PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Catalytic Improvement of Hydrocarbon Synthesis Product

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in manufacturing synthetic gasoline and in particular it relates to improvements in the anti-detonation quality of the synthetic gasoline produced by the reduction of carbon monoxide with hydrogen.

The production of normal liquid hydrocarbons and oxygenated hydrocarbons by the reduction of the oxides of carbon with the hydrogen containing gas in the presence of a suitable catalyst is now a method of record. The first work done in this field was in the presence of cobalt catalyst and the process developed is known as the Fischer-Tropsch process. The product resulting from reacting together carbon monoxide and hydrogen in the presence of cobalt was one which had a very low octane rating since it was for the most part composed of straight chain paraffinic hydrocarbons.

The next step in this field involved substitution of an iron catalyst for the cobalt catalyst. In the process using iron somewhat higher temperatures were employed and somewhat different ratio of hydrogen to carbon monoxide feed to the reaction was employed. For example whereas the older Fischer-Tropsch process was conducted at around 300—400°F., the process employing iron catalyst was carried out at temperatures from 500°—800°F. In the Fischer-Tropsch process the ratio of hydrogen to carbon monoxide in the feed to the reaction zone was about 2 moles of hydrogen per mole of carbon monoxide. In the process employing iron generally the ratio of hydrogen to carbon monoxide in the feed of the reaction zone is often of the order of about 1 mol. of hydrogen to 1 mol. of carbon monoxide, but for special purposes this ratio may be varied so that the ratio of hydrogen to carbon monoxide may be from about 2 to 4 mols. of hydrogen per mol. of carbon monoxide. The main distinction between the two processes, however, is that the quality of the gasoline formed in the process using iron as a catalyst is better with respect to its anti-detonation qualities. It is a generally accepted belief that the gasoline product produced by reducing carbon monoxide with hydrogen in the presence of an iron catalyst is of higher quality than that produced where the catalyst is cobalt.

In spite, however, of the fact that the raw gasoline from the process employing iron is of relatively good quality, nevertheless, it is customary to treat the gasoline to improve further its quality. Thus, it has been previously proposed to treat the hydrocarbon synthesis product formed by reducing carbon monoxide with hydrogen at elevated temperatures with bauxite in order to remove oxygen and to improve the octane number characteristics of the gasoline. The improvement in the octane number characteristics of the gasoline thus obtained largely arises from isomerization reactions wherein straight chain alpha-olefins are isomerized to other straight chain olefins with a shift of the double bond toward the middle of the molecule, or to a rearrangement of a straight chain olefin to form an iso-olefin.

It has been found that an unexpectedly good result is obtained by treating the hydrocarbon synthesis product in the presence of a severely deactivated and plant contaminated cracking catalyst as hereinafter defined, particularly a synthetic silica alumina gel cracking catalyst. It has been found that the anti-detonation quality of the gasoline is greatly improved and that the yields are high. The result is

[*Price* 2/-]

unexpected in that the cracking catalyst used is extremely depreciated in value for further use in ordinary catalytic cracking, inasmuch as its activity for gas oil cracking is low and that the carbon formation for a given gas oil conversion is high. However, when this used contaminated cracking catalyst is employed for treating a hydrocarbon synthesis product, there is no deleterious effect due to the spent and contaminated state of the catalyst. Its substantial deactivation for petroleum gas oil cracking results in an optimum state of activity for the treatment of the hydrocarbon synthesis product. In a large number of pilot plant runs, results obtained with used and deactivated normal cracking catalyst, have shown the latter to be superior to those obtained in conventional bauxite treating of the hydrocarbon synthesis product. This superiority, as indicated, resides in obtaining a high octane gasoline in good yields and with a relatively small amount of carbonaceous material formed during the treatment.

