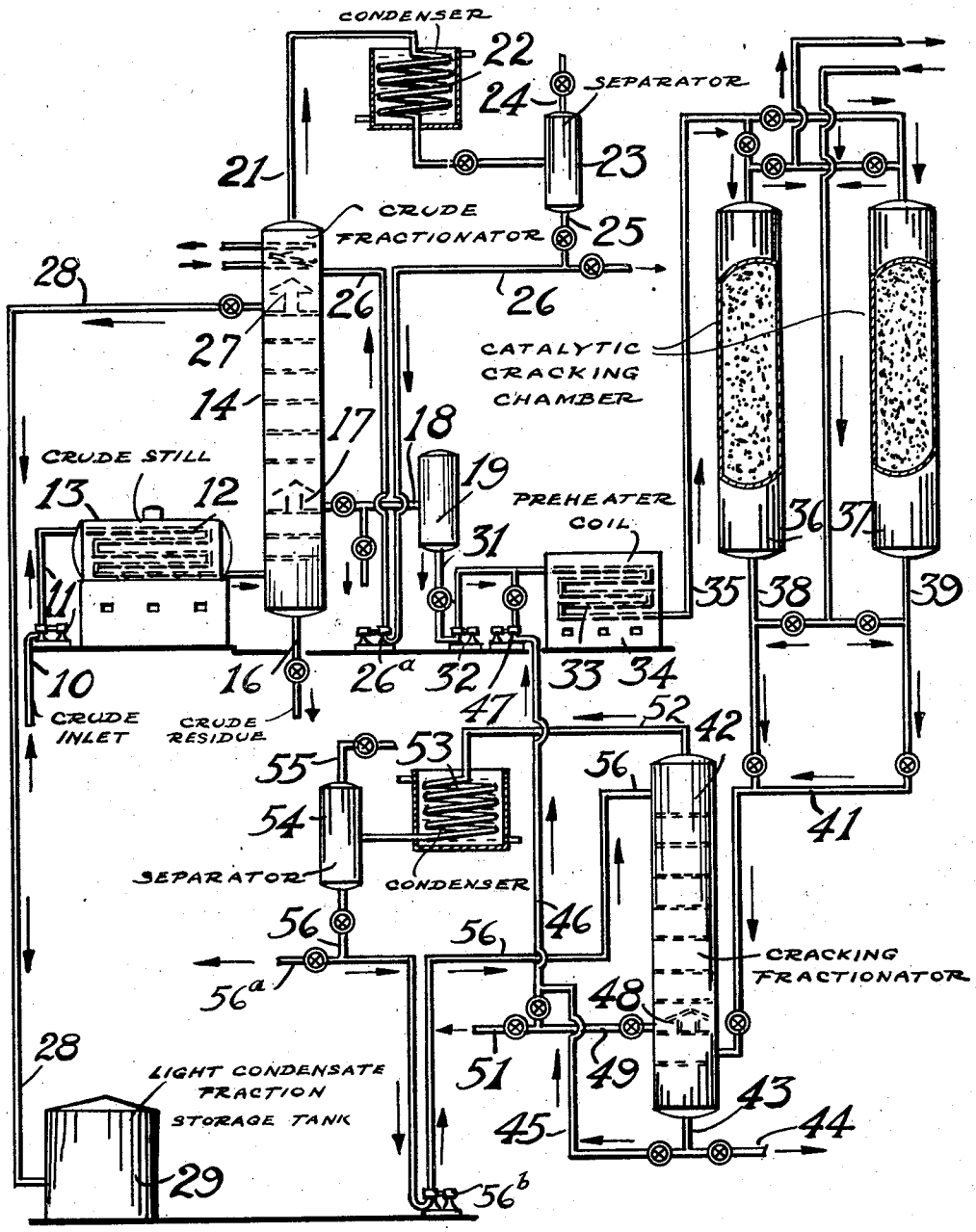
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CATALYTIC CRACKING OF HYDROCARBON OIL

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William J. Sweeney Inventor

By W. E. Currie Attorney

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CATALYTIC CRACKING OF HYDROCARBON OIL

William J. Sweeney, Elizabeth, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

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1 Claim. (Cl. 196—50)

This invention relates to the cracking of higher boiling hydrocarbons into lower boiling hydrocarbons suitable for motor fuel in the presence of a cracking catalyst capable of producing high anti-knock motor fuel, and pertains more particularly to a method of improving the anti-knock properties of the motor fuel so produced.

