

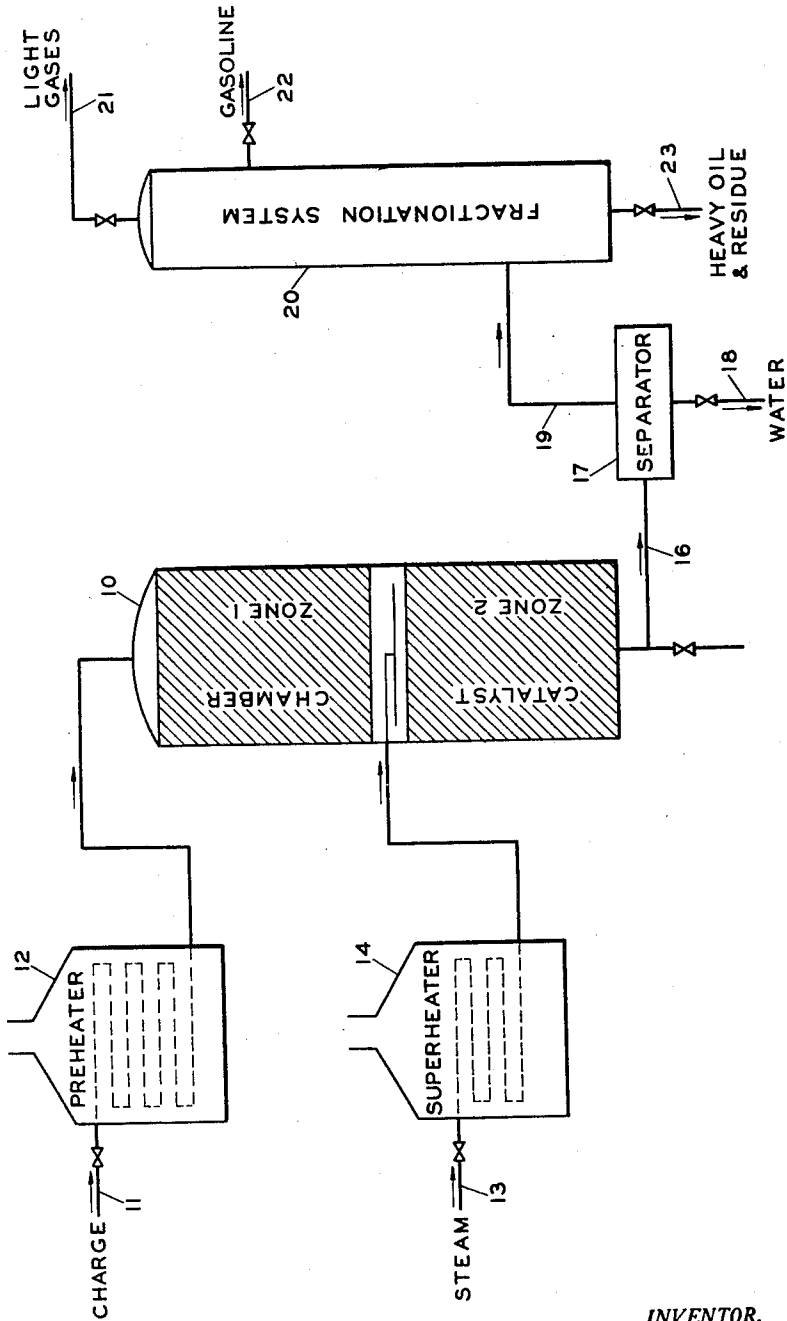
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P. H. JOHNSON

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TREATMENT OF SYNTHETIC GASOLINE

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INVENTOR.  
P. H. JOHNSON

BY *Hudson & Young*  
ATTORNEYS

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## TREATMENT OF SYNTHETIC GASOLINE

Paul H. Johnson, Bartlesville, Okla., assignor to  
Phillips Petroleum Company, a corporation of  
Delaware

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This invention relates to the treatment of gasoline to improve its properties. In one of its more specific aspects, it relates to a treatment of a Fischer-Tropsch type synthetic gasoline to improve its octane number.

I have discovered that treatment of a raw synthetic gasoline of the Fischer-Tropsch type in a two-step process greatly improves its properties. The first step comprises passing a synthetic gasoline over a cracking catalyst, such as bauxite, under conditions favorable to isomerization, and the second step comprises passing the effluent from the first step, with steam added, over the same or a different cracking catalyst under essentially the same conditions. By this treatment the ASTM and Research octane numbers of a synthetic gasoline are raised more than they would be by treating with either one or the other of the two steps.

