon monoxide and hydrogen. The hydrocarbon product of the synthesis reaction is fractionated to obtain the desired naphtha fraction boiling within the range of from 100 to about 400° F. A typical naphtha fraction has an initial boiling point (ASTM method) of 115 and an end point of 400° F.

The naphtha fraction without previous treatment to remove oxygenated compounds is passed in vapor phase over the alumina catalyst at a temperature of 700 to 900° F.

Water in the form of steam is preferably added to the naphtha vapors. Any amount may be used; suitably 5 to 50 weight per cent of the charge, preferably about 20 weight per cent, is steam. The purpose of the water is to prevent, as much as possible, cracking of the hydrocarbons. Other diluents may be used for this purpose but are, in general, less effective than steam.

The catalyst treatment results in the formation of some polymer tar. From about 2 to about 8 weight per cent of the treated naphtha is polymer tar. This is readily removed from the treated naphtha by steam distillation.

Some light gases are inevitably produced by the catalytic treatment. These are produced principally as the result of deoxygenating the oxygenated compounds.

Accordingly, the treated naphtha is subjected to fractionation to effect removal of undesirable higher and lower boiling constituents. The material higher boiling than the original charge is removed. Obviously the resulting naphtha may be further fractionated in any desired fashion depending upon the demand and specifications for each grade of motor fuel for sale or blending.

Pressures are advantageously near atmospheric, preferably within the range of from about atmospheric pressure to about 25 pounds per square inch gauge, although the process is operable at higher pressures, as 200 pounds per square inch, for example, and sometimes up to 300 pounds per square inch, usually at somewhat of a sacrifice of yield, product distribution, octane number and the like.

The catalysts employed are of the clay type which are relatively or substantially inactive for cracking virgin gas oils and heavier hydrocarbons for obtaining gasoline of a high anti-knock

value. The catalysts consist essentially of alumina and include activated alumina and fuller's earth. The catalyst may be subjected to refining, pelleting and the like, which are intended to remove impurities, place the material in better physical form for use, or otherwise render it more suitable for the process in question.

The invention is particularly advantageous in that it can employ with equal advantage many readily available, low cost catalyst, such as fuller's earth mentioned above, bauxite, and activated alumina. In particular, a typical refined bauxite catalyst such as cyclocel or porocel, are to be preferred although activated alumina is also excellent. While for economical reasons I prefer to use a product such as Riverside fuller's earth or the aforementioned bauxite catalysts, it is to be understood that the invention is not restricted to any novelty in the catalyst, per se, but rather concerns the application of the foregoing class of catalysts to a new and valuable process.

Catalyst sizes will not vary from the typical sizes conventional in the case of usual vapor phase catalytic processes, with due regard to the avoidance of undesirable pressure drop in the catalyst zone. Suitable catalyst sizes are usually for example, from 6 to 30 mesh and conventional pelleted catalysts may, of course, be employed.

The invention is in no way restricted to any specific method of contacting, being applicable to batch or fixed bed operation, or moving bed catalysts and to use with fresh or regenerated catalyst. As indicated above, the on-stream time is controlled by limiting the period at which either fresh, or regenerated catalyst is subjected to the catalytic treatment in question without regeneration or replacement.

Usually it is advantageous to regenerate the catalyst after each on-stream or treating period and thereafter resubmit it to use in the treatment zone. Such a process obviously permits the use of any conventional type of apparatus whereby catalyst is permitted to reside in the reaction zone in contact with the vapor phase naphtha for the predetermined period of time, is then withdrawn, regenerated and returned. Such apparatus is exemplified by any of the conventional fluidized or moving bed systems operating under a controlled average catalyst residence time in the treatment and regeneration zones. Among these are the structures wherein the catalyst gravitates through the treatment chamber countercurrent to the incoming feed, and after a selected period of contact moves into a regenerating chamber. The process, however, does not require these refinements and is equally applicable to fixed bed operations where after a selected period on stream, the operation is terminated and the contents of the reactor subjected to regeneration. In fact this advantage of functioning equally well with fixed bed reactors is an important factor in permitting adaption of widely available existing equipment.