It has heretofore been known that certain types of solid adsorptive catalysts, such as naturally active clays of the attapulgus type and clays of the bentonitic type which have been made active by further treatment, such as with acid, possess the power of producing gasoline motor fuel having materially higher anti-knock properties than gasoline produced by conventional thermal cracking processes.

The principal object of the present invention, in its broader aspect, is to provide a catalytic cracking process for hydrocarbon oil which will produce a high anti-knock gasoline.

A further and more specific object of my invention is to provide a method of preparing the charging oil to a catalytic cracking process which will result in the production of motor fuel of higher anti-knock properties.

Other and more specific objects of the invention will be apparent from the more detailed description hereinafter.

I have discovered that to obtain the maximum improvement in octane number of gasoline from a catalytic cracking process, employing solid adsorptive catalysts, such as active or activated clays either natural or synthetically produced, may be realized only when the initial fresh charging stock to the cracking unit is substantially free of constituents boiling within the range of the final product.

It is well known that in conventional distillation and fractionating units there is a considerable overlap of constituents present in the fractions removed from the fractionating tower. For example, when distilling crude oil to separate a 400° F. end point straight run gasoline and an intermediate gas oil fraction for cracking treatment, the gas oil so separated will contain substantial quantities of gasoline constituents boiling below 400° F. amounting in some cases to as much as 10% of the total fraction.

In the conventional thermal cracking units the presence of gasoline constituents in the gas oil charging stock does not adversely affect the quality of the final product since the octane number of the total gasoline produced is enhanced due to the reforming of the gasoline constituents in higher anti-knock constituents during the cracking process. It has been a practice in many cases to subject the heavy naphtha constituents to thermal cracking to increase the anti-knock properties and in some commercial cracking units, a high boiling gasoline fraction is passed with the gas oil through the cracking unit.

I have found, however, that, contrary to the experience gained in thermal cracking, the presence of natural gasoline constituents in the gas oil charging stock to a catalytic cracking process, employing adsorptive catalysts, adversely affects the quality of gasoline produced in that the octane number of the resulting gasoline is materially lower than when the gas oil is substantially free of gasoline constituents.

While the cause for this reduction in octane due to the presence of gasoline in the original charge has not been fully established, I have reason to believe that under conditions best suited for gas oil cracking, the catalyst has a selective action on the higher boiling gas oil constituents and very little, if any, action on the original gasoline constituents present in the charge. The original gasoline constituents appear, therefore, in the final product substantially unchanged, and since they have high knocking properties, the octane number of the final product is materially reduced. It will be understood that the above is advanced only as a possible explanation, and the invention is not to be restricted by any theory or explanation.

In accordance with my invention, the original crude oil is initially distilled and fractionated under conditions such that the gas oil fraction is substantially free of constituents within the boiling range of the final desired motor fuel product. This may be accomplished by maintaining the top temperature of the fractionating tower substantially higher than that normally maintained when producing 400° F. end point straight run gasoline to insure complete stripping of all the gasoline constituents from the gas oil. In ordinary commercial practice employing conventional bubble tower fractionators, the initial boiling point of the gas oil, after removal of the straight run gasoline, should ordinarily be at least about 50° F. higher than the final boiling point of the gasoline produced from the catalytic cracking treatment to insure that the gas oil charging is substantially free of constituents in the boiling range of the final product. For example, when producing gasoline of 400° F. end point by catalytic cracking, the initial boiling point of the gas oil charging stock

should be about 450° F. The important fact is that the gas oil being charged should be substantially free of constituents within the range of the final product.

The accompanying drawing is a diagrammatic illustration of an apparatus capable of carrying my invention into effect, it being understood that the drawing is simply for purposes of illustration as other types of apparatus may be employed.

Referring to the drawing, fresh crude oil to be distilled is introduced into unit through charging line 10 provided with pump 11 which forces the oil through a bank of tubes 12 located in furnace 13. The oil during its passage through the tubes 12 is heated to a temperature sufficient to vaporize all constituents boiling to and through the gas oil boiling range. The temperature may reach incipient cracking and the oil may be subjected to mild viscosity breaking treatment within the coil 12 or the oil may be heated to a temperature just below that at which active cracking occurs.

The heated products from the coil 12 are then discharged into the bottom section of the crude fractionating tower 14 wherein vapors separate from liquid residue and the vapors are subjected to fractional condensation. Unvaporized liquid, together with the heaviest condensate formed in the bottom section of the fractionating tower 14 is withdrawn through line 16 and removed from the system for further treatment as desired.

