

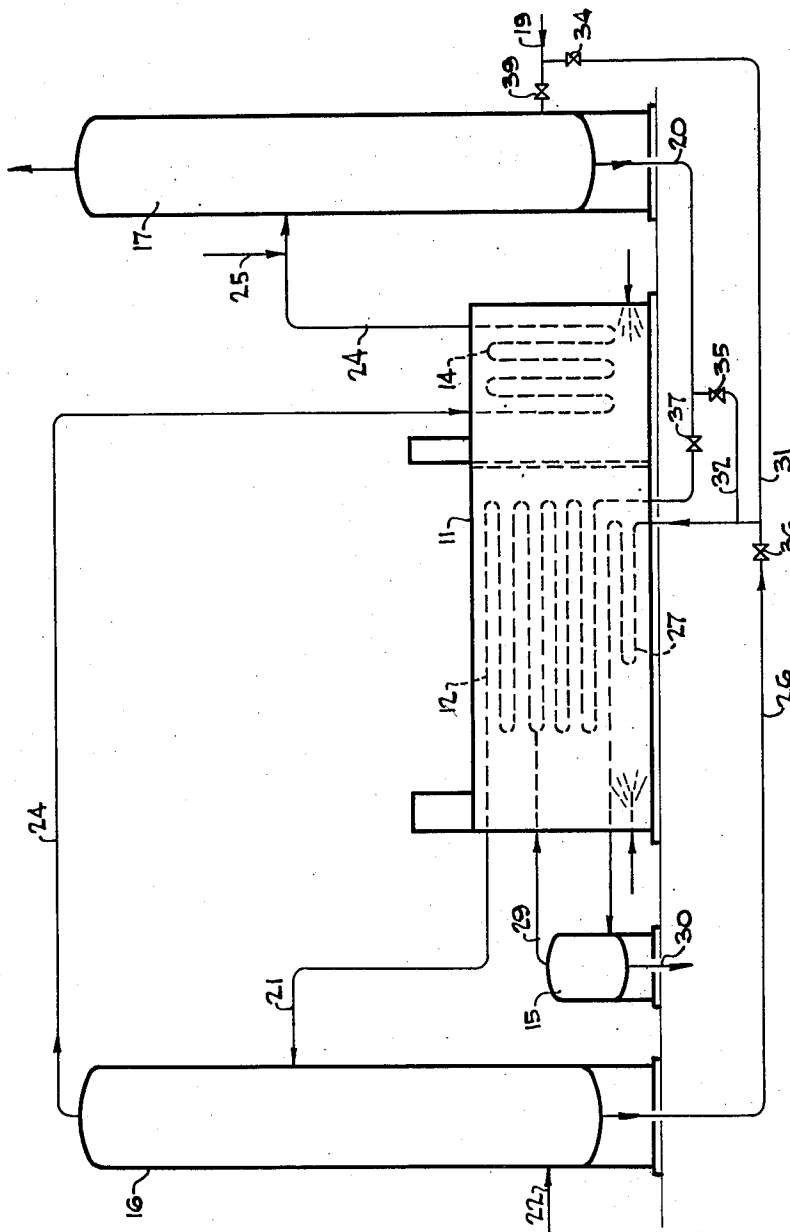
June 16, 1953

P. J. GARNER ET AL

2,642,466

PRODUCTION OF OLEFINIC HYDROCARBONS

Filed June 9, 1950



INVENTORS:

PHILIP JAMES GARNER

SIDNEY EDGAR MILES

BY

John H. Colvin
THEIR AGENT

UNITED STATES PATENT OFFICE

2,642,466

PRODUCTION OF OLEFINIC
HYDROCARBONS

Philip James Garner, Hooton, Wirral, and Sidney
Edgar Miles, Mold, England, assignors to Shell
Development Company, San Francisco, Calif., a
corporation of Delaware

Application June 9, 1950, Serial No. 167,052
In Great Britain July 28, 1949

4 Claims. (Cl. 260—683)

1

This invention relates to a process for the production of olefinic hydrocarbons, and more particularly to a process for the thermal cracking of high molecular weight paraffinic hydrocarbons, such as paraffin wax, to yield mixtures of olefinic hydrocarbons including various long-chain olefines, as for instance those containing fifteen or more carbon atoms per molecule.

