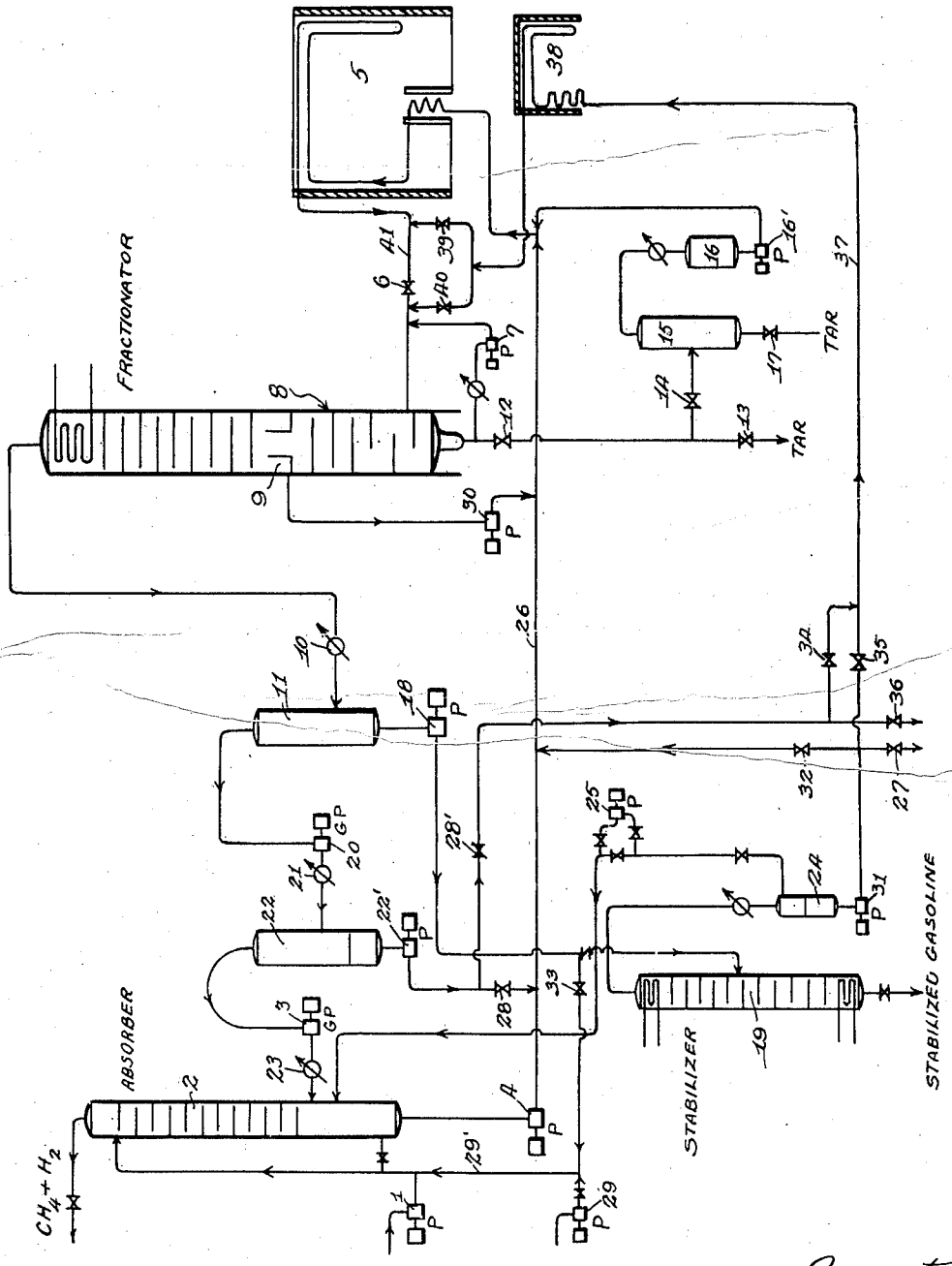
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PETROLEUM CONVERSION PROCESS

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PETROLEUM CONVERSION PROCESS

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The present invention relates to an improved petroleum conversion process capable of converting normally heavy hydrocarbons into lighter hydrocarbons while at the same time utilizing normally gaseous and liquid hydrocarbons to enhance the yield of the conversion operation and to benefit the process in numerous ways hereinafter specifically recited.