The art teaches up-grading of gasoline by means of isomerization. However, when a raw Fischer-Tropsch type of gasoline is passed over a cracking catalyst, improvement by isomerization is retarded because of high carbon deposition. The art also teaches the treatment of gasoline with steam over a cracking catalyst in which the steam aids the isomerization reaction. This method also is not entirely satisfactory, since the presence of steam inhibits the complete removal of oxygenated compounds present in this type of gasoline, resulting in poor color stability, poor odor, and poor up-grading. Although I do not know the exact reason for the poor up-grading when single-pass treating with steam, it is presumed that it may be a result of the action of oxygen-containing compounds, such as alcohols, ketones, and aldehydes, known to be present in appreciable amounts in fractions boiling in the gasoline range which result from reaction of carbon monoxide and hydrogen in the well known "Fischer-Tropsch" type of process. In the case of each method, when practiced alone, poor up-grading and poor odors are obtained when used to treat Fischer-Tropsch type gasolines.

An object of the present invention is to provide a novel and improved method for improving gasoline. Another object is to provide an improved method for removing oxygenated compounds from Fischer-Tropsch type gasoline. Other objects and advantages of this invention will become apparent from the accompanying disclosure and discussion.

In accordance with a specific embodiment of this invention, a raw synthetic gasoline of the Fischer-Tropsch type is preheated and passed

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over a cracking catalyst, such as bauxite, in a first contact zone at a temperature in the range of about 700 to about 950° F. and a pressure in the range of about 0 to about 200 pounds per square inch gauge. In the first contact zone undesirable oxygenated compounds are removed and the odor improved. Effluent from the first contact zone is then passed through a second contact zone, containing the same or a different catalyst as was used in the first zone, along with superheated steam, at a temperature in the range of about 600 to about 950° F. and a pressure in the range of about 0 to about 200 pounds per square inch gauge. Steam in the amount of about 20 to about 65 pounds per barrel of gasoline is used in the second step. The space velocity in both the first and second contact zones is about 0.5 to about 10 liquid volumes of charge per volume of catalyst per hour. The two contact zones may be the same size or they may be varied considerably in either direction, depending somewhat upon the exact nature of the gasoline to be treated. Effluent from the treatment in the second contact zone is passed through a conventional fractionating system where the desired product, such as a stabilized 400° F. end-point gasoline, is separated and recovered. The catalyst is regenerated with steam and air when it becomes contaminated with carbonaceous deposits.

Both contact zones may be of approximately equal size, or they may be varied considerably in either direction depending upon the exact nature of the material to be treated. Also both contact zones may be within the same chamber or in two separate chambers as desired.

The following specific description is of a preferred embodiment of one method for operating my process. It is understood, however, that while this is representative in general of my process, various changes may be followed in adapting the process within the scope of the invention.

A more clear understanding of some of the many aspects of my invention may be had by referring to the attached schematic flow diagram in conjunction with the following discussion.

Raw synthetic gasoline is introduced to catalyst chamber 10 through line 11 and preheater 12 at a temperature in the range of about 700 to about 950° F. and a pressure in the range of about 0 to about 200 pounds per square inch gauge. In catalyst chamber 10 the heated gasoline is first contacted with a cracking catalyst such as bauxite in zone 1. Superheated steam,

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in an amount in the range of about 20 to about 65 pounds per barrel of raw gasoline charge, is introduced to catalyst chamber 10 between zones 1 and 2 through line 13 and superheater 14. Treated material from zone 1, along with superheated steam, is passed to zone 2 at a temperature in the range of about 600 to about 950° F. where it is contacted with a cracking catalyst, the same as, or different from, the catalyst used in zone 1. Treated material is recovered from zone 2 of catalyst chamber 10 and passed through line 16 to separator 17 where water is removed through line 18. Hydrocarbon material from separator 17 is removed through line 19 and passed to fractionation system 20. In fractionation system 20 light gases are separated and removed through line 21, a gasoline product is removed through line 22 and heavy oil and residue are removed through line 23. The space velocity through each zone of the catalyst chamber is in the range of about 0.5 to about 10 liquid volumes of charge per volume of catalyst per hour.

Other catalyst may be used in the practice of this invention in addition to bauxite. Example of such catalysts are silica-alumina, brucite, alumina gel, activated natural clays such as montmorillonite, etc. Methods of preparing such catalysts are known in the art and usually include calcination at controlled temperatures to remove most of the chemically bound water. Operating conditions such as temperature, pressure, rate of flow, etc., may necessarily be altered somewhat to conform with the catalyst used. One skilled in the art will be familiar with the particular catalyst best suited for treating a particular material, and the best operating conditions to be employed.