The thermal cracking of paraffinic hydrocarbon waxes and waxy materials has been known and practiced for some time, in accordance with the teachings of the Van Peski U. S. Patent No. 2,172,228. The range of unsaturated aliphatic hydrocarbons produced thereby individually or in admixture finds application in the synthesis of a variety of useful commercial products. Waxes of various types have been the subject of such cracking conversions, the paraffin wax-containing materials being particularly valuable as cracking stock. Such materials may, for instance, include waxy material recoverable from a mineral oil distillate or residue by chilling and pressing or by known solvent extraction processes, such as solvent dewaxing of paraffinic waxy mineral oils and fractions thereof. As cracking stock, purified products are not essential, and valuable hydrocarbons can for instance be obtained from a slack wax derived by solvent extraction of a waxy mineral lubricating oil.

In the treatment of a paraffin wax-containing mineral, as for instance slack wax, to obtain olefinic hydrocarbons having at least five carbon atoms in the molecule, vapor phase cracking is effective, and to this end the material is subjected to preliminary vaporization in a flash evaporator unit at a suitable temperature which generally is just below 500° C. Thereafter cracking is effected in the vapor phase at between 500° C. and 600° C. under moderately elevated pressures up to about 60 pounds per square inch to yield the desired olefinic materials.

It is frequently found, however, that only a fraction of the initial material undergoes evaporation in the flash evaporator unit, and is much as 20 to 50% of the material may remain as a residue, herein referred to as "evaporator residue." From the standpoint of the efficiency of the cracking operation such an evaporator residue is a marked disadvantage, and the more so because such evaporator residue is not itself a product of much commercial value. Accordingly any steps which minimize the amount of evaporator residue and increase the volume of hydrocarbons passing to the cracking furnaces,

2

thereby enhancing the yield of olefinic hydrocarbons, constitute a most desirable technical advance in this particular field.

It is, therefore, a principal object of the present invention to improve the overall efficiency of thermal cracking operations for the conversion of higher molecular weight hydrocarbons to olefinic material. A more specific object is to provide a process adapted to effect a more complete conversion of waxy hydrocarbons and waxy hydrocarbon fractions to olefinic hydrocarbons suitable for the synthesis of valuable commercial products. A still more specific object is to provide an improved process for the more complete conversion of waxy hydrocarbon materials to olefinic hydrocarbons which are largely of an alpha-olefinic character.

The foregoing and other objects and the manner of their accomplishment will be more fully understood from the following description of the invention, which will be made with reference to the accompanying drawing, constituting a part of the specification, which drawing comprises a single figure representing schematically the method and apparatus for carrying out the thermal cracking of waxy hydrocarbon materials in accordance with the invention.

It has now been found that an increased yield of olefinic hydrocarbons is obtained by the thermal phase cracking of waxy hydrocarbon materials in accordance with prior practice, when the evaporator residue, resulting from the usual evaporation of the waxy stock immediately preceding the thermal vapor phase cracking, is subjected in the liquid phase to a temperature between about 390° C. and 450° C. for a period of time varying from about four hours to one quarter of an hour—which thermal treatment is hereinafter generally referred to as "soaking" or "thermal soaking" of the product—thus so modifying the nature of the residue that on further flash evaporation thereof further amounts of material are vaporized and may be effectively subjected to vapor phase thermal cracking to produce olefinic hydrocarbons, and the residue finally remaining is substantially reduced, say to an amount which is between one-twentieth and one-tenth of the amount of the original feed-stock.

Since the essential feature of the present invention is the thermal soaking of that waxy material which is not normally volatile when flashed in the evaporator up to 500° C., such thermal soaking may be applied either to the initial wax

3

feedstock, to a combination of fresh feedstock and recycle feedstock (that is to say, volatile uncracked or partially cracked hydrocarbon material which has been condensed in a fractionator and separated from the desired cracked olefinic hydrocarbons), or to the evaporator residue. However, since the evaporator residue is of smaller bulk than the other materials, it is preferred to subject only this material to the said soaking treatment since smaller capacity equipment is thus needed. Furthermore, it has been found that products yielding a higher proportion of valuable olefinic hydrocarbons on cracking are obtained by soaking the evaporator residue without admixture of fresh wax feed or fresh wax feed combined with recycle feedstock.

According to the present invention therefore the vapor phase thermal cracking of waxy material, preferably paraffin wax-containing material, at a temperature in the region of 500° C. to 600° C. includes the step of subjecting at least that part of the feedstock which is not initially vaporizable when flashed with or without steam at temperatures just below 500° C. to a thermal soaking, namely a heat treatment at between 390° C. and 450° C. for a period of 4 hours to ¼ of an hour.

