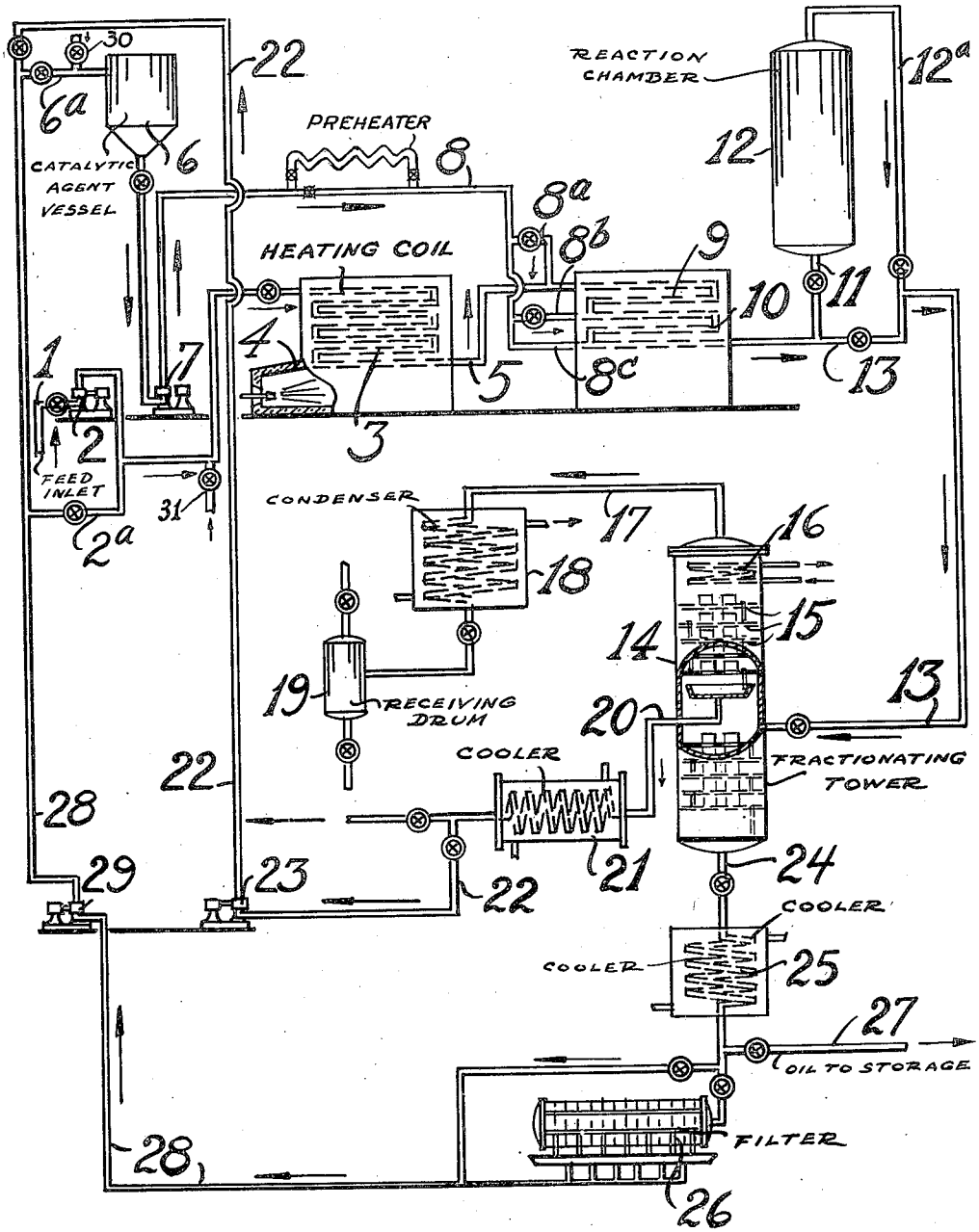
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CATALYTIC CRACKING PROCESS

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## CATALYTIC CRACKING PROCESS

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The present invention relates to the production of valuable low boiling products, suitable for gasoline, from heavier hydrocarbons, and more specifically to an improved catalytic cracking process. The invention will be fully understood from the following description and the drawing.

The drawing is a diagrammatic view in sectional elevation of an apparatus suitable for carrying out the present invention.

Many cracking processes have been proposed in the past and it has been known that the antidetonation quality of the gasoline produced is enhanced by the use of high temperatures for cracking, but in order to obtain outstanding merit in this direction, it is necessary to use temperatures which cannot readily be maintained under pressure. Operations at relatively low pressures, for example, only slightly above atmospheric pressure, results in large volumes of gas being produced which represent a considerable loss in the process.

