

July 12, 1960

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2,945,076

PROCESS FOR PRODUCING OLEFINS

Filed April 15, 1957

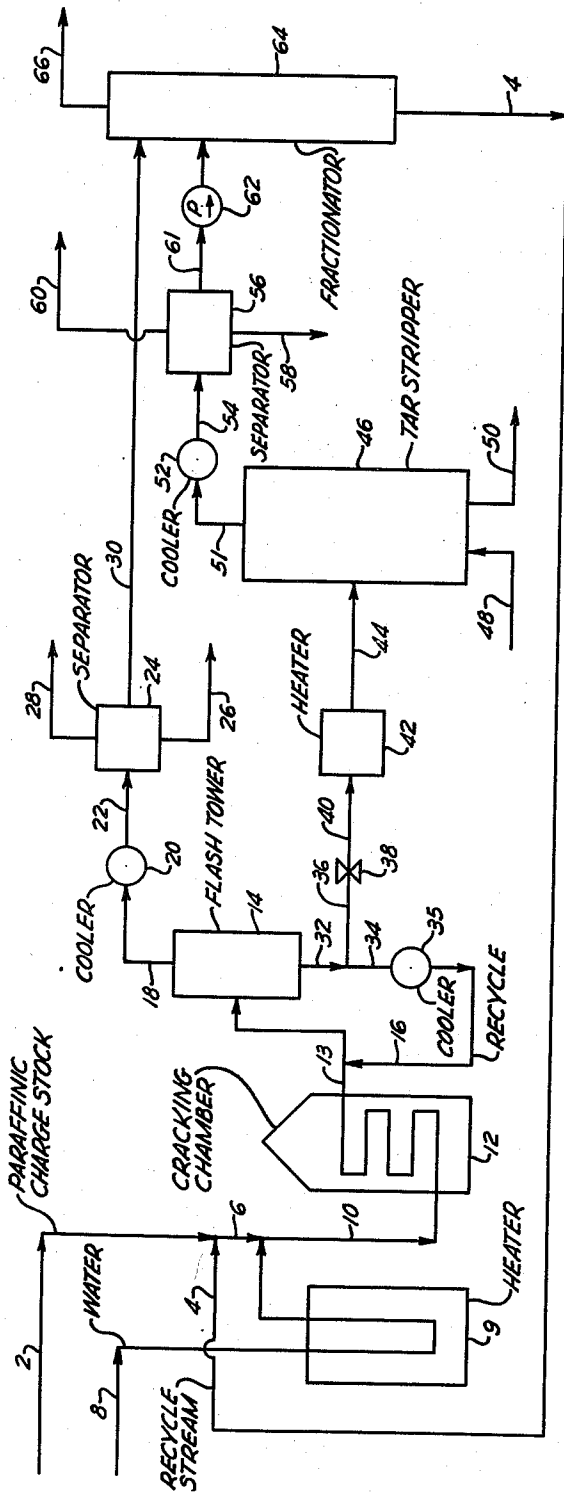


Fig. 1

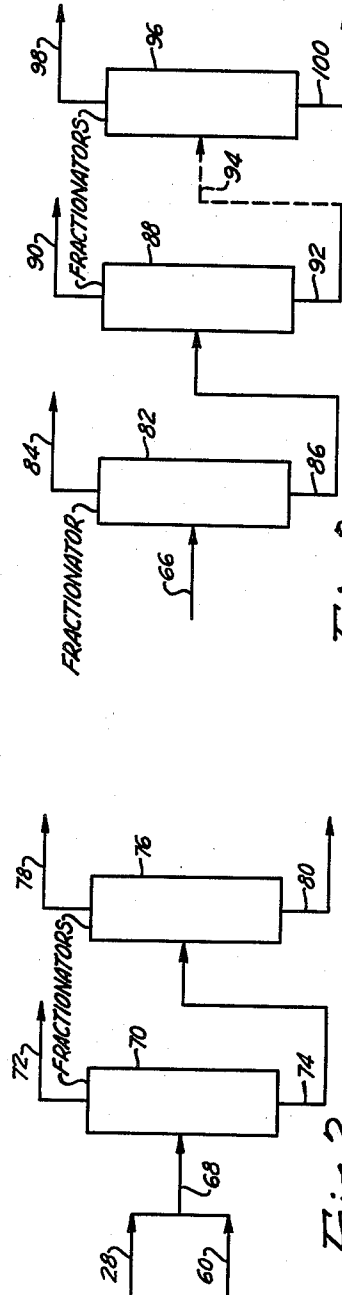


Fig. 3

Fig. 2

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2,945,076

PROCESS FOR PRODUCING OLEFINS

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Filed Apr. 15, 1957, Ser. No. 652,946

5 Claims. (Cl. 260—683)

This application relates to a process for producing olefins and more particularly to a process for producing normal alpha-olefins by cracking paraffinic stocks.

