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A. J. VAN PESKI

2,172,228

PROCESS FOR THE MANUFACTURE OF OLEFINS

Filed Oct. 12, 1936

3 Sheets-Sheet 1

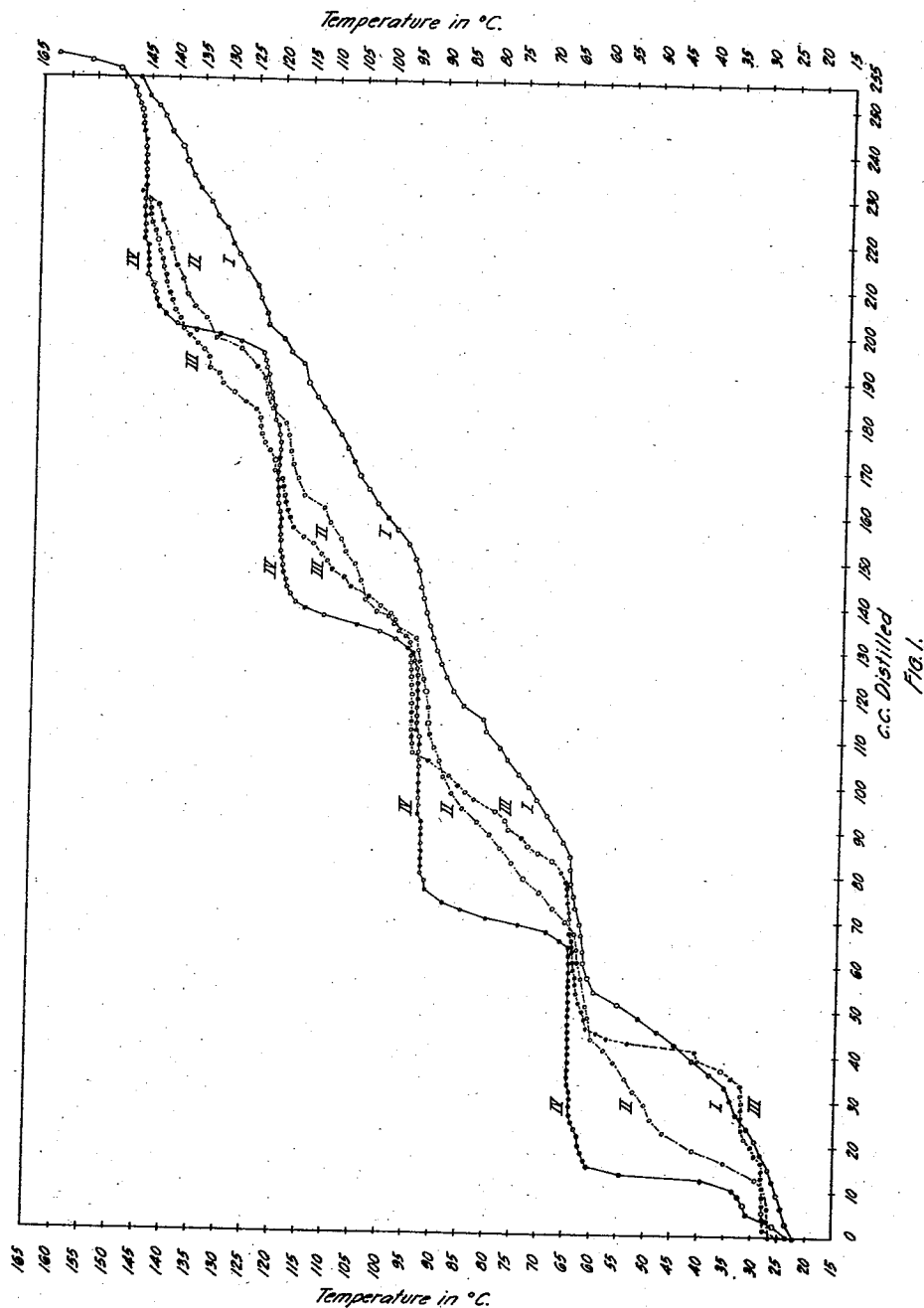


Fig. 1.

