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PROCESS OF TREATING HYDROCARBONS

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This invention relates to the cracking of hydrocarbons in the vapor phase to convert the same principally into aromatic compounds typified by benzene, toluene, and xylene.

It has been proposed to convert propane, butane and the like into benzol by cracking. The prior art workers have cracked ethane, propane and butane and mixtures thereof, in a heated tube, and obtained light oils, gaseous products and a heavy tar. However, in investigations of this character, the chemical reactions occurring were not clearly understood, and not enough importance was attached to the time factor involved in the conversion of the hydrocarbons. We have made extensive investigations to study in a somewhat exhaustive manner, the sequence of changes occurring during the cracking of hydrocarbon gases, and particularly propane and butane into aromatic compounds and oils and tar, and to further determine in a fairly quantitative degree the effect of temperature on the nature of these consecutive changes, and on the velocity with which they occur. Some of the discoveries resulting from such investigations, have been set forth in application Serial No. 364,810, filed May 21, 1929.

As an instance, our experiments show that at temperatures of 1250° to 1750° F., and under atmospheric pressure, the cracking of hydrocarbons typified by propane, butane and mixtures of the same, proceeds endothermically with an increase in volume and the formation of simple gaseous olefines to a maximum of 35 to 50% by volume, by familiar reactions in which the paraffin molecule splits into two molecules, one an olefine, and the other any simple paraffin or hydrocarbon. We have ascertained definitely that in the case of propane or butane, the heat absorbed by the endothermic reaction, reaches a maximum of about 700 B. t. u. per pound at approximately 1562° F., at which state of maximum heat content, the olefine content is approximately at the maximum. At approximately the temperature specified, this condition is attained in somewhat less than 0.002 minutes. At higher cracking temperatures within the range (1250° to 1750° F.), both

olefine content and heat content attain a somewhat higher maximum value than at the lower ones. The time consumed by this stage of reaction decreases rapidly with increase in the temperature at which it occurs.

Our experiments also indicate that continued exposure to the cracking temperature causes the olefines produced by the initial cracking to undergo an exothermic conversion or decomposition into aromatic oils and tar, after a period of no less than ten times as long as that required to effect the endothermic decomposition or conversion. A maximum yield of benzene and toluene is thus developed, accompanied by a somewhat less amount of tar, and very little carbon. During this period, relatively little change occurs in the volume of the gas. However, of course, the olefine content of the gas decreases progressively. The heat evolved during this stage in cracking, propane or butane to a maximum yield of simple aromatics is about 350 B. t. u. per pound, at a cracking temperature of 1562° F., at which temperature a period of 0.04 to 0.08 minutes is required.

We have discovered that the temperature is related to the duration of this exothermic cracking stage by the empirical formula

$$T = 1245 - 180 \log_{10} t$$

in which T = temperature in degrees Fahrenheit and t = time in minutes. This formula applies for temperatures varying approximately between 1250° to 1550° F. It is somewhat less accurate when utilizing higher temperatures up to 1750° F.

A several fold increase in the period of cracking above the shortest period above specified, which will give a virtually optimum yield of volatile oil causes relatively little change in yield. The oil produced at 1562° F. by the shorter cracking period specified contains 20% or so of unsaturates, chiefly butadiene and cyclopentadiene. The remainder is benzene, toluene and xylene. The oil produced by a longer cracking period than that specified contains over 90% benzene, and very little unsaturated hydrocarbons. The optimum yield of volatile oil is substantially

constant over the temperature range of 1250° F. to 1750° F.