To explain what is meant by a severely deactivated catalyst, the same may be defined in terms of what is known as its "D+L" value or rating. This rating is recognized in the industry as a means for determining the activity of a cracking catalyst. The test is performed by cracking a gas oil at a temperature of 850°F. in the presence of a portion of the catalyst to be tested while feeding the gas oil to the catalyst chamber at a space velocity of 0.6 volumes of oil per volume of catalyst per hour, during a two-hour period. The product is collected and subjected to an Engler distillation, the portion boiling up to and including 400°F. being collected as a distillate. The amount of material subjected to distillation is usually 100 volumes, say 100cc. The liquid condensate or distillate is measured. The material subjected to distillation minus the sum of the undistilled material remaining in the distillation flask plus the distillate, is equal to L. or the loss. The sum of the distillate quantity (D) plus the loss (L) is taken as the activity of the catalyst; and this is commonly referred to as the D+L value. A good catalyst should have a D+L value of at least 40, and many possess a D+L value of 60. A catalyst of fair activity would have a D+L of about 30. A severely deactivated catalyst, therefore, would be one which had a D+L value of the order of 20 or less.

It should also be pointed out that during use in the commercial units the synthetic silica-alumina gel catalyst becomes contaminated with iron, and this contamination of the catalyst with iron also has a deleterious effect on the catalyst in the cracking operation and lowers its D+L value.

It is pointed out that methods are known, other than that above discussed for determining cracking catalyst activity. In fact, an experienced operator can by mere observance of the performance of a catalyst in a commercial unit, determine at least qualitatively the fact that a catalyst has lost activity. For example, the yield of gasoline product and/or the degree of carbonaceous material or coke formed, based on the feed, are indications to him of the catalyst activity.

The object of this invention, therefore, is to improve the quality of a normally liquid product produced by reducing carbon monoxide with hydrogen in the presence of a synthesis catalyst.

Another object of this invention is to improve the anti-detonation quality of a normally liquid hydrocarbon synthesis product formed by reducing carbon monoxide by hydrogen containing gas without incurring severe loss of material or the formation of inordinately large amounts of carbonaceous materials.

Other and further objects of this invention will appear in the detailed following description.

In the accompanying drawing, it has been shown diagrammatically an apparatus in which a preferred modification of this invention may be carried into effect.

Referring in detail to the drawing normally liquid hydrocarbon synthesis product produced by reducing carbon monoxide using hydrogen containing gas in the presence of a metallic iron catalyst is introduced into the present treating system through line (1) and then pumped by pump (2) into retreating vessel (3) containing a fixed mass of spent and contaminated catalyst (C). This catalyst is preferably a synthetic gel containing silica and alumina and is one which has been previously used in the catalytic cracking of petroleum gas oil to the extent that it has lost activity and is therefore not usable in said last-named catalytic process. It is also generally contaminated with from 0.3 to 1.0% by weight of iron or iron compounds which have been acquired in the catalytic cracking plant by contact with iron surfaces. Either or both of these factors unfavourably reduce its activity and would render it necessary to withdraw the catalyst from the petroleum gasoline cracking process and discard it.

Under conditions which are about to be described more fully, hereinafter, the hydrocarbon synthesis product is passed in vapor phase through the reactor (3) and then withdrawn through line (4) and delivered to a fractional distillation column (5), where it is subjected to distillation. From the top of (5) a normally gaseous product is withdrawn. This normally gaseous material contains C_3 and C_4 olefins which may be sent to a polymerization plant (not shown) for the purpose of causing polymerization of said normal gaseous olefins to form polymerization products boiling in the gasoline boiling range. The main product of the present process is withdrawn from column (5) to line (7), condensed in a column (8) and collected in receiving drum (9). This material in receiving drum (9) is the gasoline fraction or cut. A small amount of heavy naphtha cut boiling in the lower gas oil range is withdrawn from tower (5) through line (10) and recycled at least in part to line (1) for further treatment.

While it has been indicated by means of the flow diagram depicted in the accompanying drawing the best manner in which the process may be operated, it has omitted a number of common engineering devices such as flow control valves, temperature recording devices, etc., and this omitted accessory apparatus would normally be used in the operation in a well conducted plant. It has, however, done this in order to direct attention to the improvements and to avoid confusion with what is old.