In its broadest aspects the present invention relates to a hydrocarbon conversion process, particularly applicable to the petroleum hydrocarbons, in which any petroleum product may be converted as a result of the action thereon by heat, time and pressure, in the presence of additional hydrocarbon or hydrocarbons which are specifically lighter than the charging stock and which may be either normally gaseous or normally liquid.

One of the objects of the invention is to convert a heavier hydrocarbon such as, for example, crude oil, fuel oil, gas oil, kerosene, or the like, into specifically lighter hydrocarbons having a lower boiling point, which for most purposes is chosen to lie within the range of the now commonly used motor fuels of commerce, the main object being at the present time the production of motor fuels having a high antiknock or octane rating, although it is to be understood that the invention is by no means limited to the production of such motor fuels, as by suitable alteration or modification of the herein described process or processes the ultimate product produced may be varied considerably as to its initial as well as final boiling point and may constitute a Diesel fuel, a heating fuel, or some hydrocarbon specialty such as solvents for the manufacture of coating compositions, cleaners-naphtha, and the like.

The inventor has recognized the fact that specifically lighter hydrocarbons which may be either normally liquid or normally gaseous, and particularly if such hydrocarbons are of the saturated or paraffin series, are capable of combining with unsaturated hydrocarbons such as the olefins, with the production of new saturated hydrocarbons, this type of reaction being for the purpose of the present invention herein termed "alkylation." This alkylation will prevent, to a considerable extent, undesirable reactions such as the polymerization of unsaturates to tars, which, as is well known, have a decided tendency to decompose into a carbonaceous material; whereas, as a result of the alkylation, the unsaturated or olefinic hydrocarbons, instead of uniting with each other, or as it is sometimes called, polymerizing, will unite with saturated hydrocarbons to form heavier hydrocarbons, which are more saturated than the original unsaturates and which, moreover, are partly branch chain and therefore are possessed of a definite antidetonant value greater than that of the corresponding straight chain hydrocarbons. Thus a mono-olefin will unite with a saturate to form a heavier saturate, whereas a diolefin will unite with a saturate to form a heavier mono-olefin which may be in the boiling range of either the product or the recycle stock.

One of the objects of the present invention therefore is to carry out a hydrocarbon conversion operation in which a mixture of comparatively heavy hydrocarbons and lighter hydrocarbons, which latter may be either some of the product produced by the process or extraneously produced light hydrocarbons which may be either normally liquid or normally gaseous, or some of both, is passed through a highly heated zone, under proper conditions of pressure, temperature and time where the conversion takes place. The conversion takes place in the presence of a sufficient amount of comparatively saturated hydrocarbons which are thus available as alkylating agents and which therefore not only alkylate the products of the operation but also prevent excessive polymerization of such unsaturated bodies as may be present or may have been formed during the operation of the process, thus reducing the production of tar and increasing the ultimate yield of the desired product.

The present invention is to be distinguished from what is ordinarily known as a cracking operation in the sense in which this term has heretofore been used. The term "cracking" has hitherto been rather loosely used as descriptive of a process in which relatively heavier hydrocarbons have been heated so as to become broken down, decomposed, or broken up, with the formation of specifically lighter hydrocarbons having a lower boiling point, as well as heavier hydrocarbons than the original material and having a higher boiling point than the original material. In accordance with the present invention, however, applicant wishes to define cracking for the purpose of his invention as the breaking up of larger hydrocarbons into smaller hydrocarbons and to reserve the term "polymerization" for the combination or aggregation of unsaturated hydrocarbons to produce hydrocarbons having a larger molecule than the constituent hydrocarbons, irrespective of the size of the original molecule. In the same manner he wishes to define alkylation as the addition of a saturated hydrocarbon to an unsaturated or olefinic hydrocarbon, with the resultant production of a hydrocarbon having a higher molecular weight

than either of the molecular constituents but characterized by its greater saturation than the original olefin.