We proposed in our above mentioned application, to take advantage of the exothermic stage of the cracking operation, to crack hydrocarbon gases to form oils in a reaction chamber in which conversion occurs at a temperature advantageously higher than that of the gas entering the same, and this without the addition of extraneous heat to the chamber; this being possible by reason of a predominance of exothermic reaction. Broadly stated, our experiments indicate that the oil forming stage in the cracking operation takes place exothermically within the approximate range of 950° F. to 1750° F., the range preferably being between 1100° F. and 1750° F. The composition of the gas to be exothermically cracked or converted may vary greatly. We have ascertained that paraffins higher than methane will absorb heat in cracking. Gaseous olefines, especially ethylene, have a positive heat of formation. In cracking to form oils of higher carbon content, methane, which has a high negative heat of formation, is formed in a relatively large amount, whether hydrogen is or is not present. These facts account for most of the exothermic effect. The maximum exothermic effect will be obtained with a gas containing a maximum concentration of gaseous olefines and a minimum concentration of paraffins higher than methane. The calculated temperature rise during the exothermic stage of the cracking of butane, for example, at approximately 1562° F., to give a maximum yield of simple aromatics, is approximately 350° F. A temperature rise, from this cause, of over 200° F. has been obtained in large scale operations, which will be specifically set forth hereafter. If a rise in temperature of 50° F. be considered the minimum which will give a practical advantage, the weight percent of gaseous olefines need not greatly exceed that of the paraffins, higher than methane.

As indicated in our beforementioned application, cracking as disclosed by us, may be applied to other hydrocarbons than the gaseous paraffins. For example, the gas formed in the pressure distillation of petroleum contains paraffins higher than methane, as well as gaseous olefines, and this product is suitable as the initial starting material.

The initial starting material may also be the gases formed in vapor phase cracking, and these are particularly suitable since they contain as high, in some cases, as 75% olefines.

Petroleum may be cracked at temperatures of 1200 to 1600° F. almost wholly to produce gases containing a large proportion of gaseous olefines, and such gases will undergo, according to our invention, exothermic cracking.

Broadly, in accordance with our present

invention, we propose to conduct the cracking operation in three stages, an endothermic stage, an exothermic stage, and a final stage in which the heat from the other stages is used to convert liquid hydrocarbons. In general, the heat required for the endothermic stage may be introduced through any confining surface. For example, the gas processed may be passed through a tube coil, through which heat is applied externally. Owing to the high velocity of the reactions occurring, cracking may be conducted economically in large scale operations at a temperature between 1300° F. and 1450° F. with the gas at a pressure of only a little above atmospheric.

The exothermic stage may be conducted in a chamber through the walls of which no heat is introduced, and in which the carbon which forms during the operation may deposit. Our experiments indicate that the maximum yield of aromatic compounds is approximately constant over a relatively wide range of cracking temperature. Therefore, owing to the comparatively long time required to effect the desired results in the exothermic cracking stage, it is permissible and desirable to conduct it at a higher temperature than is obtained in the endothermic cracking stage, and thereby reduce the size of the first reaction chamber needed. By providing this reaction chamber with adequate insulation, heat developed by the reaction may be used to attain this higher temperature without any admixture of heating gases which will lower the quality of the gases produced by the process, and this is particularly true if the initial starting materials are such and the process is carried out so as to produce a fuel gas. In extreme cases, it may be necessary to impart a helpful temperature increment prior to the exothermic cracking stage. However, if this is necessary, and if gases are used, only a small amount thereof is necessary to impart a helpful temperature increment, since little of the added heat is absorbed by endothermic reaction.

We will now proceed to describe the process broadly, by reference to the accompanying drawing, in which the figure is a diagrammatic view of an apparatus we have devised for use with the process.

Natural gas hydrocarbons, pressure still gases, oil gases, vapor phase cracking gases or the like are subjected, preferably in a tube coil 1, to sufficient preheating accompanied by endothermic cracking to initiate the exothermic stage of cracking, which is then allowed to proceed in an insulated chamber 2, under the conditions previously described, until a maximum yield of aromatic compounds and oils has developed. For example, substantially pure butane may be passed through the tube coil in which it is cracked, preferably within a temperature range of

1300° to 1400° F., and discharged into the chamber 2 at 1425° F. with a specific gravity of 1.08 (air=1.00), and an unsaturated content of over 40% by volume. This gaseous mixture may then be passed through the insulated reaction chamber, at the exit 3 of which temperature ranges of preferably 1550° to 1700° F. are developed. At temperatures within this range, the optimum yield of aromatic compounds, or oils, is obtained.

