This invention relates to the process of cracking large molecular hydrocarbons under high pressure for the production of smaller molecular hydrocarbons such as are present in high grade so-called antiknock motor fuel.

My process is distinguished from those of the prior art by a number of advantages, some of which are the obtaining of a considerably higher yield up to 78 per cent or higher of gasoline, the absence of coke formation, the possibility of fractionating in any desired ratio and the simplicity of equipment as well as the possibility of easily converting existing apparatus of the conventional type to make them suitable for the carrying out of my process. Other advantages are low cost of production and saving of fuel as can be recognized from the disclosed process.

It is the experience of those engaged in this art, that in the carrying out of cracking processes, as they are known to-day, there is formation of undesirable products along with the useful and desirable products through which the useful in useful products is diminished or the process may be interrupted. Thus the formation of coke and carbon deposits may clog the apparatus and interrupt the process and instead of the desirable gasoline other products such as hydrocarbon gases are produced in large quantities. It has always been the desire of those engaged in this art to be able to avoid or to diminish the formation of these undesirable products.

It is known in this art that the power generated by a motor fuel increases with the possibility of high compression in the cylinder of the motor and the production of cracked gasoline with a high compression stability or of so-called antiknock qualities has become highly important. Processes known as vapor-phase cracking processes were developed for the production of motor fuel with distinct antiknock properties. These vapor-phase cracking processes, operating at pressures of below 100 pounds per square inch and at temperatures of around 1000°F., are however, characterized by the production of large quantities of gas and more coke for a given amount of charging stock than previous cracking processes known as liquid-phase cracking processes. The danger of coke formation in these processes is so great, that to obtain a low coke formation, only light distillates such as kerosene and light gas oil can be cracked by this process.

Through the recognizing of certain improvements, I have overcome the difficulties of the formation of coke and the production of excessive gas quantities while still obtaining a high octane number gasoline; thus in practice they are found to be of great value.

It is proven by experience that the reaction of cracking depends upon the temperature conditions during which the conversion takes place. The best conditions are to raise the temperature of the products instantly to the required optimum cracking temperature, to keep the temperature then constant for the required length of time and to lower the temperature rapidly at the end of the reaction.

I have recognized that heavy gasolines and fuel oils can be cracked without coke formation when a reaction time of ten (10) minutes or over is used and means are provided to prevent overheating. The temperature reached under these conditions must be the optimum cracking temperature. A sudden increase in the production of gas and the beginning of coke formation start when the temperature in the cracking unit rises considerably above the optimum cracking temperature.

In many of the cracking processes, as they are practiced today, the products are heated to a temperature considerably above the optimum cracking temperature, either before they enter or while they are in the cracking zone. Then cooling takes place during the reaction and the temperature of the mixture drops below the optimum cracking temperature. I found that near the walls of the tubes a temperature often 100°F. higher than the average temperature of the products undergoing the reaction exists. The temperature then drops due partly to losses by radiation but mainly due to the absorption of heat incident with the cracking. Temperature drops of 50°F. and more are experienced in these cracking zones.

By overcoming these defects in the cracking process, I have found that both qualitatively and quantitatively the resulting yields of gasoline are very materially increased. To avoid the conditions outlined consists in providing means which prevent the temperature to deviate from the optimum cracking temperature, i. e., either to increase or decrease substantially from the optimum cracking temperature during the time in which the cracking reaction takes place and further to provide means for which the reaction time can be readily controlled.

This is accomplished by passing the preheated products to be cracked under high pressure through tubes, placed into a moderately heated furnace and adding hydrocarbon vapors pro-
duced in the process and boiling below the boiling point of gasoline, which have been heated under high pressure to temperatures above the optimum cracking temperature of the oil to be cracked. They are fed into the stream of the products to be converted and also the heated vapors are entered into the conversion unit at various points.

It is known in this art that hydrocarbon gases are useful as heat carriers in cracking processes. In some vapor-phase cracking processes, a hydrocarbon gas heated to about 1100° F. is mixed with a light gasol, vapor heated to about 900° F. in proportions to give a temperature of about 1000° F. in the mixture. The mixture is passed through a noheated vessel in which it remains for a reaction time of less than 1 second. Pressures of below 100 pounds per square inch are used. The disadvantages of these operations were outlined above.