A number of pilot plant tests or runs have been made, and data on a few of these runs is set forth below in order to show the utility of the improved process. In the runs summarized below, the catalyst employed as a spent and contaminated silica alumina gel cracking catalyst withdrawn from a commercial catalytic cracking plant. Due to preceding use, this catalyst had a very low activity (D+L of about 20) from the standpoint of its capability of promoting the cracking of natural or petroleum gas oil and was found to be uneconomical for use in catalytic cracking operations due to the fact that it had become contaminated during use in the catalytic cracking plant with harmful material such as iron and its compounds.

The conditions and results of the tests or runs which were made are set forth below in tabular form. The feed charged through to the treating vessel in the drawing was a normally liquid hydrocarbon synthesis product formed in the presence of an iron catalyst. The material had an end boiling point of about 600° F. with about 75% of the material boiling in the gasoline boiling range. The tests were made in a fixed bed unit.

Runs	Feed to catalytic Unit	I	II	III	IV
Temp. catalyst (top) °F.		914	920	898	953
Temp. catalyst (middle) °F.		918	904	899	949
Temp. catalyst (bottom) °F.		854	866	903	950
Temp. catalyst (average) °F.		895	897	900	951
Temp. lead bath, °F.		956	950	915	958
Wt. % water, based on feed		0	0	0	0
Reactor pressure, lb./sq.in. gage		0	0	0	0
Cracking period, min.		60	60	60	60
Oil feed rate V/V/Hr.		0.5	1.0	3.0	2.0
Yield Data, Based on Feed.					
Material balance, Wt. %		96.0	95.0	101.9	100.3
10lb. gasoline, vol. %		58.2	63.8	86.6	66.0
C_5—430° F., vol. %	75.3	54.8	60.2	76.5	62.0
Total C_4, vol. %	0.0	20.8	19.5	5.0	18.1
Isobutylene, vol. %	—	6.0	6.4	1.9	6.6
N-butylene, vol. %	—	8.1	9.0	2.3	8.6
Isobutane, vol. %	—	5.4	3.8	0.6	2.4
N-butane, vol. %	—	1.3	0.4	0.2	0.5
Dry gas, wt. %	0.0	15.0	11.6	3.0	9.3
Cu. ft./Bbl.	—	528	377	99	285
Hydrogen, wt. %	—	0.14	0.10	0.03	0.05
Methane, wt. %	—	1.52	0.80	0.17	0.60
Ethylene, wt. %	—	1.10	0.70	0.16	0.48
Ethane, wt. %	—	1.10	0.80	0.19	0.60
Propylene, vol. %	—	13.8	12.0	3.3	10.1
Propane, vol. %	—	2.7	1.65	0.4	1.2
Carbon, wt. %	—	4.7	2.8	1.1	1.9
Gas oil, vol. %	24.7	9.4	11.9	15.9	15.2

Runs	Feed to catalytic Unit	I	II	III	IV
10lb. Gasoline Inspection.					
Gravity, °API		63.5	64.3	65.2	63.1
% D+L at 158° F.		25.5	28.5	18.0	26
% D+L at 212° F.		56.0	57.0	44.5	56.0
% D+L at 257° F.		68.5	71.0	64.5	70.5
ASTM octane	66.4	79.3	79.9	79.5	80.7
CFR-Res. octane	71.3	89.7	90.3	90.8	92.2
CFR-Res. oct.+1.5 cc. TEL	82.6	94.6	96.7 (+2.0)		96.9 (+2.0)

In the foregoing data, it is significant to note that in run No. III a very high yield of gasoline is obtained namely 86.6 volume per cent. It is also pointed out that in run No. III an ASTM octane number of 79.5 gasoline product was formed from the material forming the feed having an octane number of 66.4. On the CFR research octane basis this corresponds to an increase of from 71.3 for the gasoline fraction of the feed stock to 90.8 for the product gasoline. It is also important to note in connection with run III that only 1.1 weight per cent. of the feed material was converted to carbonaceous material. It is also apparent from the data that for best results the contact time should be relatively low. For example, where the feed rate was 0.5 volumes of oil per volume of catalyst per hour the carbon formation was 4.7 wt. %. Where the feed rate of oil was one volume of oil per volume of catalyst per hour the carbon formation was 2.8 wt. %. In run IV the feed rate was 2 volumes of oil per volume of catalyst per hour and here the yield of 10lb. gasoline was higher than in runs I and II, the coke formation was lower and the octane improvement was excellent. The temperature here was about 950° F.