Various additional valves, pumps, and other conventional equipment, necessary for the plant practice of this invention, will be familiar to one skilled in the art and have been omitted from these schematic drawings for the sake of clarity.

Some of the many advantages of this invention are illustrated by the following example. The reactants and their proportions, and other specific ingredients, are presented as being typical and should not be construed to limit the invention unduly.

*Example*

Two runs were made using a raw Fischer-Tropsch gasoline which had a boiling range of 110 to 385° F., an ASTM unleaded octane number of 62.0 and a bromine number of 67. In each run the raw gasoline charge was passed through a calcined bauxite catalyst at an average temperature of 745° F., a pressure of 50 pounds per square inch gauge, and a space velocity of 1.4 liquid volume per volume of catalyst per hour. In the second run steam was added in the amount of 63 pounds per barrel of gasoline charge.

A third run was made in which the product of the first run was treated in the manner described for the second run except that the average temperature was 700° F.

The following data were obtained:

	Run 1	Run 2	Run 3
ASTM Octane Rating:			
0 ml. TEL.....	72.2	70.4	76.0
3 ml. TEL.....	81.3	81.6	86.2
Research Octane Rating:			
0 ml. TEL.....	77.1	73.3	82.0
Bromine Number.....	67	67	85

A comparison of runs 1 and 2 shows the octane numbers were increased more when the gasoline was passed over the catalyst alone rather than with steam. In the third run, however, the octane numbers were very materially increased, as was the bromine number.

Although the process has been described and exemplified in terms of its preferred modifications, it is understood that various changes may be made without departing from the spirit of the process as disclosed and expressed in the claims.

I claim:

1. The process of manufacturing an improved synthetic gasoline from a raw Fischer-Tropsch type gasoline, which comprises passing a synthetic gasoline stock at a temperature in the range of 700 to 950° F. through a first contact zone in the absence of steam in contact with a cracking catalyst effective for removing oxygenated materials and isomerizing hydrocarbons, and passing effluents from said first contact zone and steam through a second contact zone at a temperature in the range of 600 to 950° F. in contact with a cracking catalyst effective to further isomerize said hydrocarbons, and recovering from effluents from said second contact zone an improved synthetic gasoline stock as a product of the process.

2. A process according to claim 1 wherein each of said catalysts is an alumina-containing catalyst.

3. A process according to claim 1 wherein each of said catalysts is bauxite.

4. A process according to claim 1 wherein at least one of said catalysts is silica-alumina.

5. A process according to claim 1 wherein at least one of said catalysts is an activated montmorillonite.

6. The process of manufacturing an improved synthetic gasoline of increased ASTM and Research octane numbers from a raw gasoline containing oxygenated compounds, which comprises passing a vaporized synthetic hydrocarbon material boiling in the gasoline range and containing oxygen-containing compounds in the absence of steam through a first contact zone at a temperature in the range of 700 to 950° F. and an elevated pressure in contact with a cracking catalyst effective for removing said oxygenated compounds, improving the odor of said hydrocarbon, and isomerizing said hydrocarbon material, passing a vaporous effluent from said first contact zone and added steam in an amount in the range of about 20 to about 65 pounds per barrel of raw charge through a second contact zone at a temperature in the range of 600 to 950° F. and an elevated pressure in contact with a cracking catalyst effective to further isomerize said hydrocarbon, the space velocity of said charge through said first and second contact zones being in the range of about 0.5 to about 10 liquid volumes of charge per volume of catalyst per hour, and recovering from effluents from said second contact zone a gasoline stock of improved quality as a product of the process.

7. The process of manufacturing an improved synthetic gasoline from a raw Fischer-Tropsch gasoline stock by removing oxygenated compounds and by increasing the ASTM and Research octane number, which comprises passing a vaporized synthetic gasoline stock produced by a Fischer-Tropsch synthesis into contact with a bauxite catalyst in a first contact zone, at a temperature in the range of about 700 to about

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950° F. and a pressure in the range of about 0 to about 200 pounds per square inch gauge and thereby removing undesirable oxygenated compounds, improving the odor, and isomerizing hydrocarbons; passing vaporous effluent from said first contact zone and steam, in an amount in the range of about 20 to about 65 pounds of steam per barrel of raw gasoline charge, into contact with a bauxite catalyst in a second contact zone, at a temperature in the range of about 600 to about 950° F. and a pressure in the range of about 0 to about 200 pounds per square inch gauge and thereby further isomerizing said hydrocarbons, the space velocity of said charge through said first and second contact zones being the same and in the range of about 0.5 to about 10 liquid volumes of charge per volume of catalyst per hour, and recovering a synthetic gasoline

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of improved octane number and odor as a product of the process.

PAUL H. JOHNSON.

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