It is well recognized that when a paraffinic hydrocarbon is cracked in the sense in which the word is here used, it will break up or decompose into a number of smaller hydrocarbons. If, for example, a long chain paraffin hydrocarbon is cracked into, for instance, two new products, one of these will be a saturated product and the other one will be an unsaturated product or an olefin. This unsaturated product or olefin will possess a tendency to combine with other unsaturated products or olefins, with the formation of a long chain or high molecular weight unsaturated olefinic product. This unsaturated olefin, upon decomposition, tends to form more highly unsaturated hydrocarbons which, upon combining with each other, form tars or heavy residue which easily decompose into gases and coke. If therefore at the time of the breaking down or cracking of the original molecule there is or are present a hydrocarbon or hydrocarbons of a saturated nature and of as low molecular weight as the desired product, or lower, then these saturated comparatively light materials are available for the alkylation of the formed olefinic or unsaturated hydrocarbons, with the result that the excessive polymerization of the latter is substantially prevented not only by the ensuing alkylation but also by the spacing or jacketing effect of the saturated hydrocarbons present, which prevent to a considerable extent the contact between the formed olefinic materials present.

It has already been proposed by others to return certain hydrocarbon gases to an ordinary cracking reaction for the purpose of suppressing the amount of gas that is formed. The problem to be solved, however, is much more complex than the mere suppression of the formation of gaseous material. What applicant has accomplished is to effect the conversion of hydrocarbons without the formation of the usual large amounts of heavy residue and without the production of any waste gas other than possibly methane and hydrogen, thus utilizing to a very large degree all of the hydrocarbons charged to the process for the production of a useful end product with greatly increased yields thereof. He has found it very advantageous to return to the conversion zone of his process not only the hydrocarbons which are normally gaseous but also, in some instances, hydrocarbons which are normally liquid; in fact, he may obtain beneficial results by the return to the conversion zone of the process of any hydrocarbon lying between C_2 and C_{10}. It will at once be appreciated that some of these hydrocarbons are normally liquid, as for example from C_5 upwardly, and that some of these are to be found in normal motor fuel now in use. As a source of such hydrocarbons, as for example from C_5 and up, applicant may use some of the hydrocarbons obtained from his process, or by a previous operation of his process, or he may obtain these hydrocarbons from an extraneous source. Such hydrocarbons may be, for example, ordinary gasoline of commerce or a straight run gasoline stripped from ordinary crude oil in a stripping operation. Applicant has found it desirable to return to his conversion zone the ethane, C_2H_6, which has been found to constitute an excellent alkylating agent for the purposes of his invention. Others have already proposed to return to a cracking operation specific hydrocarbons such as the C_3's and C_4's—for example, propane, propylene, butane, and butylene—while excluding the lighter hydrocarbons such as ethane and ethylene, and also excluding the heavier hydrocarbons such as the C_5's to C_{10}'s.

Applicant has also found it advisable so to regulate the amount of alkylating agents circulating in his process as to suppress as far as possible the formation of undesired polymerization products or tars, whereby he obtains a very clean operation, with practically no carbonization of the heating zone, while at the same time obtaining high yields from the original charging stock, because of the fact that the highly unsaturated hydrocarbons normally polymerized to tar are either converted into product or made available as clean recycle stock suitable for further processing. The final product will be endowed with a relatively high antiknock value and yet of such a character that it requires but little refining. This high antiknock value can be, at least in part, attributed to the production of a certain amount of branch chain hydrocarbons which have a higher anti-knock value than the isomeric straight chain hydrocarbons of the same number of carbon atoms. Furthermore, reducing the tar production permits applicant to operate at higher temperatures, as required for production of naphthenic and aromatic compounds which have high antiknock characteristics, and also to go to high conversion per pass, on the order of 40 to 60%.

