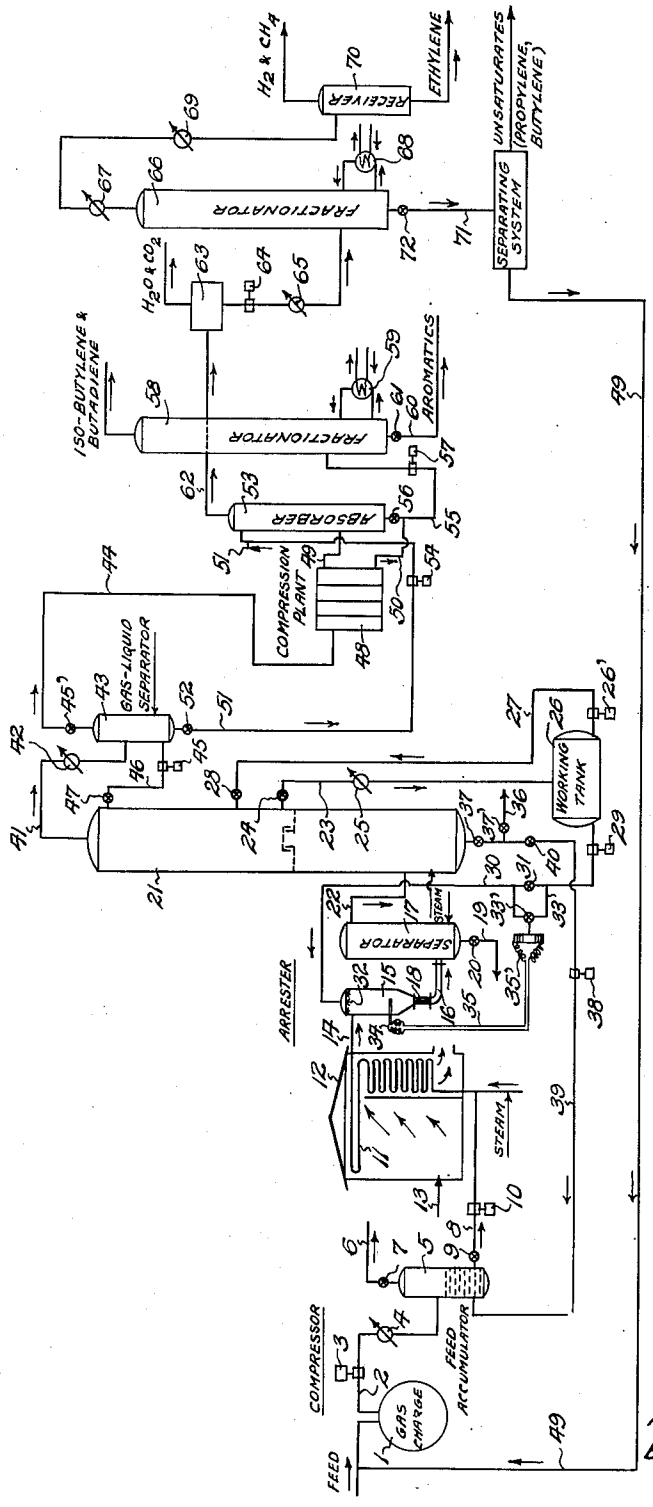
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PYROLYSIS OF GASEOUS HYDROCARBONS FOR THE PRODUCTION OF UNSATURATED COMPOUNDS

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PYROLYSIS OF GASEOUS HYDROCARBONS FOR THE PRODUCTION OF UNSATURATED COMPOUNDS

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1 Claim. (Cl. 260—683)

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This invention is directed to the pyrolysis of hydrocarbons, and more particularly to effecting the molecular decomposition of normally gaseous hydrocarbons by the application of heat in order to increase their commercial value and industrial usefulness.

Large quantities of gaseous hydrocarbons are collected currently from the casingheads of oil wells, from natural gas wells, and around petroleum refineries as a by-product of distillation and cracking operations. A relatively small portion of the gases gathered from these sources is processed for the production of more valuable materials, while enormous amounts are in a sense wastefully burned as domestic and industrial fuel.