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3 Sheets-Sheet 2

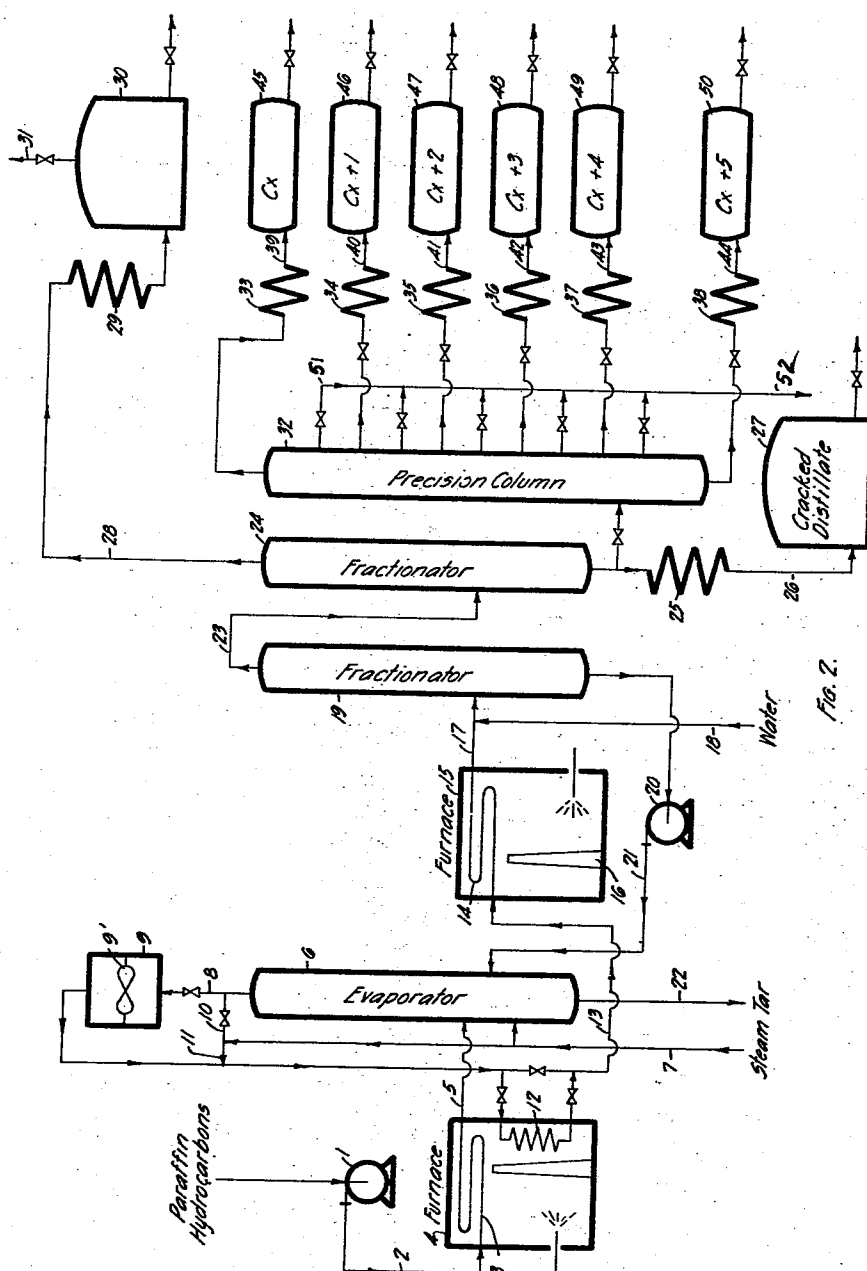


Fig. 2.

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Sept. 5, 1939.