Applicant can vary his process considerably, but it is believed that it can be fully understood from the drawing herewith submitted, which shows one type of operation which is within the scope of his invention. The drawing is a flow sheet, in purely diagrammatic form, of an operation in which the fresh charge is employed as an absorbing medium for gaseous hydrocarbons which are returned to the process. A description of the flow sheet will follow hereinafter. In the said drawing, which is not to scale, are illustrated only those instrumentalities which are absolutely essential for an understanding of the invention; nor are all the connecting lines, pumps, etc., shown, as this would only complicate the drawing, interfering with a rapid and proper understanding of the fundamental parts of the invention. Arrows have been used on the various lines which are shown merely as single lines, and any device not ordinarily understood has been properly labeled. Thus, for example, the furnace is entirely diagrammatic and is in no-wise intended as an interpretation of the mode of heating therein used. Pumps have been diagrammatically indicated by two squares connected by a line and the letter P in the pumping portion of the mechanism. Circles with arrows pointing upwardly and to the right have been employed as conventional symbols for cooling coils or condensers, which may be of the water-cooled type or other types of heat exchangers. Bubble towers have been shown merely by substantially rectangular figures having rounded ends, with the bubble trays indicated by light horizontal lines, this also having been done with the absorbers. Wherever liquid is indicated as being present in any of the containers or columns, the level shown in the drawing is not to be taken as being literally correct. With these understandings there will now be described the operation in the form shown in the drawing.

A suitable charging stock, which for example might be virgin gas oil, is introduced by means

of pump 1 into absorber 2, where it absorbs substantially all of the ethane and propane introduced into the absorber by means of gas pump 3, allowing methane, hydrogen, and hydrogen sulfide to escape at the top. The pressure on the absorber necessary for the efficient absorption of the ethane is in the neighborhood of 400 to 600 pounds per square inch, depending upon the temperature of the oil and the ratio of oil to gas.

The enriched oil is pumped from the bottom of absorber 2 by means of pump 4 and through line 26, through furnace 5, where it is heated to a temperature between 850° and 1150° F. under a pressure of from 200 to 4000 pounds on the outlet. The pressure is released by means of valve 6, the hot oil is quenched by means of cold oil introduced by means of pump 7, and the mixture is introduced into the base of fractionating column 8, where separation occurs into tar which accumulates at the bottom, cycle stock which is collected in the accumulator section 9, and gases and product which pass overhead through cooler 10 into receiver 11.

Such tar as may be formed is drawn off through valve 12 and may be sent direct to storage through valve 13, or by means of valve 14 into flash drum 15, which is held at a lower pressure than that in fractionating column 8 so that any recycle stock remaining in the tar is distilled overhead into receptacle 16 and is reintroduced into furnace 5 by means of pump 16'. Tar is drawn off from the bottom of the flash drum 15 through valve 17. The pressure held on fractionating column 8 may be from 75 to 300 pounds.

In receptacle 11 the fixed gases are to a large degree separated from the product, the latter being drawn off by means of pump 18 and introduced into stabilizer 19.

The gases passing overhead from receptacle 11 are compressed by means of gas pump 20, cooled by cooler 21 and introduced into receptacle 22 where the condensate accumulates at the bottom and the material remaining in the gaseous state is introduced into gas pump 3, from which point it is cooled by cooler 23 and enters absorber 2.

The unstabilized product from receptacle 11 which enters stabilizer 19 is stabilized to the desired initial boiling point or vapor pressure under appropriate pressure conditions which may be higher or lower than those prevailing in column 8. The overhead condensate from stabilizer 19 is condensed and accumulates in receptacle 24. Any gases remaining uncondensed may be introduced into absorber 2 by means of gas pump 25. The condensate in receptacle 24 may be introduced directly into line 26 going to the furnace 5 by means of pump 31 or may be withdrawn through valve 27 for other uses foreign to the process. The condensate in receptacle 22 may be introduced into line 26 by means of pump 22' through valve 28, or it may be vented from the system through valves 28' and 36.

If desired, light liquid hydrocarbon, such as C_5 to C_{10}, in the gasoline range, may be introduced into the absorber by means of pump 29 and line 29', or some of the unstabilized products from receptacle 11 may be introduced into the absorber by means of pump 18 through valve 33. The recycle stock in accumulator 9 in fractionator 8 is drawn off by means of pump 30 and is introduced into line 26 for passage through furnace 5. If desired, all of the liquid accumulating in receptacles 24 and 22 may be pumped into line 26 for passage through furnace 5, or such of it as desired may be withdrawn from the system for use in any manner desired.