It is quite apparent from the data that the feed rate of the fresh material from the reactants must be of the order of 2 to 3 volumes of cold oil per volume of catalyst per hour. Somewhat higher feed rates may be used, say up to 5 volumes of oil per volume of catalyst per hour where the temperature is increased up to 950 to 975° F. Another significant factor revealed by the data is that in the case of runs III and IV the gaseous products formed contain a greater proportion of olefins to paraffins. This olefinic material may be polymerized to form normal liquid hydrocarbons boiling in the gasoline range thus increasing the yield of the overall gasoline product.

Since, as previously stated, it is a known procedure to subject the synthetic gasoline produced by the reduction of carbon monoxide with hydrogen to an after treatment with bauxite for the purpose of improving the octane quality of the gasoline and otherwise upgrading the material, some comparative tests have been made in a fluid catalyst unit in which a comparison was made between a severely deactivated silica alumina gel cracking catalyst on the one hand, and bauxite on the other. The feed in both of these runs was a synthetic gasoline product which contained from 83 to 84 volume per cent. of a C_5—430° F. end boiling point fraction mixed with 12.5 to 14 volume per cent of gas oil. The conditions under which the tests were made, as well as the yields, are set forth below:—

	Feed Stock	Spent Catalyst	Bauxite
Silica-alumina gel catalyst*			
D+L activity		22	13
Temperature, °F.		816	850
Catalyst/oil ratio		9	2.5
W/hour/W**		12	12
Wt. % steam on feed		26	23
Reactor pressure, psig. (top)		9	9
Reactor feed. vol. % of total feed		95.3	93.9

	Feed Stock	Spent Catalyst	Bauxite
Yields (Output Basis)***			
10lb. gasoline, vol. %	87.7	83.2	81.2
Gravity, °API	—	64.2	64.0
%D+L at 158° F.	25.5	29.0	20.5
% D+L at 212° F.	48.5	55.5	48.5
% D+L at 257° F.	64.5	71.0	66.0
Motor octane No.	68.6	81.1	77.2
Research octane No.	80.0	94.1	88.0
Res. oct. No. +2 cc. TEL	82.0	99.1	96.8
C_5—430° F. VT, vol. %	80.1	75.5	72.0
Total C_4, vol. %	3.0	7.1	5.5
Isobutylene, vol. %		1.6	0.8
n-butenes, vol. %	2.6	4.7	4.0
Isobutane, vol. %	—	0.3	0.1
n-butane, vol. %	0.4	0.5	0.6
Dry gas, wt. %	0.2	2.9	2.0
CF/bbl.		77	60
Gas oil bottoms, vol. %	16.7	8.9	11.5
Carbon, wt. %		1.6	3.0

*Containing 12—14% alumina, the remainder being silica gel.

**In normal cracking the feed rate of oil is such that from about 1 to 3 pounds of cold oil per pound of catalyst in the reactor, are fed each hour into said reactor. Here it was 12 pounds of oil per lb. of catalyst in the reactor per hour.

***Based on actual flashed feed to the reactor.

It will be noted from the foregoing table that the cracking catalyst having a D+L activity of 22 yielded 83.2 volume per cent. of 10 pound (Reid Vapor Pressure) gasoline as against 81 volume per cent. 10 pound gasoline where bauxite was used. It will be noted further that both the clear octane rating and the rating of the leaded gasoline (TEL=tetra-ethyl lead) were superior in the run made using the spent cracking catalyst, and it is also significant to note that the carbon formation in the case of the spent catalyst was approximately 50% of that formed in the run using bauxite. It is particularly interesting to note that the research octane number (clear) was about 6 numbers better in the run using the spent catalyst than in the run employing bauxite, for this is a very important difference in this high octane range. And with 2 cc.of tetra-ethyl lead per gallon the research octane rating of the gasoline produced in the presence of the spent catalyst is increased to over 99.

As indicated, the treatment with spent cracking catalyst results in the formation of olefins and a shifting of the double bond in the olefin toward the center of the molecule. Infra-red analyses of the C_7 fraction gave the results below:—

Infra-red Analyses of C_7 Fractions.