It is therefore an object of this invention to provide economic means adapted to the profitable molecular decomposition or reconstitution of such gaseous hydrocarbons, which are primarily of the saturated type, and their conversion into unsaturated hydrocarbons useful in the field of chemical synthesis.

In the normal operation of cracking processes it is customary to employ liquid charging stocks such as reduced crude, gas oil, kerosene fractions or the like, the desired end product being primarily motor fuels of one type or another. In such operations a minimum production of gaseous fractions is desirable. Furthermore, in the manufacture of motor fuels it is customary to take advantage of every practical means of recovering liquid fractions from the gases through the employment of operations such as compression, cooling, absorption, polymerization, etc., in order to obtain the maximum yield of liquid products. However, when cracking gaseous hydrocarbons the reverse condition obtains since it is desirable to recover the maximum quantity of gaseous products, with a minimum liquid yield.

While the pyrolysis of normally gaseous hydrocarbons is not new to the art, the extent to which it is employed in the petroleum industry cannot be compared with the scale upon which liquid charging stocks are cracked. Nevertheless, developments within recent years in the field of synthetics have demonstrated the necessity of an abundant supply of unsaturated hydrocarbons from which such materials can be made, and the petroleum derivatives furnish the natural and cheapest source of supply.

Until recently unsaturated hydrocarbons were obtained largely from the decomposition of alcohol, but this situation has been reversed and the alcohols are now being made from unsaturated

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hydrocarbons derived from petroleum. This chemical aspect of the situation has directed attention to the pyrolysis of gaseous hydrocarbons for the production of unsaturated compounds from which a variety of useful materials can be made, notably plastics, lacquers, gums, resins, alcohols, rubber, anti-knock and anti-freeze compounds and kindred products, all of which are finding ready and increasingly wide commercial application.

While considerable progress has been made in synthesizing various materials from unsaturated hydrocarbons, it is believed that the potentialities of this field have scarcely been touched because of the absence of an abundant and cheap source of supply of unsaturated hydrocarbons, and since the supply has been limited in the past, further developments in the manufacture of synthetics will be governed largely by the availability and cost of unsaturated hydrocarbons in the future.

It is therefore a further object of this invention to provide means whereby unsaturated hydrocarbons can be produced in any desired amounts and upon an economic basis which will be inviting to the manufacturers of synthetics.

In accordance with this invention, the gas collected around oil fields, petroleum refineries or from natural gas wells or other sources, is passed through the heating zone of a suitably designed furnace wherein it is decomposed or molecularly reconstituted into a gaseous fraction consisting primarily of unsaturated hydrocarbons, and a heavier fraction composed largely of aromatic hydrocarbons. The latter, together with some liquid paraffinic fractions within the motor fuel boiling range, are produced as a result of polymerization reactions which proceed concurrently with the decomposition reactions.

After separating the gaseous constituents and heavier components by fractionation or otherwise, the liquid fraction may be withdrawn and further processed for the production of high anti-knock motor fuel, or it may be returned to the system with the raw feed, which is also in liquid form after having been compressed and cooled below its condensation temperature. The choice of returning the liquid fraction to the system for reprocessing in order to increase the yield of unsaturated gaseous hydrocarbons, or diverting it to motor fuel, is governed by the relative importance of the end products in relation to the market requirements.

While this invention is directed specifically to the pyrolysis of gaseous hydrocarbons for the pro-

duction of unsaturated compounds, the same general principles may be applied when cracking liquid hydrocarbons in the vapor phase for the production of high anti-knock motor fuel. The essential difference between the two operations is that in the pyrolysis of gases, unsaturated gaseous compounds is the primary end product desired, with a relatively small production of liquid hydrocarbons as a by-product; while in the cracking of liquid hydrocarbons for motor fuel, gaseous hydrocarbons are obtained as a by-product. The two are further distinguished by the wide difference in the operating temperatures. When cracking liquid hydrocarbons in the vapor phase temperatures of the order of 1000° to 1250° F. may suffice to effect the desired decomposition of most charging stocks, while in gas pyrolysis the temperature may reach 1600° F.