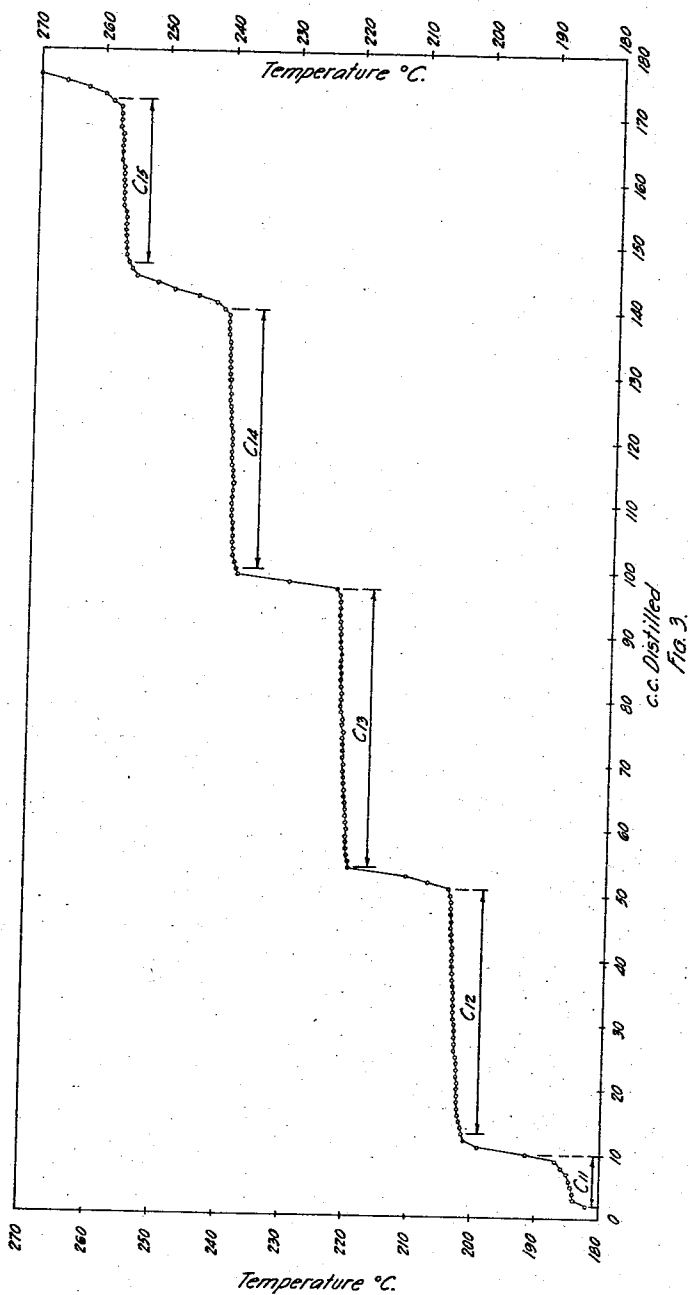
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3 Sheets-Sheet 3



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UNITED STATES PATENT OFFICE

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PROCESS FOR THE MANUFACTURE OF
OLEFINS

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Application October 12, 1936, Serial No. 105,269
In the Netherlands November 1, 1935

7 Claims. (Cl. 260—683)

This invention is a continuation-in-part of my application, Serial No. 724,883, filed May 10, 1934, and deals with a method for cracking paraffinic hydrocarbons under conditions to produce cracked oil which contains a high percentage of long chain olefins of the type which are suitable i. e. for the manufacture of high viscosity index lubricating oils by polymerization for the manufacture of high molecular alkali salts of monoalkyl sulfuric acid esters and for the manufacture of higher alcohols, ethers and the like.