In the present process the catalyst employed and the conditions generally make it feasible to employ high pressures and the previous difficulties are avoided. In the first place, the present process is operated under high pressures, for example, in excess of 100 or 200 pounds per square inch and preferably considerably higher. It is found that by the use of certain catalytic agents under these conditions, large yields of gasoline of superior anti-detonation quality are produced with relatively low gas losses. It is found that this process not only requires careful adjustment of conditions but likewise proper application of the catalyst in order to preserve the catalytic activity.

Referring to the drawing, numeral 1 denotes a feed line through which the oil is forced under high pressure by means of a pump 2. The oil passes through a heated coil 3, mounted in a furnace setting 4 and is discharged from the pipe 5 in a completely vaporized condition. At this point after complete vaporization, a catalytic agent is introduced, preferably as a slurry in a suitable carrying liquid, from a vessel 6 by means of a pump 7 and a pipe 8. Conditions are adjusted at this point, as will be disclosed below, so that the catalytic agent which is in a finely divided form is immediately dispersed through the vaporized oil and passes into a cracking zone along with the oil vapor. The catalyst dispersion may be added in small amounts and different points if desired, as at $8^a$, $8^b$, and $8^c$. The heating zone is shown on the drawing as a coil 9 mounted in a setting 10. If desired, the coil may be sufficiently large to provide time for the complete reaction, but, if a longer time of reaction is desired, the material from the coil may be passed by means of a line 11 through a reaction chamber 12. In either case, whether the products pass through the reaction chamber or through a by-pass line 13, they discharge into a fractionating tower 14 which is provided with fractionating plates 15 and a reflux coil 16. Gasoline vapors are withdrawn by vapor pipe 17 and condensed at 18 and collected at 19. If desired, an intermediate cut may be withdrawn from the middle of the tower by a line 20, cooled in the cooler 21, and may be returned for re-use by line 22 and pump 23. This material, or a portion of it, may be returned to the vessel 6 and thus may serve as a dispersing agent in which the catalyst may be introduced.

The heavier products from the tower 14 are withdrawn from a pipe 24 and after suitable cooling at 25 are passed through a filter 26 or other suitable mechanical device for removing the catalyst from the oil. Such oil is preferably sent to storage by pipe 27 but if desired a portion of it may be passed by pipe 28 and pump 29 for reuse in the process. Line 30 is provided for the addition of water or other suitable liquid carrying medium for preparing the catalyst slurry in vessel 6. Line 31 is provided for the addition of hydrocarbon gases to assist the vaporization of the oil, as explained hereinafter.

In the above description two separate coils, one for the vaporization and one for cracking are shown, but if desired both may be mounted in the same furnace setting as in previous settings without departing from the point in question.

In the operation of the process, it has been found that the most effective catalysts are natural or synthetic adsorption agents, such as adsorption clays, clays or earths treated with sulfuric, hydrochloric or hydrofluoric acid, or synthetic gels, such as silica gel or mixed or co-precipitated gels, hydro gels or the like, and especially gels of silica and alumina. Such catalysts differ considerably from metal or metal salt catalysts because of their high adsorptive character and, while capable of effecting improvements not obtained by other types of catalysts, they are also found to be readily rendered ineffective. While these materials are effective alone, they may also be fortified by the addition of other catalytic materials such as metal salts, but they are preferably used alone.

The catalysts of the type described above have been known for a long time as cracking agents, but it has been found that their effect may be entirely lost and they may be rendered entirely ineffective if they are improperly used. They have an extremely high adsorptive capacity and it has been noted that best results are obtained only when they are used in the cracking of oil vapors rather than in the cracking of oil in a liquid condition. The catalyst is employed in a fine granular or powdered condition and may be introduced in a dry state to the oil vapor. It has been found, however, that such catalyst may be employed more readily if introduced as a slurry

with a suitable liquid carrying medium. As the carrying medium, it is found that water is suitable and a thick slurry is introduced into the vaporized oil stream. If desired, an oil may be used as the agent to introduce the catalyst, but in this case great care should be taken to employ an oil which is completely vaporizable under the cracking conditions, and while it may be preheated to some degree before introduction, the material should not reach a cracking temperature before introduction.

As indicated in the previous paragraph, care should be taken in order to introduce the catalyst at a point where the oil is completely vaporized and at the same time provision should be made that a condensation of the oil vapor does not occur when the catalytic slurry is added. This can be achieved by adding the catalytic slurry at a point in the heating zone at which the input of heat is very high, and the tendency to condense may be offset to a considerable degree by preheating the slurry to as high a temperature as possible without danger of decomposition. Furthermore, the oil vapor stream may be superheated to a considerable degree so as to provide heat for immediately vaporizing the carrying agent for the catalyst and the latter is thus dispersed in the vapor stream. The amount of catalyst is small, about ½ to 10 lbs./bbl. of fresh feed, and no great difficulty is encountered in effecting its introduction once the necessity of such care is appreciated.