For a further understanding of this invention reference is made to the following description and the accompanying drawing forming a part of this specification, wherein suitable apparatus and equipment for carrying out the several steps of the process are shown diagrammatically.

Referring more particularly to the drawing, numeral 1 designates a supply of hydrocarbon gas which when obtained from the casinghead of oil wells or from natural gas wells is largely saturated in character and is composed primarily of methane, ethane, propane and butane. If the gas is collected from the various sources around an oil refinery employing cracking stills it will contain, in addition to the above constituents, some unsaturated hydrocarbons such as ethylene, propylene and butylene derived from the cracking operation, the proportion of such unsaturated hydrocarbons present in the total gas being governed by the extent to which cracking is employed in the particular refinery. However, the presence of unsaturated compounds in the gaseous charge is not objectionable, and may be considered desirable, since they are handled along with and in the same manner as the saturated gases. Whether or not they enter into the decomposition and polymerization reactions within the conversion zone is of little importance since the overall result is practically the same, either in the presence or absence of the unsaturates in moderate amounts, which is usually a relatively small proportion of the total gaseous charge, averaging perhaps five to fifteen per cent.

The gaseous charge passes through line 2 to a compressor 3 wherein it is compressed to approximately 250 pounds per square inch gauge. Leaving the compressor, the compressed gas passes through a cooler 4 where it is largely liquefied, and thence to an accumulator 5. The uncondensed portion of the gas, consisting mainly of hydrogen and methane, is withdrawn from the top of the accumulator through line 6, controlled by valve 7, and sent to the plant fuel gas-burning system. The liquefied gas collecting in the bottom of the accumulator is withdrawn through line 8, controlled by valve 9, and delivered by pump 10 to a gas pyrolysis or cracking coil 11 located in a furnace 12, fired by burners 13. The mixture of hydrocarbon gases is decomposed in this coil under temperature conditions within the range of 1300° to 1600° F., and under a pressure not in excess of approximately 300 pounds per square inch gauge. Steam is admitted to the cracking coil as an effective corrosion preventive agent.

The decomposed hydrocarbons leaving the cracking coil through line 14 enter a temperature arrester 15 wherein the temperature of the gases is substantially instantaneously reduced to a degree below that at which further decomposition can take place. This is accomplished by direct and intimate contact between the hot gases and an atomized liquid cooling agent which is preferably produced within the system as hereinafter described, thereby reducing the temperature to approximately 600° F.

In the pyrolysis of gaseous hydrocarbons under the prevailing high temperature conditions required, both the decomposition and polymerization reactions proceed with such velocity and are completed within such a short interval that it is difficult if not impossible to control the reactions to an extent which will avoid altogether the formation of some tarry substances and finely divided carbon which, if not segregated and removed from the system, will deposit upon the inner walls of the transfer lines and collect upon the fractionating trays in the bubble tower, eventually fouling the system and resulting in premature shutdowns for cleaning purposes.

I have found that while it is extremely difficult to avoid completely the formation of resinous materials and sooty coke in gas pyrolysis operations, their presence may be reduced to a negligible quantity if certain precautionary measures are followed. I have noted also that the formation of such materials is not altogether a result of the decomposition reactions per se, as is generally believed, but is due largely to the method of checking the reaction by direct contact with a cooling agent after decomposition has been effected to the desired degree.

Uniform operating conditions of time, temperature and pressure are of primary importance in gas pyrolysis operations, but regardless of the regularity attained in these conditions, resins and coke will be formed in the quenching step unless the arrester temperature is also maintained at a substantially constant level. Widely fluctuating temperatures in the arrester result in coke formation for the same reason that coke collects at unprotected and exposed spots in insulated hot oil lines.

In order to prevent such temperature fluctuations the arrester is maintained at a constant temperature under thermostatic control by means disclosed in my pending application, Serial No. 765,438 which in substance comprises automatically controlling the flow of quenching oil to the arrester, in response to the temperature fluctuations therein. Means are also provided in the above application for keeping the mixture of oil and gas in a constant state of agitation while passing through the transfer line 16 leading to the separator 17, by inserting a helical vane 18 in the line which imparts a rapid swirling motion to the materials and thereby effectively retarding the deposition of solids upon the inner walls of the line.