In the parent application I have disclosed a method whereby substantially pure normal olefins of 5 and more carbon atoms can be obtained. Briefly, the method consists of cracking hydrocarbons such as normally solid paraffin wax, in the vapor phase, and then subjecting cracked distillates comprising 5 carbon and higher hydrocarbons, produced in this operation, to a very efficient fractional distillation. I have shown that the distillation curves of these distillations, obtained by plotting boiling points versus percent distilled, exhibit plateaus, each plateau indicating a fraction consisting essentially of a single olefin. Depending upon the concentration of the paraffin wax in the cracking stock, the plateaus are more or less pronounced, the sharpness in general increasing with increasing wax content. The influence of the wax content on the sharpness of the plateaus is demonstrated in the attached Fig. 1 in which four distillation curves I, II, III, IV, are shown of distillates obtained by vapor phase cracking hydrocarbon oils containing 1%, 13.5%, 24% and 100% paraffin wax, respectively. To enable the production of substantially pure olefins of 5 and more carbon atoms, the oil should contain at least 20% wax, as determined by the Holde method, which involves the use of anhydrous ethyl alcohol and ethyl ether at sub-zero temperatures to precipitate the wax.

It is the purpose of the present invention to provide cracking conditions under which from a given paraffinic cracking stock the largest amount of long straight chain olefins is produced, and the formation of cyclic and particularly aromatic hydrocarbons from non-cyclic hydrocarbons is substantially avoided. It is another purpose to provide a cracking process whereby a paraffinic distillate which contains no extraneously added wax, can be cracked to obtain optimum yields of high molecular olefins which, upon polymerization, produce lubricating oils of high viscosity index and are very valuable

for the manufacture of alkali salts of monoalkyl sulfuric acid esters.

Straight chain olefins boiling between about 160–300° C. produce upon polymerization the best lubricating oils, quality being judged chiefly by the viscosity index. Cyclic hydrocarbons capable of participating in the polymerization, especially aromatics and in particular polycyclic aromatics, if present even in small quantities, tend to lower the viscosity index of the resulting lubricating oil. Therefore, it is the aim to produce a maximum yield of a fraction boiling between about 160–300° C. which contains a maximum proportion of straight chain olefins and which is substantially free from, i. e. contains about 10% or less cyclic hydrocarbons.

I have found that good yields of the desired long chain olefins can be obtained not only from paraffin wax or oils rich in wax, i. e. containing 20% or more wax, but also from vaporizable paraffinic oils of the type of kerosene, gas, oil, wax distillate, lubricating distillate, having characterization factors as defined by Watson, et al. in Ind. & Eng. Chem. vol. 27 (1935) pages 1460–1464, of at least 12.0. Such oils consist predominantly of paraffinic and monocyclic hydrocarbons with long aliphatic side chains of 5 and more carbon atoms, and have a relatively low content of polycyclic hydrocarbons. The content of components capable of sulfonation with concentrated sulfuric acid should be preferably below about 20%. As a general rule the higher the characterization factor is, the better is the yield of the desirable olefins. Paraffin waxes have the highest characterization factors of any known hydrocarbons and consequently give best results as hereinbefore pointed out.

By solvent extracting paraffinic oils their characterization factors can usually be raised materially, and their contents of polycyclic components can be decreased. Still greater improvements can be obtained by selectively dehydrogenating the oils under conditions to convert naphthenes to aromatics and then solvent-extracting the dehydrogenated product to separate polycyclic aromatic hydrocarbons of low characterization factors from the more paraffinic hydrocarbons of higher characterization factors.

Cracking must be carried out in the vapor phase. Since liquid phase cracking results in a smaller yield of olefins less suitable for lubricating oil synthesis the vapors should be free from liquid entrainment to insure optimum yield and quality of the desired olefins. Absence of en-

trainment is also important to avoid coke deposition in the cracking zone.

All conditions tending to cause substantial pre-cracking must be avoided or at least minimized. Such conditions include sudden pre-heating of the cracking stock, for instance, by directly mixing it with the cracked vapors for the purpose of quenching the latter, or vaporizing it at temperatures at which substantial cracking may occur, or heating the vapors from the incipient cracking temperature to the optimum cracking temperature at a relatively slow rate. Thus the evaporation temperature should not exceed about 480° C., which usually necessitates the use of a distillation aid such as steam. The time required to heat the vapors from incipient cracking temperature to the maximum cracking temperature, should preferably not be longer than about 1/3 of the total cracking time or about 1 1/2 seconds when cracking within the preferred temperature range of 550-560° C. Pre-cracking appears to cause formation of branched chain olefins and cyclic compounds, both of which are undesirable in the manufacture of synthetic lubricating oils.