	Feed	Product Run 1	Run 2
Synthesis run			
Treating run			
Catalyst	—	Spent synthetic silica-alumina	
Temperature °F.	—	900	950
V/V/Hr.	—	3	10
Pressure, psig.	—	0	0
Res. O. N. (C_5—430° F.)	75.9	91.0	87.8
Olefin type, wt. %			
Alpha	54.4	4.7	16.5
Trans	3.3	21.1	25.3
Cis	4.3	4.7	9.3
Tertiary	4.4	6.8	6.0
Tri-subst. Ethlene	2.1	6.9	3.1
Tetra-subst. Ethylene	—	33.6	13.9

Infra-red Analyses of C_7 Fractions.

Wt. % oxygen	Feed	Product Run 1	Run 2
Alcohols	0.82	0.24	0.06
Acids	1.41	0.11	0.36
Esters	0.60	0.0	0.05
Aldehydes	0.86	0.34	0.34
Ketones	0.34	0.32	0.77
Total	4.03	1.01	1.58

The olefins as synthesized are predominantly of the alpha type, with the olefinic double bond adjacent to a terminal carbon atom. After treatment with used cracking catalyst the predominant olefin types are first tetra-substituted ethylenes and second trans-olefins. Olefin isomerization occurs to an extent roughly proportional to the severity of the treatment, as indicated by the partial conversion effected in the high throughput run 2.

Now while the process of treating a hydrocarbon synthesis product has been described in detail, the hydrocarbon synthesis product may be mixed with a minor proportion of a virgin or cracked petroleum gas oil and a high quality cracked or treated product is obtained in good yields with low carbon formation.

In the accompanying drawing, and in the description of the operation of the process, the catalyst is shown and described in the form of a fixed bed. Some of the runs, however, as previously stated. were made in a fluid catalyst type of reactor. Since this technique is now known, it is deemed unnecessary to described it in detail. It will be sufficient to point out that, as usual, the catalyst is in the form of a powder having a particle size of from 20 to 200 microns, with the major portion having a particle size above 40 microns, and that the hydrocarbon in vapor form is passed upwardly through the treater containing the powdered catalyst at a velocity sufficient to form a sort of bubbling bed or dense, turbulent suspension which has come to be known as a fluidized catalyst bed. It might be added that the superficial gas velocities in fluid beds are of the order of ½ to 3 or 4 feet per second. And by "superficial velocity", is meant the velocity considered as though the reactor contained no catalyst.

To recapitulate briefly, the present invention relates to improvements in the art of catalytic treating of synthetic normally liquid naphtha hydrocarbons, usually containing oxygenated compounds associated therein, which are the product formed by reducing carbon monoxide with hydrogen preferably in the presence of an iron catalyst, usually a catalyst containing a very small per cent. of a promoter such as potassium carbonate. It has been found that by this catalytic treatment high yields of high octane number gasoline may be produced, provided the treatment is carried out in the presence of a spent and contaminated synthetic gel cracking catalyst. As compared with the prior acknowledged art of bauxite treatment of the same or a similar product, a gasoline having a higher anti-detonation rating or octane number may be obtained by practising the process.

Instead of using a spent silica alumina gel catalyst, a silica-magnesia spent catalyst (30—40 weight per cent. magnesia gel, remainder silica gel) or a spent bentonitic clay cracking catalyst may be used.

Also the catalyst in reactor (3) may be powdered and formed into a fluidized bed by causing the oil vapors to flow upwardly in said reactor at a superficial velocity of from about ½ to 2 feet per second. It is preferred to maintain a high rate of oil feed of from 10 to 15lbs. per pound of catalyst in the reactor per hour. The fluidized catalyst technique is now well understood in the petroleum oil industry.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for improving the quality of a normally-liquid hydrocarbon product obtained from a Fischer synthesis type process comprising heating the said product in a reaction zone in the presence of a siliceous cracking catalyst which has been severely deactivated and contaminated as hereinbefore defined.