The severity of gas pyrolysis temperature conditions appears to render impossible the complete absence of dust-like coke in such operations, as well as the formation of small amounts of tarry substances which apparently result from polymerization reactions which accompany those of decomposition. However, the presence of such materials in the small amounts formed present no particular problem since they may be separated from the other decomposition products and diverted from the system. To this end the mixture of liquids, solids and gases, leaving the arrester in a state of turbulence which will not permit the deposition of coke at this point, passes

through line 16 at a high velocity and enters the separator 17 wherein the velocity is greatly reduced, permitting the solids and resinous materials to settle to the bottom, while the gases and light fractions are removed with the aid of steam. The solids and heavy materials are then withdrawn through line 19, controlled by valve 20; and diverted from the system.

The overhead products from this operation leave the separator through line 22 and enter the fractionating tower 21 where further separation is effected primarily into gaseous and liquid products, a temperature gradiant of approximately 450° to 250° F. being maintained within the tower, while steam is injected into the lower section to assist in the separation. In order to control the mid-tower temperature, a stream of reflux oil is withdrawn from an intermediate point through line 23, controlled by valve 24, passed through a cooler 25 and collected in a working tank 26. Being a clean, carbon-free product of a relatively constant boiling point range, this continuous and abundant supply of oil serves the dual purpose of controlling the tower temperature and also quenching the high temperature decomposition products entering the arrester. A portion of the oil is withdrawn from the working tank by pump 26' and delivered through line 27 to the upper section of the tower, controlled by valve 28. Another portion is withdrawn by pump 29 and delivered through line 30, partially controlled by valve 31, to the spray nozzles 32 located in the top of the arrester, as a quenching medium.

The arrester is maintained under constant temperature conditions of approximately 600° F., under thermostatic control, as fully described in my pending application, Serial No. 765,438, now U. S. Patent No. 2,608,527, the mechanical means for automatically admitting the regulatory flow of oil through the by-pass 33 consisting essentially of a valve 33' actuated by a motor, a magnet or other suitable device 35', electrically controlled by the make-and-break contact of the thermostat 34 connected through a conduit 35 with a source of current (not shown) and said device. Valve 33' may be magnetically actuated to the open or closed position as the thermastatic circuit is established or broken by the rise or fall of the temperature in the quenching chamber. The thermostatic element 34 inserted through the wall of the chamber is electrically connected with the magnets 35' through conduit 35 and with a source of current (not shown) in such a manner as to control the movement of the valve mechanism 33' to the open or closed position in response to the fluctuation of temperature in the chamber. When the temperature rises above the desired point, valve 33' is opened automatically, admitting more oil to the chamber; when the temperature falls, the valve is closed, diminishing the flow of oil, thus maintaining an even temperature in the quenching chamber.

In the initial operation of the gas pyrolysis system herein described it is necessary to prime the fractionating tower with a sufficient quantity of oil, preferably a naphtha cut of approximately 300° to 400° F. boiling range, for temperature control and quenching purposes, but thereafter condensation of a part of the products of decomposition and polymerization are more than sufficient for these requirements and there is a gradual but slow accumulation of oil in the system. The excess of oil may be withdrawn from the bottom of the fractionating tower through line 36, controlled by valves 37 and 37', and further processed for high anti-knock motor fuel, or it may be returned to the feed accumulator by pump 38 through line 39, controlled by valves 37 and 40, and again decomposed for the production of additional unsaturated gaseous hydrocarbons.

The overhead leaving the top of the fractionating tower through line 41 passes through a cooler 42 and into a gas-liquid separator 43, the liquid accumulating in the bottom of the separator being largely aromatic in character. A portion of this liquid is returned to the top of the tower as a reflux temperature control medium by means of pump 45, through line 46, controlled by valve 47.