An average cracking temperature of between 500° and 600° C. and preferably between 550° and 560° C. must be maintained. The vapors should be held at a uniform cracking temperature for as long a portion of the total cracking time as possible. Deviations from the optimum temperature range cause a reduction in the yield of the desired 160-300° C. fraction, or a reduction of percent olefins contained therein, or both. Thus, when in a series of cracking tests, the temperatures were changed from 560° to 540° and 570° C. respectively, under otherwise optimum conditions, the yields of olefins on the basis of converted cracked stock were as follows:

Average cracking temperature, °C.....	560	540	570
Reaction time in seconds.....	3.4	6.8	3.2
Yield of olefins, volume percent of the corresponding fraction, boiling—			
Up to 300° C.....	39.7	37.1	35.3
Up to 160° C.....	17.4	15.3	15.9
Between 160-220° C.....	12.0	11.1	11.7
Between 220-300° C.....	10.3	10.7	7.7

Within a temperature range of 550-560° C. the cracking time should not exceed 6 seconds and is preferably limited to between 2.5 and 5 seconds as may be seen from the following typical data:

Reaction time in seconds.....	8.0	3.4	2.2
Average cracking temperature, °C.....	560	560	560
Yield of olefins, volume percent of the corresponding fraction, boiling—			
Up to 300° C.....	35.3	39.7	38.6
Up to 160° C.....	15.5	17.4	14.7
Between 160-220° C.....	11.4	12.0	10.5
Between 220-400° C.....	8.4	10.3	13.4

Cracking time as herein defined is computed by the approximate formula:

$$\text{Time} = \left[\frac{A}{\text{Mol. wt. of cracking stock}} + \frac{B}{\text{mol. wt. of diluent gas}} \right] \times 22.4 \times \frac{T}{273}$$

in which V=volume of cracking space in liters,
A=throughput of cracking stock in grams per second,
B=throughput of diluent gas in grams per second,
T=average cracking temperature in ° C.

Diluent gas in the above formula refers to an inert gas such as steam, carbon dioxide, nitrogen, hydrogen. It has been found that to obtain optimum conversion of the hydrocarbon vapors, it is desirable to dilute these vapors with a sufficient amount of an inert gas so that the partial pressure of the hydrocarbon vapor in

the mixture is not more than about 60% and preferably between 30 and 50% of the total pressure in the cracking zone.

Since normally a distillation aid is required in the vaporization of the hydrocarbon oil to avoid pre-cracking, as hereinbefore explained, there will usually be enough of inert diluent present, and in general, one must guard against an excess rather than a lack of diluent. While an excess of diluent gas, if very great, may adversely affect the olefin yields, its main disadvantage lies in that it seriously reduces the charging capacity of the cracking unit.

The total pressure in the cracking zone may be varied between about 1 and 5 atmospheres, higher pressures tending to increase the yield of the 160-300° C. fraction, but also tending to reduce the amount of olefins contained therein.

At the end of the cracking period the cracked vapors must be abruptly cooled, preferably by quenching with water, although other quenching media, such as normally gaseous liquefied hydrocarbons, may also be used. The use of cracked distillates or fresh feed oil for quenching should be avoided for reasons already mentioned. In the quenching operation, the temperature of the cracked vapors should be lowered to a temperature of about 480° C. or lower, at which temperature olefins are sufficiently stable to resist material isomerization or cyclization over short periods of time.

An uncracked portion of hydrocarbons contained in the quenching mixture may be recirculated through the cracking zone without danger of impairing the quality of the olefins, provided the tarry material formed during cracking is carefully separated therefrom by fractional distillation.