Condensate formed in the intermediate section of the fractionating zone is collected in a trap out tray 17 from which it is withdrawn through line 18 to an accumulator tank 19. This fraction constitutes the charging stock to the catalytic cracking unit to be later described. The temperature at the top of the fractionating tower is controlled so that the initial boiling point of the gas oil condensate collected in trap out tray 17 is sufficiently above the final boiling point of the motor fuel distillate, obtained from the catalytic cracking unit, to insure that the gas oil is substantially free of constituents boiling within the range of the final cracked distillate. A temperature differential of 50° F. is ordinarily sufficient.

Vapors remaining uncondensed in the fractionating tower 14 pass overhead through line 21 to a condenser 22 wherein normally liquid hydrocarbons are condensed as distillate. Products from the condenser 22 pass to a receiver 23 wherein the distillate separates from normally gaseous constituents. The gases are vented from receiver 23 through line 24 and the distillate is withdrawn through line 25 and passed to suitable storage not shown. If desired, a portion of this distillate may be pumped back through line 26 to the fractionating tower 14 as reflux therefor.

When operating in the manner so far described, where no intermediate condensate between the distillate and gas oil condensate fraction is separated, the end point of the distillate will be materially above the end point of the distillate obtained from the catalytic cracking unit by reason of the fact that the top temperature of the fractionating tower is controlled to produce a gas oil of high initial boiling point.

If desired, a crude distillate may be collected in receiver 23 which has an end point substantially the same as the catalytic cracking distillate. To accomplish this, a light condensate fraction boiling between the distillate and the initial boiling point of the gas oil condensate may be separated. To this end, the upper section of the tower 14 may be provided with a separate trap out tray 27 for collecting said light condensate. This light condensate, which will be in the nature of heavy naphtha or light kerosene, is withdrawn from trap out tray 27 through line 28 and passed to storage 29. This light fraction may be subjected to separate and independent catalytic or thermal cracking under conditions best suited for this type of material or otherwise utilized as desired.

The gas oil collected as charging stock for the catalytic cracking unit is withdrawn from the accumulator tank 19 through line 31 and is forced by means of pump 32 through a preheating coil 33 located in furnace 34. The oil during its passage through the preheating coil 33 is heated to a vaporizing temperature. The vapors so preheated then pass through transfer line 35 leading to either of two catalytic reaction chambers 36 and 37 depending on which is being employed for cracking. In this connection it will be understood that a plurality of catalytic reaction chambers are provided so that one or more may be employed for carrying out the cracking operation while the remainder are undergoing regeneration.

The catalyst chambers 36 and 37 contain a catalyst mass capable of effecting the desired conversion. As already mentioned, the catalyst may consist of solid adsorptive catalysts of the clay type, naturally active such as attapulgus clay or fuller's earth or bentonitic clays treated to be made active such as activated clays marketed under the trade name Filtrol, Tonsil, Marsil and Terrana. In addition to natural clays, synthetic compositions of silica and alumina may likewise be employed.

The oil vapor during its contact with the catalyst within the catalyst chamber undergoes conversion into lower boiling hydrocarbons within the motor fuel boiling range. In addition to the direct splitting of high molecular weight hydrocarbons into lower molecular weight constituents, the catalyst effects other molecular rearrangements resulting in the formation of aromatic and olefinic hydrocarbons having high anti-knock properties.

The conversion of hydrocarbons within the reaction chamber results in the formation of carbonaceous deposits on the surface of the catalyst which rapidly reduces the activity thereof so that it becomes necessary to discontinue the cracking operation from time to time to regenerate the catalyst. The reduction in activity of the catalyst is reflected not only in reduction in yield but in the octane number of the gasoline produced.

It has been found that to obtain best results, the temperature of the catalyst chamber and the total volume of oil vapors treated with the catalyst between regenerations must be controlled within relatively narrow limits. It has been found that other factors being constant, the amount of normally gaseous constituents formed increases with the temperature and that within certain limits there is a corresponding increase in octane number of gasoline produced. The amount of octane number improvement for each unit of temperature rise, however, gradually decreases, whereas the amount of gaseous constituents formed for each unit increases. There is therefore a definite limit in the temperature of reaction beyond which any advantage gained by increase in octane

number of the gasoline is more than offset by loss in ultimate yield due to the formation of gases. The maximum temperature limit will vary somewhat with individual oils and other factors. The maximum limit for oils so far investigated is about 900° F. For virgin gas oils from Mid-Continent crudes, the preferred temperature to obtain maximum octane improvement with minimum gas loss is approximately 850° F. In other types of oil the temperature may be as low as 820° F. The reaction temperature may be maintained by preheating the oil vapors to the required amount within the preheating coil **33** or the catalyst chamber may be subjected to sufficient heating to maintain the catalyst at proper temperature.