Regeneration may be carried out in any conventional manner for catalysts of this class, for example, at temperatures of about 1050° F. and usually under pressure, as for example, 90 pounds per square inch gauge, with the continuous recirculation of an appropriate flue gas containing, for instance, about 5 volume per cent oxygen until carbonaceous deposits are removed. It is to be understood however that the specific method of regeneration is immaterial to the present invention insofar as the catalyst is placed thereby in fully regenerated condition. In short the

temperatures and pressures are not critical and may be varied widely, and the regenerating gas may comprise steam or any other conventional medium, usually circulated in a suitable diluent to control rate of regeneration.

The catalyst is regenerated after from 10 to 30 volumes of naphtha per volume of catalyst have been treated. After regeneration the catalyst is again placed on stream.

Example

A typical crude hydrocarbon product resulting from the synthesis of hydrocarbons from carbon monoxide and hydrogen in molar proportions of about 1:2 with an iron catalyst has the following analysis:

Gravity, ° API.....	51.8
Bromine number, cgs./gm.....	104
Neutralization number, mg. KOH/gm.....	16.8
ASTM distillation, ° F.:	
IBP	106
10%	142
50%	264
90%	576
EP	660
Recovery, percent.....	94.0
Residue, percent.....	Coke

The high bromine number and neutralization number are indicative of the high content of olefinic and oxygenated compounds typical of hydrocarbon synthesis products.

The crude product was cut at the 400° F. point into two fractions:

Fraction:	Wt. per cent
IBP, 400° F.....	75.3
400° F., EP.....	24.7

The naphtha fraction, the physical properties of which are listed in the following table, was treated in accordance with this invention.

The naphtha fraction was vaporized and preheated to about 350° F. and passed over 4/8 mesh bauxite (Regular Porocel) at a space velocity of 1.02 v./hr./v. Steam was added to the charge to give a feed containing 20.7 weight per cent water vapor. The recovered naphtha was subjected to steam distillation to remove light and heavy ends resulting from the treatment. Physical properties of the raw, treated and steam distilled naphtha are tabulated below.

	Raw Naphtha	Treated Naphtha	Steam Distilled Naphtha
Gravity, ° API.....	60.2	61.5	61.7
Aniline Point, ° F.....	55.2	82.4	84.2
Bromine Number, cgs./gm.....	124	120	113
CFRM Octane Number:			
Clear.....	63.6	77.4	78.1
1 ml. TEL/gal.....	68.7	81.6	81.7
3 ml. TEL/gal.....	75.7	83.2	83.7
CFRR Octane Number:			
Clear.....	70.9	89.9	89.4
1 ml. TEL/gal.....	75.4	94.4	94.4
3 ml. TEL/gal.....	86.1	96.2	96.2
ASTM Distillation, ° F.:			
IBP.....	115	110	127
10%.....	142	156	160
50%.....	228	226	225
90%.....	354	362	344
EP.....	398	448	390
Recovery, per cent.....	98.0	98.0	98.0

The overall yield of treated naphtha was about 88.3 weight per cent of the naphtha charged. Only 3.8 weight per cent of the charge was converted to gaseous materials. The water make was 4.3 weight per cent of the naphtha feed,

while the carbon deposition amounted to 0.6 weight per cent.

Little cracking or dehydrogenation took place under the operating conditions.

Referring to the data in the foregoing tabulation, it will be seen that the CFRM octane number was increased approximately 14 points by the bauxite treatment, while the CFRR octane number was increased approximately 19 points.

The bauxite treatment resulted in increasing the end point of the treated naphtha due to the formation of heavy polymer materials. These were removed by the steam distillation of the treated naphtha. No significant increase in octane values was obtained by steam distillation. Approximately 4 per cent by volume of the treated naphtha is removed as polymer tar in the steam distillation.

The finished naphtha which has been bauxite treated and re-run for removal of polymer tar is substantially non-corrosive and is gum-stable over long storage periods.