2. A process according to claim 1 wherein the catalyst is a silica alumina catalyst, a silica magnesia catalyst or a bentonitic clay catalyst.

3. A process according to claim 2 wherein the catalyst contains silica and alumina gels in the ratio of 88—86 parts by weight of silica to 12—14 parts of alumina.

4. A process according to claim 2 wherein the catalyst contains silica and

magnesia gels in the ratio of 70—60 parts by weight of silica gel to 30—40 parts of magnesia gel.

5. A process according to any of the preceding claims wherein the catalyst contains iron material to the extent of from 0.3% to 1.0% by weight.

6. A process according to any of the preceding claims in which the said liquid product is fed to the reaction zone at a space velocity of from 2—5 and preferably 2—3 volumes of cold oil per volume of catalyst per hour.

7. A process according to any of claims 1 to 5 wherein the catalyst is maintained in the form of a fluidized bed of finely powdered solid.

8. A process according to claim 7 wherein the hydrocarbon vapors are passed upwardly through the fluidized bed at a superficial velocity of from ½ to 4 feet per second.

9. A process according to claim 7 in which the said synthetic product is fed to the treating zone at a velocity such that from 10 to 15lbs. of oil per lb. of catalyst in reactor are fed in each hour.

10. A process for improving the quality of a normally-liquid hydrocarbon product obtained from a Fischer synthesis type process as described herein and with particular reference to the accompanying drawing.

Dated this 18th day of March, 1948.

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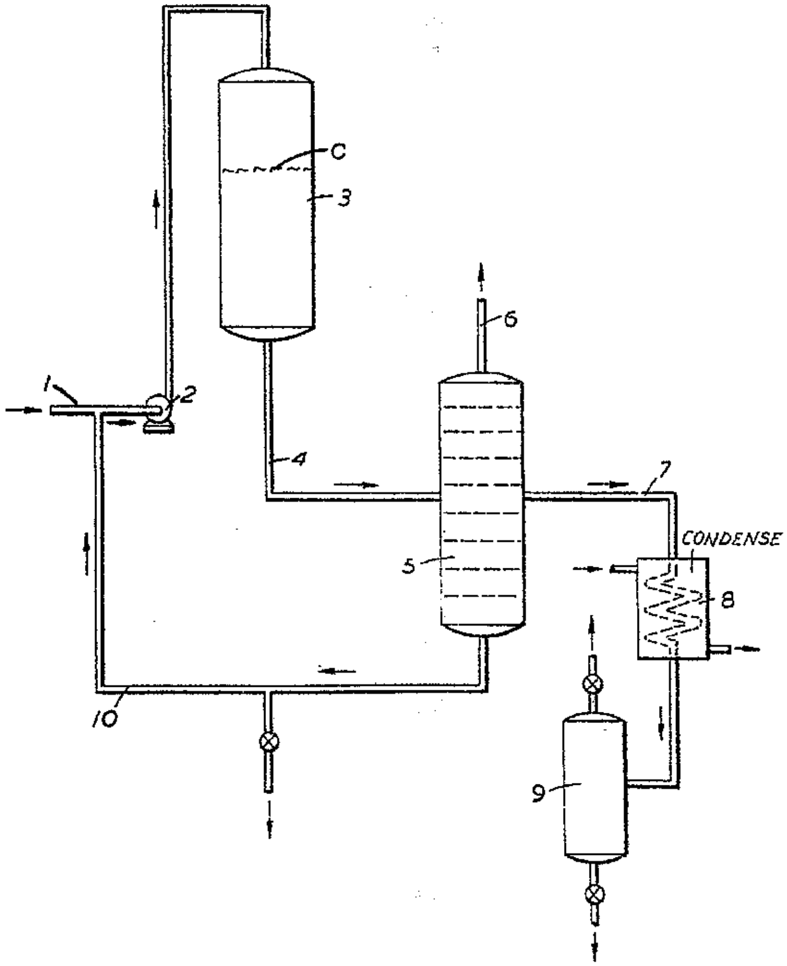
641,121 COMPLETE SPECIFICATION 1 SHEET

[This Drawing is a reproduction of the Original on a reduced scale.]



H.M.S.O. (Ty.P.)