In accordance with a preferred embodiment, the invention comprises in a vapor phase thermal cracking of a hydrocarbon slack wax at a temperature intermediate of 500° C. and 600° C., the step of subjecting at least that part of the feedstock which cannot be readily initially vaporized in a flash evaporator at 480° C. to 500° C., to a thermal soaking, namely a heat treatment at a temperature of from about 400° C. to 440° C., and preferably between 405° C. and 425° C., for a period of time of from about 2 hours to 1 hour, the longer period of soaking being applied at the lower temperature.

In the preferred method of practicing the present invention the vapor phase cracking of the hydrocarbons is effected in the presence of superheated steam which may be, and preferably is, present in the flash evaporator and the flash evaporator residue is subjected without admixture with initial feedstock material or recycle feedstock to the foregoing specified thermal soaking treatment after which it is subjected to vaporizing treatment in the flash evaporator with further amounts of fresh feedstock and/or recycle feedstock.

The invention will now be further illustrated by reference to the accompanying diagrammatic drawing which shows a plant for cracking slack wax in accordance with the novel process. The plant represented in the drawing comprises a furnace 11 with a preheating coil 12 and a cracking coil 14, a soaking tank 15, flash evaporator 16 and a fractionator 17.

Fresh feed of slack wax comprising Colon (Venezuela) residual slack wax at a temperature of about 100° C. is introduced through the pipe 19 at the bottom of the fractionator 17 wherein it mixes with hot recycle feedstock, and the mixture at 340° C. to 360° C. into which steam may be injected flows through pipe 20 to the preheating coil 12 in the furnace 11, where its temperature is raised to about 480° C. to 500° C. Thence it is passed by a pipe 21 to the flash evaporator 16 where it mixes with preheated steam initially at a temperature of about 440° C. and a pressure of 60 to 90 pounds per square inch (gauge) intro-

4

duced into evaporator 16 through the pipe 22. The mixture of the resulting vaporized hydrocarbons and steam then passes through the pipe 24 to the vapor phase cracking coil 14 in the furnace 11 where the temperature is about 540° C. to 560° C. and where cracking takes place in about 15 to 25 seconds. The mixture from the cracking coil 14 passes via the pipe 24 to a fractionator 17 and receives an admixture of quenching water from the pipe 25 to assist condensation. A mixture of olefinic hydrocarbons is withdrawn from the top of the fractionator 17 and condensed hydrocarbons (re-cycle feedstock) are recycled with fresh feed admitted via pipe 19. The plant pressure is maintained at from about 10 to about 25 pounds per square inch gauge.

The evaporator residue which accumulates in the base of the evaporator 16, is passed via a pipe 26 through a coil 27 in the furnace 11 to the soaking tank 15. The volume of this tank 15 and the conditions in coil 27 are so related to the throughput rate of the plant that the required soaking conditions are established in this tank, for example 2 hours residence at 410° C. The soaked residue leaves the tank 15 through the pipe 28 and joins the stream of material in the coil 12.

A pipe 30 leading from the base of the soaking tank 15 is used to bleed off continuously a quantity of evaporator residue equivalent to from about 5% to about 10% of the fresh feed. The exact quantity thus bled off is adjusted to be the minimum consistent with the prevention of coking and may generally be regarded as waste; in some cases, however, it is convenient to subject it to a soaking treatment in a location other than that of the continuous process described above. Bled-off residue soaked in this way is preferably accumulated in a storage vessel until a convenient quantity has been obtained for soaking treatment; this soaking is thus carried out as a discontinuous or batch treatment.

Valved lines 31 and 32, provided with valves 34 and 35, respectively, and valves 36, 37 and 39, in lines 26, 20 and 19, respectively, make it possible to pass either fresh feed from the line 19 or a recycle feed from the line 20, or mixtures of these two, as well as evaporator residue, to the soaking tank 15, by means of valve manipulations which are evident from the drawing.

Since the placement of required pumps, temperature recorders and controls, other valves, level controls and the like will be evident to one skilled in the art, various auxiliary equipment has been omitted from the drawing.

It will be readily understood that the process described above may be modified by allowing the evaporator residue to accumulate either in the evaporator or in a suitable storage vessel and then to carry out the soaking as a separate operation distinct from the main cycle of operations, for example in a separate apparatus.

The advantage derived from the thermal soaking step of the present invention is illustrated by the comparative results obtained in the vapor phase thermal cracking of vaporizable material obtainable from soaked and unsoaked evaporator residues produced in a plant cracking operation using a waxy feed stock comprising a Colon short residue slack wax. From the pertinent data, which are given in Table I, it can be seen that the soaking of the evaporator residue reduced substantially the final residue which had to be discarded as waste.