It is also known that high pressure in cracking is a favorable factor, as it improves heat transfer conditions and aids in preventing overheating. Increased pressure gives also decreased gas formation and higher yields of gasoline. A high pressure unit has another advantage over the low pressure cracking unit because for the same size which consists in a larger throughput while avoiding the necessity of large size reaction chambers.

With this process illustrated in the following example, I have succeeded in accomplishing cracking under high pressure in a mixed phase of vapors and liquids at a constant reaction temperature producing a high octane number gasoline avoiding coke formation and keeping the production of gas at a minimum.

Thus crude oil products or crude oils are charged into a flash tower from which heavy tar is periodically withdrawn. The overhead vapors are fractionated into a hydrocarbon gas, a gasoline, and a distillate. The distillate contains hydrocarbons of the kerosene, gasoil and fuel oil type. The distillate is heated under pressure to a temperature at which cracking will not take place. The hydrocarbon gas, part of which is being continuously withdrawn, is heated under pressure to a temperature above the cracking temperature of the distillate, and part of the olefinic hydrocarbons present in the gas oil will undergo a reaction of condensation forming higher boiling cyclic hydrocarbons.

The preheated distillate and the one part of heated gas are introduced into a tubular reactor zone, the quantity of the gas being so controlled that the optimum cracking temperature of the distillate results instantaneously. A rapid mixing of both streams is secured by passing it through a nozzle in which the pressure is lowered by about 25 pounds. The reaction starts immediately and being endothermic, it absorbs heat. The absorbed heat is resold by adding further quantities of the heated gas at various points into the cracking zone. The losses of heat by radiation are prevented by placing the tubular cracking unit into a furnace which is moderately heated.

When the reaction has progressed to the end, after a cracking time of ten (10) minutes or more, the reaction is rapidly terminated by lowering the pressure and admixing colder products such as are to be cracked later on and whereby the temperature of the mixture is then passed into a flash tower for the separation of the tar and then into a fractionating tower.

In this way, I accomplish various desirable functions, which are rapid heating and cooling, the conversion under high pressure at a constant temperature of high molecular weight hydrocarbons, removing by fractionation any of the desired products and recycling products desired for further conversion, prevention of coke formation and the production of the highest possible yields of gasoline with high anti-knock characteristics.

One typical example of the application of this process is described in detail in the following process.

The fresh feed such as crude mineral oil products obtained from crude mineral oils, tars or similar materials, is stored in a tank 1, from which by means of pump 2 it is passed through the heat exchangers 3 and 4. Thus preheated to a temperature of around 350° F., the feed is mixed at point 5 with the products emerging 20 from the cracking zone, whereby the temperature of the cracked products is rapidly lowered to about 750° F. and the cracking reaction is suddenly brought to a stop.

The mixture of fresh feed and of cracked 25 products is processed into a vaporizer 6 which is heat insulated and maintained at a definite temperature by refluxing oil from bottom of the fractionating tower 10 by means of the reflux pump 11 and the reflux line 12. The pressure of this tower is around 25 pounds per square inch. A heavy tar, collecting at the bottom of the vaporizer, is either continuously or periodically withdrawn and passed through the heat exchanger 4 and the cooler 7 into the storage tank 8.

The vapors leaving the vaporizer are partly cooled in the heat exchanger 9 and enter the fractionating tower 10. The temperature of this tower is controlled by gasoline reflux taken from the receiving vessel 18 by means of the reflux pump 22 and the reflux line 23. A temperature of about 350° F. prevails at the top and a temperature of about 540° F. prevails at the bottom of the tower which operates at a pressure of about 25 pounds per square inch. Distillates at various temperatures can be taken off. In this example only two products are taken. These vapors pass through the heat exchanger 3 and 16, the cooler 17 and they enter the receiving drum 18. The gasoline leaving the bottom of the receiving drum is sent into the gasoline storage tank 19. Part of the cracked gas leaving the top of the receiving drum is sent into the gas holder 20. The other part of the gas is passed through the gas scrubber 21 in which corrosive products such as hydrogen sulphide are removed. The purified gas is heated in the heat exchangers 14 and 18, compressed to a pressure of about 1000 pounds per square inch and picked up by the high pressure pump 24. By means of the control valves 25 and 26 the gas is divided into two streams and passed through a number of tubes placed in the furnace 27. The temperature of the gas is raised to about 2080° F., during this the olefinic hydrocarbons present in the gas are converted into gasoline rich in cyclic hydrocarbons.