In the preferred form of our invention, the conduit 4 through which the gaseous mixture is discharged from chamber 2, has introduced therein by way of valved pipe 5, preheated crude petroleum or fractions suitable for cracking. This latter material, namely, the crude petroleum or other fractions suitable for cracking, is mixed with the hot gases and introduced into a second reaction chamber 6, and there cracked in the vapor phase, (by utilizing the heat from the hot gases) at a temperature varying approximately between 900° and 1200° F., for a period long enough to produce a profitable yield of volatile oils, in which hydrocarbons other than aromatics predominate. The volatile cracked product of the operation is a mixture of vapor phase gasoline with benzol produced by the cracking of the gases.

If desired, some, or all of the hot gas diverted through the line 8 may be fed through the by-pass 12 and be mixed with the combined vapors passing from the converting chamber 6 to the scrubber 13. In the latter, the gaseous mixture is subjected to cooling, and scrubbing, by means of oil, and from the tower 13, fuel oil and tar, with some gas oil, is discharged by way of the pipe 19 to any suitable storage.

The remaining portion of the gaseous mixture from the tower 13 is discharged by way of a conduit 14 into a fractionating column 15 which operates in the presence of uncondensable gases, and is provided at its top with any suitable form of reflux condenser. From this column, gas oil is withdrawn through the pipe 20, by which some or all of it is fed into the line 5 for recycling purposes. A pipe 34 which communicates with the pipe 20, allows some or all of the gas oil from that pipe to be discharged to a suitable storage.

The portion of the mixture which remains uncondensed after passage through the column 15, is discharged from the top of the latter through a pipe 16, and this material will consist of gas, gasoline vapors and benzol vapors, which are led through a condenser 17, and then into an accumulator 18, from which the benzol and gasoline may be discharged by way of a conduit 21. Any gas entering the accumulator 18 may be discharged through the pipe 22, into an absorber 23, in which it may be contacted with ab-

sorbing oil from the pipe 24. The enriched oil will be discharged from the absorber 23 by way of a pipe 25, that leads the mixture to the still 28. In the latter, heat is applied to the mixture to distill off ethylene, propylene, butylene, etc., and crude benzol plus vapor phase gasoline, and the vapors leave this still through the pipe 29 and the condenser 30. The crude benzol and vapor phase gasoline are separated from the remaining gases, and the liquids accumulate in the receiver 31, from which they may be discharged through a pipe 32, into any suitable storage. Gases such as ethylene, propylene, butylene etc., are discharged from the accumulator 31, through a line 33, from which some or all of the same may be withdrawn through a pipe 33a as a product or products of the process. However, we prefer to return some or all of these gases through the line 33, into a recycle conduit 27, which leads the same to the inlet 7 of the primary heater 1.

As is usual in absorption systems, the denuded oil from the still 28 may be returned through the pipe 24 to the absorber 23 for reuse in the latter.

Any gases which remain after passage through the absorber 23 are discharged from the top of the latter through the pipe 23a, into a line 26, from which some or all of the gas may be discharged. As the line 26 communicates with the line 27, however, this gas or a part of it may be recycled back to the entrance of the heater 1.

For the purpose of controlling the exothermic reaction in the chamber 2, the endothermically cracked material which passes through the pipe 2a from the heating coil 1, may be mixed with hot or cold diluent gases introduced through a pipe 35, having suitable branches 36 and 37. For example, a cold diluent gas, to control the cracking, may be fed into the pipe 2a through the pipes 36 and 35, or combustion products or other heating gases, to add sensible heat, may be introduced through pipes 37 and 35.

The foregoing is a typical example of the process, but of course, it may be varied in many respects, as will be appreciated by those skilled in the art.