If the product is to be a Diesel oil, for instance, then the pressure held on furnace 5 will be high, say in the neighborhood of 2000 pounds, as under high pressure conditions in the furnace a more saturated product will be produced. However, if a high octane gasoline is desired, this outlet pressure will be lowered to perhaps 200 to 1000 pounds per square inch. It is not advisable to carry over 300 pounds pressure on fractionating column 8 due to the difficulty of securing efficient separation between the fractions when working at much higher pressures than this. Pressure on stabilizer 19 will depend on the type of product made. If, for instance, it is desired to make Diesel oil, pressure may be held at about 100 pounds; or if it is desired to make motor gasoline, pressure on the stabilizer will be held in excess of that on fractionating column 8. The pressure which is held on receptacle 22 will depend upon how much propane it is desired to withdraw from the system. Pressure which is held on absorber 2 will depend upon how much ethane it is desired to absorb and how much absorption oil is available for the task.

In an operation where it is desired to supplement the alkylating effect of the gases by the alkylating effect of extraneous light liquid hydrocarbon, the latter may be introduced into the absorber along with the charging stock by means of pump 29, or, failing an outside source, some of the unstabilized product itself may be used for this purpose.

By means of this apparatus, it is possible to vary not only the amount of liquefied gas and light liquid hydrocarbons being fed to furnace 5 but also their composition. For instance, a gas can be returned which is substantially all ethane, or which is largely ethane and propane, or which is largely ethane, propane and butane. Naturally the composition of the light liquid is determined by what is available from outside sources or by the product itself, whichever is used.

The advantages of this type of operation are that a minimum of heavy tar and a minimum quantity of waste gases useful only for fuel will be produced. By utilizing substantially all of the ethane as an alkylating agent, the butane is made available either for a gasoline blending agent or for other purposes, and any excess propane which it is not desired to recirculate is also made available for other purposes. Propane and butane have a much wider field of application for outside uses than does ethane, which is largely used for fuel; therefore it is important that the ethane be consumed in this operation along with such propane as is desired.

Contrary to prior practice, in which the cracking of different boiling ranges of stock has been done in separate coils under different conditions, so-called "selective cracking", applicant has found that it is more advantageous to use a rather long range cracking stock. By the use of a long range stock, the heaviest hydrocarbons begin to decompose in the earlier part of the coil, and any gases formed in said decomposition are available during the remainder of the passage through the coil for alkylating with lighter decomposing hydrocarbons, thereby minimizing the amount of gas which leaves the conversion zone.

By the use of light, largely saturated paraffinic alkylating agents in the conversion zone, the formation of tar, which it is assumed is largely the result of interaction between highly unsaturated hydrocarbons, is avoided or greatly minimized by what is apparently a selective alkylating action.

By varying the pressure and temperature on the conversion coil and the amount of alkylating agent recirculated, a wide variety of products can be secured. For instance, at low pressure on the order of 400 pounds and high temperature on the order of 1050° F. a highly olefinic product results, whereas at lower temperatures on the order of 980° F. and pressures in the neighborhood of 2000 pounds, a much more highly saturated hydrocarbon results. The initial and end boiling points of the product may also be regulated at will within wide limits. The end point of the product is controlled by means of the cooler in the top of fractionating column 8. The initial boiling point of the product is controlled by the amount of reboiling done in stabilizer 19.

The process may be used for the reforming of naphtha or motor fuel which has insufficient antiknock rating, while at the same time converting a high boiling point stock into high octane motor fuel. It has been found in this process that when using ethane as an alkylating agent it can be entirely consumed in the process, resulting in only methane and hydrogen leaving the system out of the top of the absorber tower 2, which is a result never hitherto attained, and in the description of most of the prior art processes involving gas return the statement is made that ethane is practically a useless gas which cannot be employed in the process and must be wasted.