Other factors remaining constant, the total volume of oil vapors treated with the catalyst between regenerations affects both the yield and octane number of the gasoline produced. The catalyst exerts its maximum activity during the initial portion of the cracking period, for, as already mentioned, the activity tends to reduce as the cracking progresses. Moreover, freshly prepared catalyst is normally more active than catalyst which has been subjected to repeated regenerations.

The total volume of oil vapors treated by the catalyst between regenerations will depend upon the activity of the catalyst which in turn will depend upon the number of cracking-regeneration cycles to which the catalyst has been subjected. When cracking East Texas virgin gas oil of 34.7 A. P. I. gravity, for example, at a temperature of 850° F. employing commercial Filtrol as a catalyst, the volume of oil vapors treated by the catalyst between regenerations may range from 2.5 volumes of liquid oil per volume of catalyst for freshly prepared catalyst down to .5.

The volume of oil vapors treated by the catalyst between regenerations may be varied by modifying either the feed rate or the length of cracking periods. For example, a cracking process employing a feed rate of .6 volume of liquid oil per volume of catalyst per hour operating on a four-hour cracking period between regenerations will treat the same total volume of oil vapors per period as a two-hour cracking period with a feed rate of 1.2 volumes of liquid feed per volume of catalyst per hour.

For any given temperature and catalyst, the yield of gasoline produced by a single passage of oil through the catalyst chamber is initially a function of the rate of feed, or contact time, but since the activity of the catalyst diminishes as the cracking proceeds, it will be evident that the length of cracking periods is an important factor in the yield of gasoline produced.

The feed rate is preferably regulated to obtain an average gasoline yield over the cracking period of at least 30 per cent and preferably 35 or more per cent. The actual feed rate may vary from .3 to 1.2 volumes of liquid oil per volume of catalyst per hour depending on the length of cracking period, it being understood that the total volume of oil treated per volume of oil treated per volume of catalysts between regenerations should not exceed 2.5 and preferably should be between .5 and 1.5. The feed rate may be maintained uniform throughout the cracking period or it may be reduced to compensate for the reduction in activity of the catalyst. The length of the cracking period may vary from a maximum of four hours to a quarter of an hour or less. While the shorter periods of operation necessitate more frequent regenerations, the time for each regeneration is correspondingly decreased so that the cracking capacity of catalyst chamber over a given period is not materially reduced. Moreover, the shorter cracking periods makes possible a better control of the regenerating conditions and more complete restoration of catalyst activity.

Conversion products from the catalytic reaction chamber **36** or **37**, as the case may be, are withdrawn through lines **38** or **39** respectively, which merge with line **41** leading to a fractionating tower **42**. Vapors introduced into tower **42** are subjected to fractionation to condense constituents boiling above the desired boiling range.

The total condensate formed in the tower may be withdrawn from the bottom of the tower through line **43** and removed from the process through line **44** or a part or all of the total condensate may be recycled through lines **45**, **46** and pump **47** to the inlet side of the preheating coil **33** and subjected to further cracking treatment.

In lieu of withdrawing the total condensate from the bottom of the tower **42**, a trap out tray **48** may be provided for separately collecting a light fraction of said condensate The lighter fraction so collected is withdrawn from the tower through line **51** or recycled through line **46** and pump **47** to the preheating coil **33**. When recycling insufficiently converted condensate, it is preferred to remove from the process the highest boiling fraction amounting to from 5 to 15% of the total condensate formed in the tower **42** through lines **43** and **44**, since this highest boiling fraction tends to form coke deposits on the catalyst more rapidly and thus reduces length of cracking periods between regenerations.

Vapors remaining uncondensed in the fractionating tower and consisting of motor fuel constituents and constituents boiling below the desired motor fuel range pass overhead from fractionating tower **42** through line **52** to a condenser **53** wherein the desired cracked distillate fraction is caused to condense. The products from the condenser **53** pass to a receiver **54** which functions to separate uncondensed normally gaseous constituents from the liquid distillate. The normally gaseous constituents are vented from the receiver through line **55** and the distillate is removed from the process through line **56**.

The gases separated in receiver **54** and removed therefrom through line **55** may be passed to a suitable adsorption unit (not shown) or otherwise treated to remove light motor fuel constituents contained therein.