The recycled gas to be cracked entering the system at 7 from the pipe 27, serves the dual purpose of providing the last increment of temperature to the oil for vapor phase cracking, and contributing benzol to the gasoline product. If the higher temperatures in the 900 to 1200° F. range are used for vapor phase oil cracking in the chamber 6, the gas yield from this source will be increased and the olefine content increased at the same time. The higher the olefine content, the greater the benzol yield will be, so it will be profitable to crack all of such gases to obtain benzol. All the gas cannot always be used to introduce heat into the vapor phase cracking

chamber 6, so a part can be diverted through the pipe 8, and separately scrubbed, cooled and freed from benzol in the scrubber 10 and absorber 11. In such case, the recycled gas would be richer, and a higher benzol conversion would be obtained. The fraction of the gas so diverted through the pipe 8, will depend chiefly on the way the heat conserving devices are employed.

Other gases will be added to the recycled gas at 7 only, if natural gas fractions or low boiling fractionator concentrates or other gases giving a profitable yield of benzol are available for the purpose. However, we desire to have it understood that we may introduce into the heater 1, either some or all of the gases from the line 27, or some or all of the material entering the coil 1 may come from the entrance pipe 40.

Only the gas discharged at 26, not that at 8, will contain benzol yielding gaseous constituents in any considerable amount. This gas can be scrubbed with the oil to be cracked, if desired, and the desirable soluble hydrocarbons retained in the cycle. A high oil rate in the oil absorber 23 will concentrate such gases (propylene, propane, butylene, butane) in the gasoline from which they can be removed by a rectifying column to add to the recycled gas. Such operations will in part accomplish the result of increasing the benzol yield which the supplementary absorber 11 achieves with an additional investment for the equipment.

It will be observed that for the purpose of extracting the liquids from the gases, any suitable separating apparatus may be employed instead of the absorption system. Conventional compression apparatus or refrigerating apparatus might be used for this purpose. Furthermore, any suitable fractionating equipment may be used to split the liquid mixtures wherever desired.

From the foregoing, it will be understood that we have provided an improved three-stage process, in which raw gases, recycled gases, or a mixture of such gases are first passed through suitable means to cause an endothermic reaction, then subjected to a controlled exothermic reaction, and subsequently mixed with heated or vaporized oil for utilizing the heat from the gases to subject said oil to vapor phase cracking.

It is believed from the above description that our improved process and the advantages thereof may be readily understood by those skilled in the art, and we are aware that various changes may be made in the details disclosed, without departing from the spirit of the invention, as expressed in the claims.

What we claim and desire to secure by Letters Patent is:

1. The process of converting hydrocarbons, comprising continuously thermally treating raw hydrocarbon fluids in a zone to produce

a gaseous mixture of aliphatic hydrocarbons containing an olefine content sufficient to insure subsequent exothermic conversion and having a temperature suitable for exothermic conversion, then subjecting said mixture in a second zone without the addition of heat and in the absence of a catalyst to exothermic cracking at a temperature between 1100° and 1750° F., controlled as to duration and final temperature to continuously convert the olefines into crude benzol, then introducing into the mixture in a third zone while the mixture is in heated condition resulting from the cracking, a relatively heavy hydrocarbon oil, and thereby decomposing a portion of said oil, and finally separating the crude benzol and gasoline so produced.

2. The process of converting hydrocarbons, comprising continuously thermally treating raw hydrocarbon fluids in a zone to produce a gaseous mixture of aliphatic hydrocarbons containing an olefine content sufficient to insure subsequent exothermic conversion and having a temperature suitable for exothermic conversion, then subjecting said mixture in a second zone without the addition of heat and in the absence of a catalyst to exothermic cracking at a temperature between 1100 and 1750° F., controlled as to duration and final temperature to continuously convert the olefines into crude benzol, then introducing into the mixture in a third zone while the mixture is in heated condition resulting from the cracking, a relatively heavy hydrocarbon oil and thereby thermally decomposing a portion of said oil separating the crude benzol and gasoline so produced, and returning a portion of the residual gas to the inlet of the first mentioned zone.

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