As an example of actual operating conditions and results obtained, the following may be mentioned: Starting out with a straight run naphtha obtained from Kansas crude, having a gravity of 52.5° A. P. I. and an Engler distillation range of from 253° F. to 439° F., and with an L–3 octane number of 23, an outlet temperature at the end of the coil in furnace 5 of 1020° F., an outlet pressure of 2000 pounds per square inch, and a pressure on the absorber of 400 pounds, there was obtained a volume yield of liquid corresponding to 93.5% from the material fed into the process. The amount of 400° F. end point gasoline in the final liquid withdrawn from the process was 93.2% (the remainder being 28° A. P. I. gas oil), and the octane rating of this gasoline in accordance with the standard L–3 method was 60. The amount of gas produced per barrel of charge was 163 cubic feet; and this gas, which was discharged from the process, was found to consist entirely and solely of methane, CH_4. There was no hydrogen, ethylene nor ethane in it. The product as discharged from the operation was a lemon yellow color and was easily refined, having an odor very similar to that of the straight run gasoline. The percentage of gas recycled to the process, in percentage of gas to liquid volume, assuming the gas were all liquid, was 72%. The analysis of the liquefied gas which was fed to the furnace 5 was as follows:

	Per cent
Methane	2.7
Ethylene	1.4
Ethane	47.9
Propylene	3.3
Propane	44.7

There were no gases having a higher than C_3 carbon content at any time in any of this mixture of gases fed to the furnace.

As a second example, when cracking a 35° gravity Kansas virgin gas oil at 930° F. and under 2000 pounds pressure, a yield of 90.5% by volume of 407° F. end point gasoline was secured with 9.9% of heavy tar and 2.3% of recycle stock. It will be noted that the volume yield of these products adds up to more than 100%, which is accounted for by the large increase in volume of the light gasoline. There was produced 292 cubic feet of fixed gas per barrel of gas oil charge leaving the top of the absorber which consisted of

	Per cent
H_2	15.0
CH_4	84.5
C_2H_4	0.5
	100.0

As a third example, cracking 35° A. P. I. Kansas gas oil in which the recycle stock from accumulator 8 was withdrawn from the system and not recycled, there were produced

	Per cent
405° F. end point gasoline	51.1
Recycle stock	42.7
Tar	3.4

228 cubic feet of gas per barrel of charge left the top of the absorber, having a composition of

	Per cent
H_2	4.8
CH_4	87.5
C_2H_4	3.4
C_2H_6	4.3
	100.0

There was drawn off from the system 132 cubic feet of gas per barrel of charge, having the following analysis:

	Per cent
C_2's	55.3
C_3's	44.7
	100.0

The L–3 octane number of the gasoline was 70.9, which, by the addition of 1 cc. of lead tetraethyl, rose to 73.1. The liquid volume of the gas entering the furnace was 51.3% of the total material entering the furnace, and the composition of this gas was 56.2% ethane. The outlet temperature of the furnace was 1050° F. and the pressure 750 pounds per square inch.

As a fourth example, a charge consisting of four parts of 35° A. P. I. Kansas gas oil with one part of 82° A. P. I., 14-pound Reid vapor pressure natural gasoline, initial boiling point 90° F. and final boiling point 295° F., was charged to the system without returning any recycle oil. The furnace outlet temperature was 980° F. and the pressure 2000 pounds per square inch. There was produced a volume yield of liquid products recovered of 97.6% based on the charge. These products were:

	Per cent
Gasoline	42.8
6.4 pounds Reid vapor pressure 68.0 octane by the L–3 method	
Recycle	51.1
Tar	3.7

There was produced in addition 295 cubic feet of

gas per barrel of charge, leaving the top of the absorber and having the following composition:

	Per cent
CH_4	96.1
C_2H_4	0.2
C_2H_6	3.7
	100.0

The present process is also to be completely distinguished from any process of gas conversion in which an extraneous gas is added to a process. It will be noticed that in the present process it is the gas produced in the process which is entirely utilized, and in some cases heavier liquid products such as from C_5 to C_{10} are employed, and these may be either extraneous or produced in the process, but in any event extraneous gas or hydrocarbons normally gaseous are not employed. The process may therefore be considered as substantially a conversion process in which heavier hydrocarbons are converted into those which have a higher Baumé gravity or lower specific gravity and which have a lower boiling point than the initial materials, while at the same time avoiding the manufacture or production of excessive amounts of hydrocarbons having a higher boiling point than the initial material and converting lighter hydrocarbons into heavy hydrocarbons useful in the desired product.