The means by which to accomplish the aforementioned conditions may vary. In Fig. 2, an illustrative flow diagram of a cracking process is shown, which meets the various requirements. Referring to Fig. 2, paraffin hydrocarbons from a source not shown are forced by pump 1 in line 2 through heating coil 3 in furnace 4, in which they are heated to a vaporizing temperature below about 480° C. Heating should be relatively gentle to avoid local overheating, a high velocity through coil 3 therefore being desirable. The heated oil is then transferred through transfer line 5 into an evaporator 6, where at least a portion of the oil is vaporized. Live steam, which is preferably superheated, or any other heated inert distillation aid such as carbon dioxide, nitrogen, hydrogen, etc. is introduced through line 7 into the evaporator 6 to aid in the vaporization of the

oil. The resulting vapors, which normally contain entrainment, are now treated to eliminate such entrainment. For instance, the vapors may pass through line 8 into an apparatus 9 known as a "centrifix", which consists of a vertical cylindrical vessel containing stationary blades 9' which impart to the passing vapors a whirling motion, in consequence of which the entrained liquid is thrown against the wall of the vessel and returns to the evaporator 6; or the vapors may pass through an expansion valve 10 in line 11 to effect vaporization of entrainment, and steam may be injected into line 11 on the low pressure side of valve 10, if desired; or the wet vapors may pass

through drying coil 12 located in furnace 4, where they may be heated to approximately incipient cracking temperature, if desired.

The thoroughly dried vapors proceed through line 13 to cracking coil 14 in furnace 15. The first portion of the coil is located in the hottest part of the furnace in the vicinity of the bridge wall 16. A high vapor velocity is maintained through that portion of the coil to obtain an optimum heat transfer, and the vapors are spontaneously heated to the required cracking temperature of about 560° C. Vapors and flue gases may flow concurrently to achieve greatest rate of heat transfer. In the last portion of the coil, the vapors are held at this temperature for the necessary time to effect cracking.

The cracking vapors enter transfer line 17 in which they are quenched to below about 480° C. A suitable quenching medium, such as water, normally gaseous liquefied hydrocarbons, etc. is introduced into line 17 through line 18. The quenched mixture containing cracked distillate, gas, unconverted paraffinic hydrocarbons, tar, distillation aid and quenching medium, enters fractionator 19 in which tar and unconverted paraffinic hydrocarbons are separated as liquids. These liquids are conveyed by pump 20 in line 21 to evaporator 6, where paraffinic hydrocarbons are re-evaporated and tar is allowed to escape through bottom drain 22. The vaporized portion of the charge is transferred from fractionator 19 through transfer line 23 to fractionator 24, where it is further fractionated into a heavier distillate fraction which may be run through cooler 25 in line 26 to rundown tank 27, while a light fraction passes through vapor line 28, condenser 29 into receiving tank 30, where liquid hydrocarbons are separated from gas. Gas goes through line 31 to a gas plant not shown.

The bottom stream of fractionator 24 instead of going to storage in tank 27 may be further fractionated in a precision column 32, provided with sidestrippers, not shown, in accordance with the invention described in the aforementioned parent application Serial No. 724,883. Several fractions, having substantially constant boiling points, i. e. at least 80% of such fractions boiling over a temperature range of less than about 3° C., may be taken from column 32 and be passed through condensers 33—38 in lines 39—44 into tanks 45—50, respectively. This bottom stream may consist entirely of such substantially boiling fractions, or may contain small intermediate fractions boiling between the larger constant boiling fractions. These intermediate fractions may be withdrawn if desired through manifold 51 and be discarded through line 52.

In a specific example, paraffin wax having a melting point of 54° C. and an average molecular weight of 390, was heated in coil 3 to 470° C. and evaporated in evaporator 6 at a pressure of 4.8 atmospheres. 10.1% by weight of steam was introduced into the evaporator through line 7 at a temperature of 445° C. The vapors in which the partial pressure of the hydrocarbon was about $\frac{1}{3}$ of the total pressure, were passed at a pressure of 2.9 atmospheres through separator 9 to remove entrained liquids.