The oils employed for the present process should be distillates capable of complete vaporization under the conditions prevailing and the conditions of temperature and pressure should be adjusted so as to obtain complete vaporization. The oil is preferably preheated to 800° or 850° F. or higher before introduction of the catalyst and the pressure imposed at coil outlet should be at least 200 pounds per square inch, although it is preferable to use considerably higher pressures, say 250 to 1000 or 2000 pounds. If the oil cannot be vaporized under these conditions then it should be redistilled so as to produce a lower boiling cut which can be so employed. It is found, however, that the introduction of a considerable amount of lighter oil, such as naphtha or hydrocarbon gases, assists the vaporization of heavier stocks, especially when vaporization is carried out in a coil such as provided here, in which the tube size is such as to prevent stratification of the vapor from the liquid phases. In this way it is often possible to avoid redistillation and to accomplish cracking of stocks in vapor phase which could not be employed if used in absence of the lighter stock. A lighter oil is also improved somewhat as to volatility and antidetonation quality. Heavy oils may be distilled or cracked previously by conventional methods in order to obtain a lower boiling stock which can be vaporized under the temperatures and pressures disclosed, but even naphtha stocks may be used with such heavy oils if sufficient light oil is added to insure complete vaporization of oily constituents.

A coil is preferably provided to serve as the cracking zone so that heat may be added during cracking, that is to say while the catalyst and the oil vapors are in contact, and the time is provided so that a substantial yield of gasoline is obtained. It is preferable to provide a coil and upflow drum for reaction space and it is found that catalyst stratification occurs in the drum and effects additional decomposition, so that a greater degree of cracking may be afforded than is possible in the limited coil space available. Temperature during the cracking reaction is, as stated above, above about 900° F. and adjusted so as to prevent condensation of the heavier fractions of the feed stock or reaction products. While temperature in excess of 1000° F. may be used, it has been found that with an effective catalyst, temperature generally need not be above 1000° F. with pressure of 200 to 500 pounds and preferably higher with higher temperatures. These conditions in combination with the use of a siliceous catalyst of the class disclosed above introduced where the oil is in the vapor phase are the essential elements.

The oil discharged from the cracking zone may be cooled and clay separated, but it is preferred to separate a light distillate suitable for gasoline and a heavier oil which carries the catalytic material. The catalyst may be separated from this oil by mechanical means such as filtration or centrifugation from liquid oil or by vapor by means of cyclone separator but some of the clay appears to accumulate in the reaction drum, if it is employed, and this effects an increase in octane number of the gasoline produced. In the process it is possible to obtain very high yields of gasoline from gas oils with low gas yields and it is not ordinarily necessary to use recirculation methods as are commonly employed in cracking processes.

*Example*

Three different feed stocks, a light natural gas oil, an intermediate natural gas oil and a mixture of the total distillate cracking stocks available at one refinery, being a wide cut, were subjected to a process of cracking in the presence of a siliceous catalyst. In each case the oil was passed rapidly through a coil, the catalyst, which was a highly treated acid clay, being added after the oil had been substantially completely vaporized and thence to an unheated reaction chamber. In two of the operations the insufficiently cracked gas oil fraction was recycled through the coil. The third operation was once-thru. The following tables show the data on the three runs, the operating conditions of temperature, pressure and the amount of catalyst, and also the yields of gasoline, gas oil, tar and gas. The properties of the gasoline produced in each case are also given. The high octane numbers of the gasoline particularly should be noted:

| Feed stock | Light natural gas oil | Intermediate natural gas oil | Mixture containing total cracking stocks |
|---|---|---|---|
| Operating conditions: | | | |
| Coil outlet temperature °F. | 940 | 980 | 985 |
| Pressure, pounds | 250 | 250 | 250 |
| Catalyst—pounds/barrel of fresh feed | 12.3 | 7.7 | 2.4 |
| Type of operation | Recycle | Recycle | Once thru |
| Yields on fresh feed: | | | |
| Gasoline—volume percentage—400° F end point | 41.7 | 52.0 | 59.1 |
| Cracked gas oil—volume percentage | 35.9 | 10.6 | 12.4 |
| Tar—volume percentage | 16.7 | 30.6 | 16.7 |
| Dry gas—weight percentage | 9.1 | 12.5 | 15.6 |
| Properties of gasoline: | | | |
| A. P. I. gravity | 60.2 | 59.8 | 54.7 |
| O. N.—A. S. T. M. | 75.7 | 75.8 | 74.3 |
| Aniline point | 87 | 75.5 | 73 |
| Acid heat | 113 | 114 | 117 |

The present invention is not to be limited by any theory of the mechanism of the operation, the use of any particular temperatures or pressures or catalytic agents, but only to the following claims in which it is desired to claim all novelty inherent in the invention.