When the process is initiated in the apparatus, the cracking is carried out at comparatively low temperatures until sufficient gas is generated to build up the gas cycle. This is done to avoid formation of tarry and heavy end products at the higher temperatures due to the absence of alkylating hydrocarbons. During this period the fractionating, absorbing and stabilizing columns become filled with gas and the temperature may be progressively increased until the pressure has been built up to the desired operating conditions at which time the system becomes stabilized. After a prolonged run, if it is desired to clean the furnace tubes, the valves on the pressure apparatus are closed to maintain the pressure, the oil discharged from the tubes, the tubes cleaned and reconnected and the valves are opened. The system may then be quickly brought to stabilized operating conditions for the reason that the system is under a substantial recycle gas pressure when operations are resumed. In some instances, when cracking very light stock, when once the process is in full operation, the necessity for withdrawal of tar is almost entirely eliminated, as all the heavy materials are alkylated into light products, or the polymerization of olefins to heavy products is prevented. In either event, the formation of tar and products heavier than the raw materials is greatly reduced.

One method of utilizing the excess C_3's and C_4's is shown. Any excess C_3 and C_4 which it is not desired to return to the furnace through line **26**, or to vent from the system through valves **27** and **36**, can be passed through valves **34** and **35** and line **37** to small heater **38** where the gaseous mixture is heated to 1050° to 1100° F. to convert a substantial percentage of it into olefins. The heated gases are then introduced into the transfer line **41** of furnace **5** through either of the valves **39** or **40**, where they meet the cracked oil coming from furnace **5**. These olefinic gases react with the cracked oil either in the transfer line or in fractionator **8**, thereby increasing the yield of liquid product. This process makes possible the utilization of the ethane in the cracked gases, at the same time converting a large portion of the C_3's and C_4's into motor fuel without overloading the coil in furnace **5** with gaseous material.

The apparatus illustrated is, of course, purely exemplificative; and, saving for himself such modifications as will readily occur to those skilled in the art to which the application appertains, applicant claims:

1. The process of converting hydrocarbons into motor fuel which comprises absorbing gases predominantly ethane in the oil to be cracked under at least 300 pounds of pressure and cracking the resulting mixture at about 980° to 1100° F. under at least 200 pounds pressure, thereby producing a mixture of hydrocarbon products; separating the mixture into four fractions which consist of (1) a mixture of hydrogen and hydrocarbons having 1 to 4 carbon atoms per molecule, (2) hydrocarbons within the gasoline boiling range, (3) a recycle stock within the gas-oil boiling range, and (4) tar; returning (3) to the cracking zone; withdrawing (2); employing cooling and compression on (1) to liquefy some of the therein contained C_3 and C_4 hydrocarbons; heating said C_3 and C_4 hydrocarbons to high temperatures to convert them to olefins; introducing the highly heated olefins into the converted oil; at least partially separating a C_2–C_3 fraction from (1) by absorption in gas-oil; bleeding a gas predominantly hydrogen and methane from the process; and passing the C_2–C_3 gas-enriched gas-oil to the cracking zone.

2. The process of converting hydrocarbons into motor fuel which comprises absorbing gases predominantly ethane in the oil to be cracked under at least 300 pounds pressure, and cracking the resulting mixture at a temperature of 950° to 1100° F. under at least 200 pounds pressure, thereby producing a mixture of hydrocarbon products; separating the mixture into four fractions of which (1) consists of a mixture of hydrocarbons having 1 to 4 carbon atoms per molecule, (2) consists of hydrocarbons within the gasoline boiling range, (3) of a recycle stock within the gas oil boiling range, and (4) tar; returning (3) to the cracking zone; withdrawing (2) and (4); employing cooling and compression on (1) to produce a liquid predominantly C_3 and C_4, and feeding this liquid to a heating zone where it is converted partially into olefins, delivering said mixture to the converted oil; and substantially separating the rest of the hydrocarbons from methane and hydrogen by absorption of C_2 and C_3 hydrocarbons in the oil to be cracked, bleeding a gas predominantly hydrogen and methane from the process, and passing the C_2 and C_3 gas-enriched oil to the cracking zone.

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