

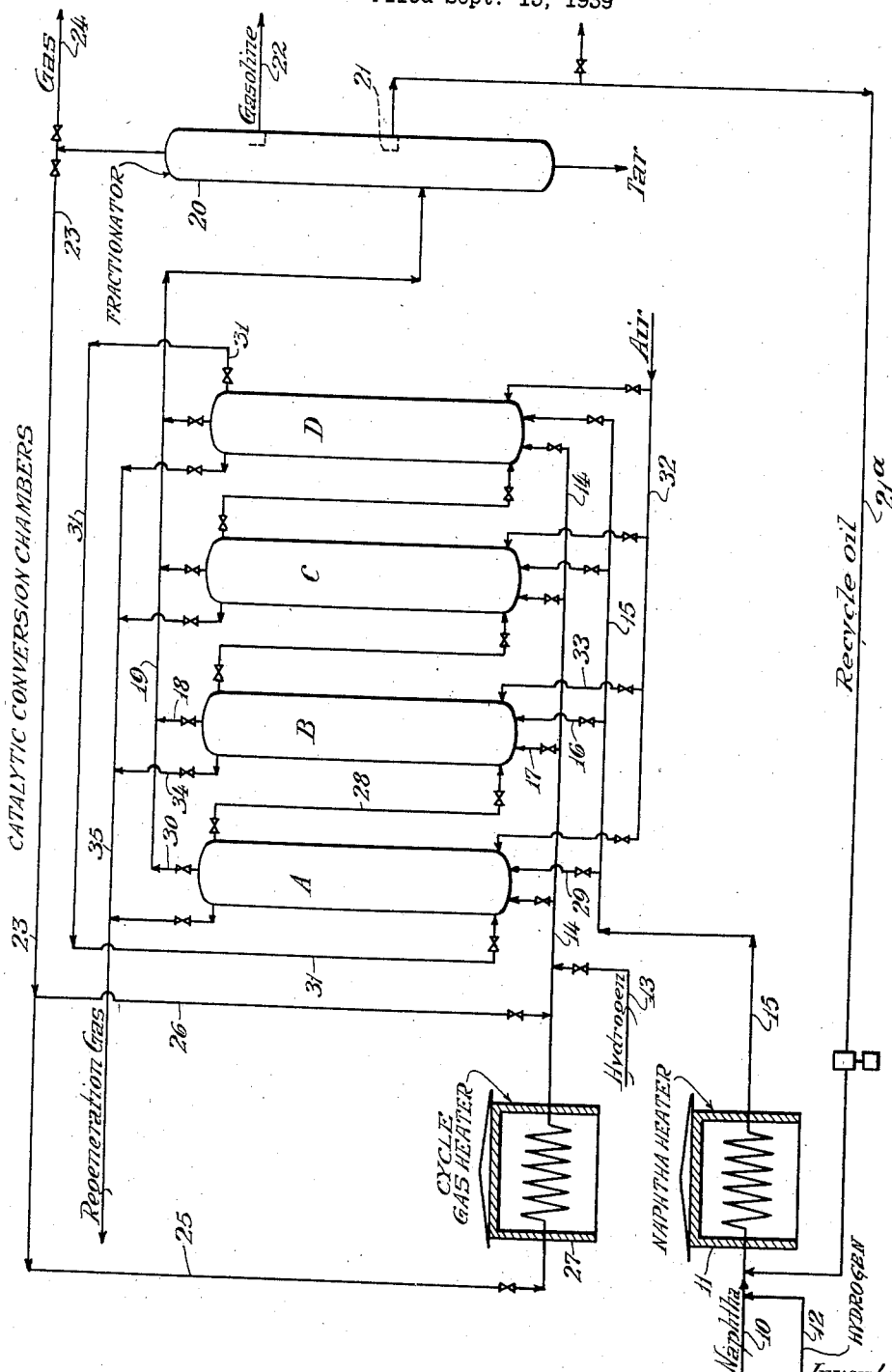
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CATALYTIC TREATMENT OF PETROLEUM DISTILLATES