We claim:

1. An improved process for producing gasoline from heavy oils which comprises forcing the stream of oil through a narrow, constricted passageway and heating the same under pressure during flow to a temperature above 700° F., the temperature and pressure conditions being interadjusted to effect complete vaporization of the oil, then adding to the oil vapor stream a finely divided adsorptive siliceous catalyst as a dispersion in an easily vaporizable liquid whereby the liquid is immediately vaporized and the catalyst dispersed in the oil vapor without condensation thereof, maintaining contact between the oil and the finely dispersed catalyst under pressure in excess of 100 pounds per square inch and at cracking temperature, for time sufficient to effect conversion of a substantial part of the oil to gasoline, then cooling the product and separating the gasoline from the catalyst.

2. Process according to claim 1 in which the cracked product is cooled so as to condense a fraction of the oil heavier than gasoline and the condensate is filtered to separate the catalyst.

3. Process according to claim 1 in which the pressure is within the range from 100 to 1,000 pounds per square inch.

4. Process according to claim 1 in which an aqueous dispersion of the siliceous catalyst is introduced into the oil stream after complete vaporization.

5. Process according to claim 1 in which the stream of oil vapor and catalyst is passed into an enlarged reaction zone, wherein at least a part of the catalyst is accumulated.

6. Process according to claim 1 in which said cracking temperature is between about 900 and 1000° F. and said pressure is between about 200 and 500 pounds per square inch.

7. Process according to claim 1 in which about one-half pound to 10 pounds of said catalyst is used per barrel of said oil.

8. An improved method for producing gasoline from heavier hydrocarbons by cracking said heavier hydrocarbons while completely vaporized in the presence of a dispersion of a solid adsorptive siliceous catalyst comprising preheating a mixture of said catalyst and a hydrocarbon oil heavier than gasoline and which is capable of complete vaporization under the cracking conditions used, to a temperature below that causing decomposition of the oil and under a pressure above 100 pounds per square inch, then bringing the preheated mixture into a zone of high heat input wherein it is mixed with a stream of superheated oil vapor separately preheated to a substantially higher temperature while avoiding condensation of said vapor and the resulting mixture is quickly heated to a temperature above about 900° F. at which said hydrocarbon oil heavier than gasoline is completely vaporized and maintaining contact of the oil vapors and the catalyst at said temperature and pressure for sufficient time to effect substantial conversion of the oil to gasoline.

9. An improved process for producing gasoline from heavier hydrocarbons which comprises forcing a hydrocarbon distillate heavier than gasoline through a long, narrow constricted passageway and heating the same while flowing therethrough to a cracking temperature adjusted with the pressure and the nature of the oil so as to cause complete vaporization and superheating, then adding an oil dispersion of a solid adsorptive siliceous catalyst to the said superheated oil vapors so that the dispersing medium is immediately vaporized while avoiding condensation of the previously vaporized oil, and maintaining contact of the oil vapors and the catalyst at cracking temperature and under substantially superatmospheric pressure for sufficient time to effect substantial conversion of the oil to gasoline.

10. An improved process for producing gasoline from heavier hydrocarbons which comprises forcing a hydrocarbon distillate heavier than gasoline through a narrow constricted passageway and heating the same under pressure during flow to a temperature above 700° F., the temperature and pressure conditions being interadjusted to effect complete vaporization of the oil, then adding to the oil vapor stream a finely divided adsorptive siliceous catalyst whereby the catalyst is immediately dispersed in the oil vapor without condensation thereof, and maintaining contact between the oil vapor and the finely dispersed catalyst under pressure in excess of 100 pounds per square inch and at cracking temperature, for a time sufficient to effect conversion of a substantial part of the oil to gasoline.

11. Process for preparing motor fuel by cracking a relatively heavier hydrocarbon oil feed stock which is completely vaporized at the temperature and pressure used in the cracking operation, comprising passing a suspension of a solid adsorptive siliceous catalyst in said vaporized hydrocarbon oil through a cracking zone maintained at a pressure above 100 pounds per square inch and a temperature above about 900° F. for sufficient time to effect substantial conversion of the oil to gasoline.

12. Process according to claim 11 in which said pressure is between 200 and 500 pounds per square inch.

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