TABLE I

Effect of thermal soaking on vaporization of evaporator residue

Run No.	1	2	3	4
Feed	Colon Evaporator Residue			
	Unsoaked		Soaked	
Evaporator level, cm.	8	25	25	8
Vaporizer temperature, °C.	490	476	488	482
Evaporator bottom temp., °C.	424	425	425	423
Unit pressure, p. s. i. g.	20	20	20	20
Steam/hydrocarbon ratio w./w.	1.0:0.20	1.0:21	1.0:23	1.0:22
Residue as percent on feed	75	57	36	45

¹ Temperature of liquid in evaporator.

The conditions of soaking the evaporator residue referred to just before and the results are shown in Table II.

TABLE II

Soaking colon slack wax evaporator residue

Temperature of soaking chamber, °C.	425
Residence time in soaking chamber, minutes	45
Gas evolved, percent wt. on feed	2.6
Distillate evolved, percent wt. on feed	2.2
Mol. wt. of soaked material	1600
Mol. wt. of feed	1725

¹ Mol. wt. calculated from refractive index and melting point.

The soaked residue had the appearance of heavy fuel oil, but it still had a definite set period. An increase of 30% in the residence time produced a material which was still liquid at room temperature.

When the steam/hydrocarbon vapor products of runs 1 and 4 (Table I) and equivalent steam/hydrocarbon vapor product produced from fresh Colon slack wax feed were thermally cracked separately and under similar conditions to produce olefinic hydrocarbons, and the respective cracked products were quenched and fractionated, and the C₉—C₁₈ cracked distillate fraction was separated therefrom, the results were as given in Table III. Data are also included for similar runs using soaked and unsoaked Concepcion evaporator residues.

TABLE III

Thermal cracking using evaporator residues as feed

Feed	C ₉ —C ₁₈ cracked distillate		alpha-olefin content ratio ¹
	Percent (on feed)	Br No.	
Fresh Colon feed	30.8	85	100
Colon evap. residue	11.2	64	57
Soaked Colon evaporator residue	35.2	63	61
Concepcion evap. residue	10.2	70	63
Soaked Concepcion evap. residue	15.6	66	—

¹ Ratio = $\frac{\text{alpha-olefin content of c. d. of run}}{\text{alpha-olefin content of c. d. fresh Colon wax run}}$

The material increase in the C₉—C₁₈ cracked distillate product from the soaked evaporator residues, while maintaining comparable bromine numbers and alpha-olefin contents as compared with the unsoaked evaporator residues is apparent from the tabulated data in Table III. At the same time the alpha-olefin content is as much

as about 60% of what it is for the fresh waxy feed.

According to a further modification of the process of this invention there is introduced into the soaking tank selected hydrocarbon fractions with the object of establishing therein equilibrium conditions which tend to produce larger amounts of products subsequently vaporizable for the desired cracking operation. Thus hydrocarbon fractions of gasoline boiling range may be introduced to increase the yields of waxy products suitable for vapor phase cracking from the material undergoing soaking. Since this modified technique involves maintaining sufficient pressure in the soaking tank to keep the more volatile hydrocarbon gasoline boiling range fraction liquid, it is generally more conveniently carried out with batchwise soaking.

The additional cracked unsaturated hydrocarbons which can be made available by subjecting the initial feedstock or evaporator residue to a thermal soaking as specified above with the subsequent application of vapor phase cracking conditions to the material so treated constitute a range of products of very considerable value and interest in a diversity of syntheses of interest both in the chemical and petroleum fields. The nature of these additional unsaturated products may perhaps differ a little from those obtained by the vapor-phase cracking of the untreated initial waxy feedstock but the differences, if any, do not detract from their value as raw materials for various commercial manufactures.

Although the improvement upon which the present invention is predicated may be applied in general to any evaporator residues resulting from the vaporization of waxy hydrocarbon materials to produce hydrocarbon vapors suitable for vapor phase thermal cracking to olefinic hydrocarbons, the usual distillate waxes are generally substantially completely vaporizable under the indicated evaporator conditions. However, even then the more difficultly vaporizable residual material resulting from the vapor phase cracking of the vaporized distillate waxes may be advantageously subjected to the soaking treatment in accordance with the invention. The invention is particularly applicable to hydrocarbon stocks containing those higher boiling, higher molecular weight, paraffinic hydrocarbons such as the iso- or branched-chain paraffin hydrocarbons which are not sufficiently branched in character to constitute material suitable for lubricating oil manufacture. Such isomeric paraffin hydrocarbons are characteristic components of petroleum residual slack waxes.