The distillate removed from receiver **54** may be employed as motor fuel but is preferably subjected to further refining treatment which may include stabilizing treatment such as distillation, acid, clay, mild hydrogenating treatment and purifying treatment or any desired combination of such refining operations to produce a final motor fuel product.

The gasoline so produced will have an octane number of at least 75 and usually 80 or higher regardless of the composition of the charging stock providing said stock is substantially free of constituents within the range of the final cracked product.

As previously mentioned, as the cracking reaction is being carried on in one of the reaction chambers **36** and **37**, the other is undergoing regeneration so that the cracking operation may be carried out continuously without inter-

ruption. The regeneration may be accomplished by passing an oxidizing gas, such as air, in admixture with a diluent gas, such as steam or cooled recycle combustion gases, through the catalyst bed to burn off the carbonaceous deposits contained thereon. The temperature in the reaction chamber during regeneration should be maintained below 1000° F. to avoid fusing the catalyst and permanently reducing the activity of the catalyst. The amount of air contained in the gases may be increased as the regeneration proceeds and the regeneration is continued until the catalyst is substantially free of carbon.

The following comparative examples will serve to illustrate some of the advantages of my invention, it being understood that the operating conditions and results obtained are illustrative rather than limitative.

Example I

An East Texas gas oil of 34.7 A. P. I. gravity, 167 aniline point and having an initial boiling point of 398° F., a mid-point of 567° F. and a final boiling point of 750° F. was passed at a rate of .3 volume of liquid feed per volume of catalyst per hour through a bed of Attapulgus clay maintained at a temperature of 825° F. for 4 hour cracking periods.

The process produced 21.8% by volume of 400° F. stable gasoline of 47 A. P. I. gravity having an aniline point of 109 and an octane number of 55.5. The process also produced .9% by weight of gas.

Example II

The same gas oil was fractionated to produce an oil fraction having an initial boiling point of 478° F. and a mid-point of 575. This fraction was cracked under the same conditions and with the same catalyst as Example I. In this case, 20.6% of stable gasoline of 58.4 A. P. I. gravity and having an aniline point of 70 and an octane number of 80 together with 2.6% by weight of gas was recovered from the process.

When comparing results obtained from the two examples, it should be noted that while the yield of gasoline produced in Example II was slightly lower, the octane number of the gasoline obtained was 24.5 points higher. The slight increase in yield and the exceedingly lower anti-knock properties of the gasoline produced in Example I may be explained as due to the presence in the final product of uncracked low anti-knock gasoline constituents present in the original gas oil charge. In this connection the slight difference in yield does not express amount of unconverted gasoline constituents carried over into the final distillate, since the amount of cracking accomplished in both cases was not the same due to the presence of the relatively more refractory and unconvertible gasoline constituents in Example I. That the extent of cracking is not the same in both cases is evident from the difference in gas yield. It will be noted that the yield of gas in Example II is approximately three times that produced in the first case.

Example III

A similar stock having a 33.3 A. P. I. gravity, an aniline point of 172, an initial boiling point of 450° F. and a mid-point of 603° F. was passed at the feed rate of .6 volume of liquid feed per volume of catalyst per hour over commercial Filtrol while maintaining a catalyst temperature of 860° F. on four-hour periods. 33.3 per cent of stable 10 Reid vapor pressure gasoline was produced having an A. P. I. gravity of 57.2 and an octane number of 78.

Example IV

The same feed stock was cracked under the same conditions and with the same catalyst as in Example III except that the cracking process was operated on two-hour cracking periods instead of four. 38.5 per cent stable 10 Reid vapor pressure gasoline was produced having an octane number of 80.

Having thus described the preferred embodiment, it is understood that my invention embraces such other variations and modifications as come within the spirit and scope thereof. It will also be understood that in the accompanying claim it is my intention to claim all novel features of my invention as broadly as the art will permit.

I claim:

In the catalytic cracking of hydrocarbons to produce a motor fuel containing gasoline constituents, wherein uncracked gas oil vapors are contacted with a solid adsorptive catalyst, the steps of providing a liquid starting material consisting of gas oil which contains gasoline constituents, removing from such gas oil substantially all constituents within the gasoline boiling range so that the resulting uncracked gas oil fraction will have an initial boiling point from about 450° F. to about 478° F. and converting the resulting gas oil fraction free of gasoline constituents in the presence of a catalyst to produce a gasoline motor fuel having a materially higher anti-knock value than a gasoline motor fuel produced under substantially the same conditions and catalyst from the gas oil fraction which contains the gasoline constituents.

WILLIAM J. SWEENEY.