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CATALYTIC TREATMENT OF PETROLEUM
DISTILLATES

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This invention relates to a process of treating hydrocarbon oils and particularly petroleum naphthas by the action of catalysts whereby the chemical composition of the hydrocarbons is largely altered particularly in the direction of producing aromatic hydrocarbons from open-chain or aliphatic hydrocarbons. A primary object of the invention is to convert catalytically paraffinic naphthas and gasoline of low knock rating into gasoline of high knock rating for use as a motor fuel in internal combustion engines. Another object of the invention is to aromatize paraffinic naphthas by the action of metals or compounds of metals selected from the IV, V and VI groups of the periodic system, in the presence of hydrogen under controlled conditions of pressure and temperature to obtain dehydrogenation rather than hydrogenation. A further and more specific object of the invention is to condition the catalyst employed in the process by treating it preliminarily with a gas mixture preferably produced in the process and thereby obtain larger yields of the desired aromatic hydrocarbons with less degradation to carbon and carbonaceous materials. Still another object of the invention is to provide a process with a plurality of reaction chambers which are employed in rotation and regenerated in rotation by treating with an oxygen-containing gas for removal of carbonaceous deposits from the catalyst, after which the catalyst is conditioned with hydrogen-containing gas before reuse.

As previously indicated, the catalysts which we prefer to employ are compounds of the IV, V and VI group metals or the metals themselves and in particular the elements of the left series or sub-group "A." Preferred examples of such compounds are chromium, molybdenum, and vanadium oxides. Titanium, cerium, thorium and tungsten oxides are also of importance. The catalyst may be prepared by various methods such as the ignition of the nitrate of the metal, ignition of the ammonium salt of the metallate, such as ammonium chromate, heating the hydroxide, etc. In general, we prefer to employ a support for the catalyst and in particular we prefer to employ aluminum oxide as a support. The alumina should be in a porous form presenting extensive surface, such as Al_2O_3 gel. The aluminum oxide or bauxite may be impregnated with the catalyst metal nitrate or the ammonium metallate, for example, and ignited. The catalyst metal oxide may suitably be present on the alumina in the ratio of about 2 to 10%. The catalyst may be granulated and screened to

about 5 to 50 mesh, the 10 to 20 mesh size being generally preferable.

The invention is illustrated by a drawing which shows diagrammatically suitable apparatus for carrying out the process, including a pipe heater for vaporizing the naphtha and a series of catalytic reaction chambers. Referring to the drawing, the stock to be treated is introduced by line 10 into heater 11. A typical stock is a heavy naphtha fraction from Mid-Continent crude having an initial boiling point of about 250° F., a 50% point of about 350° F. and an end point of about 425° F. Various distillate stocks, either straight run or cracked, may be employed and another example is a heavy gasoline having a 10% point of about 300° F. and 90% point of about 450° F.

In the heater 11 the naphtha is vaporized and the vapors are heated to a temperature generally within the range of about 875 to 1075° F. at which temperature the vapors are introduced into one or more of the catalyst chambers A, B, C or D. The pressure within the catalyst chambers, while in operation, is suitably about 30 to 450 pounds per square inch, the preferred pressure range being about 100 to 250 pounds per square inch. Higher pressures must be avoided to prevent hydrogenation in the process with the production of less aromatic hydrocarbons and a motor fuel of low knock rating. The treating rate may suitably be about 0.04 to 10 volumes of naphtha liquid per volume of catalyst per hour.

In order to extend the life of the catalyst and control the reaction more accurately to produce a maximum dehydrocyclization, it is necessary to maintain a certain concentration of hydrogen in the catalyst mass during the reaction. We prefer to employ about 2 to 8 mols of hydrogen per mol of hydrocarbons treated. However, the amount of hydrogen may be reduced to as little as 0.4 mol in some cases. Hydrogen may be introduced by line 12, passing through the heater with the naphtha or it may be introduced by line 13 connecting with distributor 14 for introduction into the end of the catalyst chamber in operation. Instead of addition hydrogen in this manner, however, we may recycle hydrogen-containing gases from the process as will be hereinafter more fully described.

Leaving naphtha heater 11, the naphtha vapors are conducted by line 15 to one of the catalyst chambers A, B, C or D. For example, it may be conducted by connection 16 to the bottom of chamber B. Gases are introduced simultane-

ously from header 14 and connection 17. The mixture of hydrocarbons and hydrogen passes through a bed of the catalyst previously described contained in chamber B and hydrocarbons leaving the chamber B by connection 18, leading to header 19 by which they are conducted to fractionator 20. Unconverted naphtha distillates heavier than the desired motor fuel product may be separated by trapout 21 and conducted back to the process by line 21a. The desired motor fuel is withdrawn at trapout 22 and the fixed gases containing hydrogen, methane, C₂, C₃ and C₄ hydrocarbons are withdrawn from the top of fractionator 20 by line 23. A portion of the gases may be discarded by vent 24 while the major portion is recycled to the process through lines 23, 25 and/or 26. The gases which are recycled vary somewhat in composition depending on the conditions of operation, the efficiency of the catalyst and the age of the catalyst. With a fresh catalyst of high activity, the hydrogen content in the recycle gas may reach 90 to 95%. Later in the run, the hydrogen content of the gases may drop to as low as 45%.