The dry vapors then were conducted through cracking coil 14 in which they were rapidly heated and cracked at an average temperature of 545° C. for 2.9 seconds at an average pressure of 2.7 atmospheres. The time required to heat the dry vapors to the desired cracking temperature was about $\frac{1}{4}$ of the total cracking time. The cracked

vapors leaving the cracking furnace were quenched with water to a temperature of about 400° C. The quenched product was fractionated in column 19 into a light fraction boiling up to 300° C. and a heavier fraction, the heavier fraction returning to evaporator 6. From the light fraction a distillate boiling up to 300° C. was prepared, which constituted 60% by weight of the converted charge. This distillate had a specific gravity at 15° C. of .771 (52° A. P. I. gravity), a McIlhiney bromine number of 93.5 and the following A. S. T. M. distillation:

Initial boiling point.....	62° C.	
10%.....	104	18
20%.....	135	
30%.....	165	
40%.....	191	
50%.....	221	
60%.....	243	
70%.....	260	20
80%.....	275	
90%.....	291	
95.5.....	300	
Residue.....	2.5	
Loss.....	2.0	

A fraction amounting to 70% of the above distillate had a boiling range from 160° to 300° C. This fraction contained 80% by volume of olefins, of which 23% consisted of C₁₀—C₁₂ olefins, 56% of C₁₃—C₁₈ olefins and 21% of C₁₉ and higher olefins. When polymerizing the 160° to 300° C. fraction with AlCl₃, a lubricating oil of a viscosity index of above 120 was obtained.

200 milliliters of a close cut fraction boiling from 200—300° C. from the above distillate was subjected to an analytical distillation in a precision column, and the distillation curve shown as Fig. 3 exhibiting the typical plateaus, was thereby obtained.

According to this analysis in which 176 milliliters out of the 200 were actually distilled, the fraction was composed as follows:

	Normal olefines	Other hydrocarbons	
	Percent	Percent	
Below undecylene.....		1	45
Undecylene.....	3		
Undecylene to dodecylene.....		2½	
Dodecylene.....	19		
Dodecylene to tridecylene.....		1¼	50
Tridecylene.....	22½		
Tridecylene to tetradecylene.....		1¼	
Tetradecylene.....	20		
Tetradecylene to pentadecylene.....		3	
Pentadecylene.....	12		
Above pentadecylene.....		14	
Total.....	76½	23¼	55

On the basis of the actually distilled fraction, the above total percentages are:

	Per cent	
Normal olefines.....	87	60
Other hydrocarbons.....	13	

In another cracking test, a Borneo paraffin distillate having a characterization factor of 12.1 was cracked under the optimum conditions herebefore described. A cracked fraction boiling up to 200° C. contained about 10% aromatics was refined and polymerized and yielded a lubricating oil having a viscosity index of 104. Variations from the optimum conditions, such as cracking at higher temperatures or for longer periods of time, were immediately reflected in a loss of yield of the desired olefins or increase in the aromatic content of the cracked distillate

or both. Thus, for instance, when cracking the same stock at 600° C. instead of 560° C. the content of aromatics in the distillate rose to above 16%, and the viscosity index of the lubricating oil produced by polymerization of the refined distillate dropped to 88.

On the other hand, when a mixture of 60% paraffin wax and 40% of a highly aromatic gas oil was cracked under optimum conditions and a gasoline so obtained was polymerized, the resulting lubricating oil had a viscosity index of only 20.

The long chain olefins which are produced when subjecting a paraffin oil of a low content of cyclic hydrocarbons, or mixtures of such paraffin oil with paraffin wax, to my cracking process, are useful not only for the manufacture of high viscosity index lubricating oils, but also for the production of washing, wetting and emulsifying agents. These agents may be prepared by treating selected olefins, for instance those of 13-18 carbon atoms, with sulfuric acid under conditions to produce mono-alkyl sulfuric acid esters, the alkali salts of which are known to be excellent hard water detergents. The long chain olefins may also be used for the preparation of other high molecular compounds, such as higher alcohols, ethers and the like.