The invention claimed is:

1. In the process for producing olefinic hydrocarbons by vapor phase thermal cracking of waxy hydrocarbons wherein a paraffin wax-containing material is vaporized substantially at a temperature below about 500° C. and without substantial cracking thereof and thereby is separated from a difficultly vaporizable fraction and the vaporized portion is subjected to thermal cracking in the presence of steam at a temperature in the range of from about 500° C. to about 600° C., the improvement which comprises the steps of subjecting at least a substantial portion of the separated difficultly vaporizable fraction to a thermal soaking at from about 390° C. to about 450° C. for a period of time of from about 1/4 of an hour to about 4 hours, thereafter subjecting it to the aforesaid vaporizing operation, and subjecting the

resulting vaporized portion to the aforesaid vapor phase thermal cracking operation.

2. In the process for producing olefinic hydrocarbons by vapor phase thermal cracking of waxy hydrocarbons wherein a paraffin wax-containing material is vaporized substantially at a temperature below about 500° C. and without substantial cracking thereof and thereby is separated from a difficultly vaporizable fraction and the vaporized portion is subjected to thermal cracking in the presence of steam at a temperature in the range of from about 500° C. to about 600° C., the improvement which comprises the steps of subjecting at least a substantial portion of the separated difficultly vaporizable fraction to a thermal soaking at from about 400° C. to about 440° C. for a period of time of from about 1 to about 2 hours, after which the soaked material is subjected to the aforesaid vaporizing operation and the resulting vaporized portion is subjected to the aforesaid vapor phase thermal cracking operation.

3. A process for producing olefinic hydrocarbons from paraffin wax-containing material which comprises heating a petroleum residual slack wax to a temperature of from about 480° C. to about 500° C. and separating the heated material at that temperature and without substantial cracking thereof into a vapor fraction and a difficultly vaporizable residue fraction, subjecting the separated vapor fraction in the presence of steam to thermal cracking within the range of from about 540° C. to about 560° C. for a period of time sufficient to effectively convert the vaporous hydrocarbons into olefinic hydrocarbons without substantial formation of coke therefrom, promptly quenching the cracked product vapors and fractionating and condensing the vapors, subjecting the separated difficultly vaporizable residue fraction from the initial vaporization to a thermal soaking at from about 390° C. to about 450° C. for a period of time of from about ¼ of an hour to about 4 hours, and combining the soaked residue with heated fresh feed material after which it is subjected to the aforesaid vaporizing operation and the resulting vaporized por-

tion is subjected to the aforesaid vapor phase thermal cracking operation to produce an additional quantity of olefinic hydrocarbons from the initially difficultly vaporizable residue fraction.

4. A process for producing alpha-olefinic hydrocarbons from a mixture consisting essentially of high molecular weight paraffinic hydrocarbons, including normal paraffin wax hydrocarbons and branched-chain paraffin hydrocarbons, which process comprises heating said mixture to a temperature of from about 480° C. to about 500° C. and separating the heated material at that temperature into a vapor fraction and a difficultly vaporizable residue fraction, the residue fraction comprising a substantial proportion of high molecular weight branched-chain paraffin hydrocarbons, subjecting the separated vapor fraction in the presence of steam to thermal cracking within the range of from about 540° C. to about 560° C. to effectively convert the vaporous hydrocarbons into alpha-olefinic hydrocarbons, promptly quenching the cracked product vapors and fractionating and condensing the vapors, subjecting the separated difficultly vaporizable residue fraction from the initial vaporization to a thermal soaking at from about 390° C. to about 450° C. for a period of time of from about ¼ of an hour to about 4 hours, and combining the soaked residue with fresh feed mixture after which it is subjected to the aforesaid vaporizing operation and the resulting vaporized portion is subjected to the aforesaid vapor phase cracking operation to produce an additional quantity of olefinic hydrocarbons from the initial difficultly vaporizable residue fraction.

PHILIP JAMES GARNER.
SIDNEY EDGAR MILES.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,008,550	Halloran et al. -----	July 16, 1935
2,172,228	Van Peski -----	Sept. 5, 1939
2,374,338	Dunham -----	Apr. 24, 1945
2,532,615	Ewell -----	Dec. 5, 1950