A number of similar naphtha fractions were treated with comparable results. Slight differences in composition due to differences in operating conditions in the synthesis reactor have little effect on the finally treated naphtha fraction.

The catalyst was regenerated periodically by burning off the carbon with an oxygen-containing gas. The maximum temperature during the regeneration was approximately 1300° F. After 40 cycles the catalyst was still active.

Removal of oxygenated compounds from the raw naphtha as by extraction with ethylene glycol, results in lowering of the octane value and neutralization number of the raw naphtha but has no other apparent significant effect.

From the foregoing it will be apparent that the present invention provides an effective and economical means for making an essential improvement in naphthas of the present specific class.

It is to be understood that this invention is generally applicable to all synthetic naphtha products of the catalytic reduction of carbon monoxide with hydrogen, in the presence of typical catalysts for this process, such as, those of the iron group, e. g., cobalt, iron, nickel or ruthenium at the well established operating temperatures and pressures which characterize the respective catalysts. As is also known the optimum conditions vary for equivalent catalysts, being in somewhat lower ranges for cobalt catalysts, typically 400° F. and around atmospheric pressure. Obviously the synthesis catalysts may include conventional additions of activators and promoters, such as alkali or alkaline earth metal oxides, alumina, titania, etc.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. In a process for the synthesis of motor fuel hydrocarbons by the interaction of carbon monoxide and hydrogen in the presence of a catalyst of the iron group, the improvement comprising separating from the products of the synthesis reaction a hydrocarbon fraction boiling within the range of from about 100° F. to about 400° F. and

containing oxygen-containing compounds produced by the reaction, and passing said fraction in vapor phase in admixture with steam in an amount within the range of from about 5 to 50 weight percent of the hydrocarbon-steam mixture into contact with fuller's earth at a temperature within the range of from about 700 to about 900° F. and at a pressure within the range of from about atmospheric to about 25 pounds per square inch gauge for a period of time effective to substantially improve the octane value of said fraction.

2. A process for the production of motor fuel hydrocarbons which comprises reacting carbon monoxide with hydrogen at a temperature within the range of from about 500 to about 700° F. and a pressure within the range of from about 150 to about 550 pounds per square inch gauge in the presence of an iron hydrocarbon synthesis catalyst, separating from the products of the synthesis reaction a hydrocarbon fraction boiling within the range of from about 100° F. to about 400° F. and containing oxygen-containing compounds produced by the reaction, and passing said fraction in vapor phase in admixture with steam in an amount within the range of from about 5 to 50 weight per cent of the hydrocarbon-steam mixture into contact with fuller's earth at a temperature within the range of from about 700 to about 900° F., under conditions of contact time effective to substantially improve the octane value of said fraction.

3. A process for the production of motor fuel hydrocarbons which comprises reacting carbon monoxide with hydrogen at a temperature within the range of from about 500 to about 700° F. and a pressure within the range of from about 150 to about 550 pounds per square inch gauge in the presence of an iron hydrocarbon synthesis catalyst, separating from the products of the synthesis reaction a hydrocarbon fraction boiling within the range of from about 100° F. to about 400° F. and containing oxygen-containing compounds produced by the reaction, and passing said fraction in vapor phase in admixture with steam in an amount within the range of from about 5 to 50 weight per cent of the hydrocarbon-steam mixture into contact with fuller's earth at a temperature within the range of from about 700 to about 900° F., under conditions of contact time effective to substantially improve the octane value of said fraction, and subjecting the resulting hydrocarbon fraction of improved octane value to fractionation to effect removal of materials higher boiling than the untreated hydrocarbon feed.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,264,427	Asbury	Dec. 2, 1941
2,347,682	Gunness	May 2, 1944
2,398,674	Schulze	Apr. 16, 1946
2,425,960	Schulze	Aug. 19, 1947

FOREIGN PATENTS

Number	Country	Date
112,274	Australia	July 3, 1939
735,276	Germany	May 11, 1943