Gases which are obtained from fractionator 20 are heated in cycle gas heater 27 and then pass at a high temperature through header 14 and into one or more of the catalyst chambers previously mentioned, the cycle gas generally passing first through a bed of freshly regenerated catalyst before entering the naphtha conversion chamber. For example, the cycle gas from heater 27 may pass by header 14 into the base of the catalyst chamber A containing freshly regenerated catalyst. The hot catalyst contained therein (at a temperature of 900 to 1000° F. or higher) is considerably modified in activity and tempered by the hydrocarbons contained in the recycle gas.

The gas then passes from the top of chamber A by line 28 to the bottom of chamber B which is in operation. When the activity of the catalyst in chamber B has become appreciably exhausted which may require about 5 to 20 hours of operation, certain valves are adjusted and the hot gases from cycle heater 27 are diverted to catalyst chamber D which is freshly regenerated. The valves in line 28 are closed. At the same time valves in connections 16 and 18 are closed and naphtha vapor is permitted to enter chamber A by connection 29. The treated hydrocarbons are withdrawn by line 30 into header 19 previously mentioned. The recycle gases which are introduced at the bottom of chamber D are conducted by line 31 to the bottom of chamber A where they mix with the hydrocarbon vapors being treated therein. This process is repeated at regular intervals.

After the catalyst in chamber B has been substantially exhausted as just mentioned, it may be regenerated by means of an oxygen-containing gas introduced through manifold 32 and connection 33. The exhausted regeneration gases are withdrawn by line 34 and manifold 35. At the start, the amount of oxygen in the regenerated gases is maintained at a low concentration, about 0.2 to about 5%, the remainder of the gas being inert non-combustible gas such as nitrogen or flue gas. In this way, we control the temperature of the catalyst undergoing regeneration and prevent overheating of the catalyst and permanent degeneration. Spent regeneration gases from line 35 may be passed in indirect contact with a stream of water thereby generating steam from the heat contained in the gases.

The following scheme will show the operating cycles in the process according to one method of running:

Present cycle

5 Chamber

- (A) Hydrogen through fresh catalyst
- (B) In operation on naphtha with hydrogen coming from (A)
- (C) Regenerating
- (D) Regenerated and hot

Next cycle

- (A) Operating on naphtha with hydrogen from (D)
- (B) Regenerating
- (C) Regenerated and hot
- (D) Cooling with hydrogen

Next cycle

- (A) Regenerating
- (B) Regenerated and hot
- (C) Cooling with hydrogen
- (D) Operating on naphtha with hydrogen from (C)

25 When the temperature of the catalyst after regeneration is considerably higher than the desired hydrocarbon conversion temperature, we may recycle unheated gas through 26 directly to the reaction chamber just regenerated and thereby reduce the temperature to the desired point. Where the temperature of the regenerated catalyst is very high, for example 1200 to 1400° F. in the case of some of the more rugged catalysts, we may conduct the regeneration in such a manner as to leave the catalyst completely regenerated at a high temperature and thereupon pass recycle gas therethrough without preliminary cooling of the catalyst. The hydrogen and hydrocarbon gases have a desirable conditioning or moderating effect on the catalyst so that when the naphtha vapors are passed over such a catalyst, the dehydrocyclization which takes place is more readily controllable. Less destructive reaction of the naphtha hydrocarbons initially with excessive carbon formation takes place and more of the naphtha hydrocarbons are converted to the aromatic hydrocarbons desired.