I claim as my invention:

1. A process for producing olefins from solid paraffins and highly paraffinic distillates predominating in crystallizable paraffins, which comprises vaporizing the paraffinic material without substantial cracking thereof, subjecting the vapors, by indirect application of heat thereto and in the presence of steam, to a temperature within the approximate range of 540° C. to 570° C. for a time period of from three to six seconds and under a pressure below 75 pounds per square inch, then promptly quenching the heated vapors to prevent continued conversion thereof, and fractionating and condensing the vapors.

2. A process for producing olefins from a paraffinic hydrocarbon mixture having a boiling range not below that of kerosene and a characterization factor of at least 12.0, which comprises vaporizing the paraffinic mixture without substantial cracking thereof, subjecting the vapors by indirect application of heat thereto and in the presence of steam, to a temperature within the approximate range of 540° C. to 570° C. for a time period of from 2.5 to 6 seconds and under a pressure not above 5 atmospheres, then promptly quenching the heated vapors to prevent continued conversion thereof, and fractionating and condensing the vapors.

3. A process for producing olefins from a paraffinic hydrocarbon mixture having a boiling range not below that of kerosene and a characterization factor of at least 12.0, which comprises vaporizing the paraffinic mixture without substantial cracking thereof, removing entrained liquid from the resulting vapors, rapidly heating by indirect application of heat the dry vapors in the presence of steam to a temperature within the approximate range of 540° C. to 570° C. for a time

period of 2.5 to 6 seconds and under a pressure not above 5 atmospheres, then promptly quenching the heated vapors to prevent continued conversion thereof, and fractionating and condensing the vapors.

4. The process of claim 3 in which the partial pressure of the hydrocarbons in the vapor mixture is between 30% and 60% of the total pressure.

5. A process for producing olefins from a paraffinic hydrocarbon mixture having a boiling range not below that of kerosene and a characterization factor of at least 12.0, which comprises vaporizing the paraffinic mixture without substantial cracking thereof, subjecting the vapors by indirect application of heat thereto in the presence of steam and under a pressure of not above 5 atmospheres, to an effective cracking temperature within the approximate range of 540° C. to 570° C. for a time period of from 2.5 to 6 seconds, the time of heating from incipient to the effective cracking temperature being not more than one-third of the total cracking time, then promptly quenching the heated vapors to prevent continued conversion thereof, and fractionating and condensing the vapors.

6. A process for producing olefins, suitable for the production of synthetic high viscosity index lubricating oils by polymerization, from a paraffinic hydrocarbon mixture having a boiling range not below that of kerosene and a characterization factor of at least 12.0, which comprises vaporizing the paraffinic mixture without substantial cracking thereof, subjecting the vapors by indirect application of heat thereto and in the presence of steam to a temperature within the approximate range of 540° C. to 570° C. for a time period of from 2.5 to 6 seconds and under a pressure not above 5 atmospheres, then promptly quenching the heated vapors to a temperature below 480° C. to prevent continued conversion thereof, fractionating and condensing the vapors to produce a distillate comprising a fraction boiling between 160° to 300° C.

7. A process for producing olefins from a paraffinic hydrocarbon mixture having a boiling range not below that of kerosene and a characterization factor of at least 12.0, which comprises heating and vaporizing the paraffinic mixture without substantial cracking thereof in a vaporization zone and with the aid of steam, removing entrained liquid from the vapor mixture, rapidly heating in a separate heating zone by indirect application of heat the dry vapor mixture to an effective cracking temperature within the approximate range of 540° to 570° C., the total cracking time being from 2.5 to 6 seconds and the time of heating from incipient to effective cracking temperature being not more than one-third of the total cracking time, under a pressure not more than 5 atmospheres, then promptly quenching the heated vapors to prevent continued conversion thereof, and fractionating and condensing the vapors.

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