The gaseous products leaving the top of the separator through line 44, controlled by valve 45', consist of a mixture of saturated and unsaturated hydrocarbons composed primarily of C_2, C_3 and C_4 compounds. This gaseous mixture is sent to a gas separating system where separation is effected into its component parts by ways and means well known to the art, utilizing such methods as are adapted to the recovery of the desired constituents.

In its simplest form and by way of illustration only, such an operation consists in first compressing the gas for the recovery of liquid fractions. The gas passing through line 44, for example, is conducted to a gas compression plant 48, operating preferably in a succession of increasingly higher pressure stages, combined with intermediate cooling between the stages. The uncondensed gases leaving the compression plant through line 49 go to an absorption tower 53, maintained at approximately the same pressure as that employed in the highest compression stage, usually between 200 and 500 pounds per square inch gage.

The liquid withdrawn from the bottom of the gas-liquid separator 43 through line 51, controlled by valve 52, is delivered by pump 54 to the top of the absorption tower as an absorption medium for extracting iso-butylene and butadiene from the gases because of their greater affinity for aromatics than the other C_4 compounds, i. e., normal butylene and butane.

The enriched aromatic liquid withdrawn from the bottom of the absorber through line 55, controlled by valve 56, together with that withdrawn from the compression plant through line 50, is delivered by pump 57 to a fractionating column 58 equipped with suitable fractionating plates (not shown) and a reboiler 59, wherein the iso-butylene and butadiene fractions are recovered as an overhead product, while the aromatic liquid is withdrawn from the bottom of the fractionator through line 60, controlled by valve 61. This liquid may be further fractionated to remove the paraffinic hydrocarbons liquefied in the compression operation, the aromatics then being recovered as finished product.

The overhead products leaving the absorber 53 through line 62 are processed in suitable apparatus shown diagrammatically at 63 for the removal of water and carbon dioxide by the action of reagents such as calcium chloride and silica gel. The remaining gases are then passed consecutively through a compressor 64, a cooler 65 and into a low temperature fractionator 66, preferably of the bubble tower design, also equipped with a reboiler 68. This fractionator is maintained under a pressure of about 500 to 1000 pounds per square inch gage, and at a tempera-

ture of about −90° to −175° F. Reflux for the top of the tower is provided by cooling and condensing a portion of the overhead product in a reflux condenser **67**, through which a suitable refrigerant, such as, for example, expanding liquid ethane or propane, is passed. An additional cooler **69**, of a similar type is provided to further condense the overhead product which is collected in a receiver **70**, and which consists essentially of ethylene.

The liquid products withdrawn from the bottom of the fractionator through line **71**, controlled by valve **72**, consisting primarily of ethane and C_3 and C_4 hydrocarbons, of both the saturated and unsaturated types, may be further fractionated by similar methods for the recovery of other unsaturated constituents such as propylene and butylene, as will be apparent to those skilled in the art, the remaining saturated hydrocarbons being returned to the feed for reprocessing.

What I claim:

A process for refining hydrocarbons, comprising: thermally converting normally gaseous hydrocarbons of the saturated methane series type into those of the unsaturated ethylene series type, passing gaseous and light liquid hydrocarbons constituting products of such conversion through a primary fractionating zone, removing converted gaseous hydrocarbons as an overhead product from the fractionating zone and liquid hydrocarbons from the bottom of said zone, cooling the overhead hydrocarbons removed from the top of said fractionating zone and passing the same through a separating zone, effecting in said separating zone a separation of gaseous hydrocarbons from a low-boiling liquid aromatic fraction, compressing the gaseous hydrocarbons discharged from said separating zone and passing the same through an absorber, delivering the aromatic liquid fraction to the top of said absorber for countercurrent flow relationship to the ascending compressed unsaturated hydrocarbon gases, whereby to cause the aromatic liquid hydrocarbons to absorb and remove selectively from the contacted gases iso-butylene and butadiene, fractionating the last-named liquid hydrocarbons to separate iso-butylene and butadiene as overhead products, and treating the hydrocarbon gases removed from the top of said absorber to recover ethylene therefrom.

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