The high boiling condensate leaving the bottom of the fractionating tower 10 is aspirated by the high pressure pump 13 and compressed to a pressure of about 1000 pounds per square inch. The aspirated condensate is passed into the tubular heating zone 14 placed in the furnace 15. The oil is then heated to a temperature at
which substantial cracking will not take place which is around 800° F. The oil thus preheated is sent to the cracking zone 32 placed in the furnace 33. The cracking zone consists of a number of tubes with a diameter of around three inches. At point 34, before entering the cracking zone, the high boiling condensate is mixed with the gas coming from the gas heating coils, placed in the furnace 37. Both streams are rapidly mixed in a nozzle placed near point 36 (the nozzle is not shown). The proportions of the gas are so controlled that a temperature of about 850 to 860° F. instantaneously results in the mixture. The cracking reaction starts and absorbs heat. An additional quantity of the heated gas is therefore introduced into the cracking zone at point 38. Heat losses by radiation are prevented by moderate heating of the furnace 36. The length of the tubes is so adjusted that a reaction time of 10 minutes or more is obtained and the reaction time is also controlled by increasing or decreasing the amounts of heated gas introduced at point 38. A pressure of around 900 pounds per square inch is maintained in the cracking zone by means of the pressure control valve 31.

The cracked products, leaving the reaction zone with a temperature of around 960 to 980° F., are decreased in pressure by the valve 31 and mixed with the fresh feed at point 5, whereby the temperature is quickly decreased and the reaction brought to a stop.

The temperatures given above are for illustration purposes only; they may vary within reasonable limits for different charging stocks. The temperature of the oil leaving the preheating zone 34 may range between 700 and 800° F., but differences between the temperatures of the products entering the cracking zone and the products leaving the cracking zone should not exceed 25° F. The temperature to which the gas is heated before entering the cracking zone 32 may be somewhat above or below 1050° F.

It is not required that the pressure must be maintained at around 1000 pounds per square inch. The pressure may vary considerably between 300 and 3000 pounds per square inch. It is usually found advantageous to preheat the oil and the gas at pressures of 10 to 15 pounds above those used in the cracking zone. In the vaporizer and the fractionating tower, pressures of below 50 pounds per square inch are found satisfactory.

It will also be understood that instead of three different furnaces as shown in the drawing, only two or even one may be used if by proper combination or design the above outlined temperature conditions can be secured.

Having thus described one typical example of my process, I do not bind myself to the exact details given in the above description, but rather consider this as one example illustrating the general broad idea of my invention.

I claim:

1. The method of cracking hydrocarbon oils comprising the steps of mixing fresh charge oil with cracked products, passing the mixture to a vaporizing zone and separating vapors and gases from unvaporized liquid, fractionating the overhead products to obtain non-condensed gases, a motor fuel and a condensate, passing said condensate at a pressure of above 300 pounds per square inch through a heating zone and heating it to a temperature of below 800° F., heating 20 non-condensed gases at the same pressure to a temperature of about 1050° F., passing the mixture through an outside heated tubular cracking zone of such length that the reaction time is at least 10 minutes, introducing additional heated 25 non-condensed gases to keep the temperature of the mixture constant until said condensate is cracked, mixing the cracked products with cooler fresh charge oil to bring the temperature of the mixture below 800° F. and passing the 30 mixture into said vaporizing zone.

2. The method of cracking hydrocarbon oils comprising the steps of mixing fresh charge oil with cracked products, passing the mixture to a vaporizing zone and separating vapors and gases from unvaporized liquid, fractionating the overhead products to obtain non-condensed gases, a motor fuel and a condensate, passing said condensate at a pressure of above 300 pounds per square inch through a heating zone and heating it to a temperature of about 800° F., heating non-condensed gases at approximately the same pressure to a temperature of about 1050° F., mixing a part of the heated gases with the heated oil and passing the mixture through a cracking zone in which a reaction time of at least ten minutes is obtained, introducing additional heated non-condensed gases to keep the temperature of the mixture constant until part of the condensate is cracked, mixing the cracked products with cooler charge oil to bring the temperature of the mixture to below 800° F., and passing the mixture into said vaporizing zone.

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