Instead of employing in our process a catalyst disposed in stationary beds, we may also employ a moving bed arrangement of the catalyst. In this arrangement the catalyst is fed continuously or intermittently into an elongated reaction chamber from which it is withdrawn at the bottom continuously or intermittently. Hydrocarbon vapors are passed through the granular catalyst the same way as hereinabove described for a fixed bed catalyst. In a moving bed operation, the recycled gases may pass through the freshly regenerated catalyst in the upper part of an elongated reaction chamber and thereafter combine with the hydrocarbon vapors introduced into the reaction chamber at a lower point, flowing concurrently with the catalyst and being withdrawn at the base of the reaction chamber. Regeneration of the spent catalyst withdrawn from the base of the reaction chamber may be carried out in a separate regenerating unit and the hot regenerated catalyst may be introduced directly into the top of the elongated reaction chamber in a manner well understood in the art.

Having thus described our invention, what we claim is:

1. The process of converting petroleum naphtha of low knock rating into aromatic motor

fuels of high knock rating which comprises passing the vapors of said naphtha in contact with a solid aromatizing contact catalyst at an elevated temperature of about 875 to 1075° F. in the presence of about 0.4 to 8 mols of hydrogen per mol of naphtha hydrocarbon treated and a pressure of about 30 to 450 pounds per square inch, and preconditioning said catalyst at a high temperature with a current of hydrogen-containing hydrocarbon gas before contacting with said naphtha vapors.

2. The process of claim 1 wherein the said hydrogen-containing hydrocarbon gas employed for preconditioning the said catalyst is derived from the reaction with said aromatizing catalyst.

3. The process of aromatizing open-chain hydrocarbons contained in petroleum naphtha which comprises subjecting the vapors of said naphtha together with hydrogen to the action of a solid aromatizing contact catalyst at a temperature of about 875 to 1075° F. and a pressure of about 30 to 450 pounds per square inch, separating the product of aromatization into a motor fuel fraction, a heavier fraction and a gaseous fraction containing excess hydrogen, recycling the gaseous fraction in the process and contacting it with fresh catalyst at a high temperature of about 900 to 1400° F. before contacting said catalyst with said naphtha hydrocarbons.

4. The process of claim 3 wherein said fraction heavier than gasoline obtained from the process is vaporized and recycled with said naphtha vapors to said aromatizing catalyst.

5. The process of claim 3 wherein said hydrogen-containing gas is heated to an elevated temperature before contacting it with said fresh catalyst.

6. The process of aromatizing open-chain hydrocarbons contained in petroleum naphtha which comprises vaporizing said naphtha and subjecting the vapors at a temperature of about 875 to 1075° F. to the action of a solid aromatizing contact catalyst contained in a first reaction zone, separating from the products of the reaction aromatic gasoline and hydrogen-containing hydrocarbon gas, conducting said hydrogen-containing hydrocarbon gas at a high temperature into contact with fresh aromatizing catalyst contained in a second reaction zone and thence in

series into said first catalyst zone in admixture with said naphtha vapors, continuing the reaction until the catalyst in said first reaction zone becomes substantially deactivated, interrupting the reaction and regenerating the catalyst in the said first reaction zone by passing therethrough a current of an oxygen-containing gas, whereby carbonaceous matter deposited on the catalyst in said zone is removed, altering the flow of said naphtha vapors and said hydrogen-containing gas to permit said gas to flow through said freshly regenerated catalyst in said first reaction zone while naphtha vapors are being conducted into said reaction zone in which the catalyst has been preconditioned by contacting with said hydrogen-containing hydrocarbon gas, and continuously repeating the steps above described.

7. The process of claim 6 wherein at least three reaction zones are provided and the vapors of said naphtha are treated successively and in rotation in the succeeding zones, the catalyst in said zones being successively regenerated by combustion with oxygen-containing gas and then conditioned by contacting with said hydrogen-containing hydrocarbon gas before said naphtha vapors are treated therewith.

8. The process of claim 6 wherein the temperature of the catalyst undergoing preconditioning is above the temperature employed in said aromatization step.

9. In the process of aromatizing petroleum naphtha wherein the vapors of said naphtha are contacted in the presence of hydrogen with a solid aromatizing contact catalyst at a temperature of about 875 to 1075° F. and a pressure of about 30 to 450 pounds per square inch, the improvement comprising initially treating said catalyst at an elevated temperature in the range of 900 to 1400° F. with hydrogen-containing hydrocarbon gas, whereby the initial hydrocarbon destructive activity of said catalyst is reduced before contacting with said naphtha.

10. The process of claim 9 in which the naphtha is treated at the rate of about 0.04 to 10 volumes of liquid naphtha per volume of catalyst per hour.

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