Olefins, particularly normal alpha-olefins, are often extremely desirable for use in many chemical reactions. For example, a convenient and extensive use for olefins resides in the Oxo process wherein they are reacted with hydrogen and carbon monoxide in the presence of a catalyst, generally cobalt carbonyl, at high pressures and moderate temperatures to produce a product predominating in aldehydes having one more carbon atom than said olefins. The aldehydes produced are often, in turn, hydrogenated to the corresponding alcohols. Since primary straight chain aldehydes and, particularly, the corresponding alcohols are extremely valuable commercially, it is apparent that normal alpha-olefins would be considered attractive as charge stock in the Oxo process.

In accordance with the present invention, paraffinic hydrocarbons such as petroleum waxes, are subjected to well-defined cracking and recovery operations wherein a large conversion of said hydrocarbons to a product predominating in normal alpha-olefins is obtained. At the same time, secondary reactions likely to result in the production of undesirable diolefins and isomerization, polymerization, decomposition, etc., products are inhibited.

As an illustration of but one embodiment of my invention, a flow diagram of the present process is shown in Figures 1, 2 and 3 of the drawings, which drawings are hereby incorporated in and made part of the present application.

A paraffinic charge stock is introduced into the system by line 2, preferably in the molten state at a temperature of about 200° to about 300° F. Prior to its introduction into the cracking zone, the charge can be joined by a recycle stream, described and defined hereinafter, in line 4. In order to vaporize the combined charge in line 6, water is introduced in the system by line 8 and converted to steam in heater 9 by any convenient means, for example by gas burners, not shown, to a temperature of about 900° to about 1200° F. The temperature of the steam should be high enough to vaporize the combined charge from line 6 but low enough to prevent appreciable cracking thereof before its entry into the cracking zone. The pressure of the charge in line 6 and of the steam produced in line 8, though not critical, should be sufficient to overcome pressure drop through the system. I have found that a pressure between about 15 to about 40 pounds per square inch gauge is sufficient for such purpose. In order to obtain efficient and optimum vaporization of the charge stock and to control the contact time of the charge stock in the cracking chamber, the ratio of steam to charge stock is extremely important. In general at least about 2 percent by weight, and preferably about 3 to about 40 percent by weight, of steam, based upon the total charge stock, is sufficient to vaporize the charge stock satisfactorily and maintain the desired contact time. As charge stock any paraffinic hydrocarbon

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such as wax, natural as well as synthetic, is suitable, although a petroleum wax is preferred. It is further preferable that the wax be substantially free of oil. While waxy materials containing up to about 41 percent by weight of oil have been used successfully, a preferred charge would contain less than about 16 percent by weight of oil. Best results are obtained using petroleum paraffins having a melting point of about 130° to about 140° F. and an oil content of less than about one percent by weight.

The molten charge stock and steam are combined in line 10 and passed through cracking chamber 12 wherein the vaporized charge stock is cracked and a hydrocarbon mixture predominating in C₂ to C₂₀ olefins, in the present example, is obtained. In order to obtain satisfactory cracking in chamber 12, careful control of the reaction conditions therein is required. The temperature must be at least about 1000° F. in order to crack the charge stock at a reasonable rate, but should be maintained below about 1250° F. in order to inhibit secondary reactions and prevent excessive coking in chamber 12. Preferably a temperature of about 1000° to about 1175° F. and a pressure of about one to about three atmospheres is extremely satisfactory. The residence time is similarly extremely important in order to obtain satisfactory cracking and inhibit secondary reactions. In general a residence time, dependent, of course, upon the remaining variables, is about 0.2 to about 6.0 seconds, particularly about 0.5 to about 3.0 seconds.

The mixture of cracked products and steam removed from cracking chamber 12 is passed to flash tower 14 by line 13. Before this mixture is passed into flash tower 14, it is quickly cooled from cracking temperature to a temperature of about 600° to about 800° F., preferably to a temperature of about 675° to about 725° F. to forestall further cracking and/or secondary reactions. This time interval is extremely important and must be less than about 2 to about 3 seconds, preferably between about 0.02 to about 0.10 second. The cooling is effected by a recycle stream from line 16, the composition of which will be defined hereinafter. The purpose of flash tower 14, which is operated at a pressure of about 10 to about 30 pounds per square inch gauge and a temperature of about 600° to about 700° F., is to effect a separation of the steam and lighter products from the heavier liquid products produced in the cracking operation. Moreover sufficient recycle of heavier product is thus provided to cool the cracked product before its entry into flash tower 14. A mere separation of steam, as condensed water, from the total cracked products would be exceedingly difficult because of a tendency to form an emulsion therewith.

Under the pressure and temperature conditions existing in flash tower 14, set forth above, the products removed from the top of the tower through line 18 comprise C₁₂ to C₂₀ and lighter hydrocarbons, preferably C₁₆ to C₁₈ and lighter hydrocarbons, and water as steam. The products are then passed through cooler 20 wherein the steam is condensed to water. The temperature in cooler 20 is not critical as long as it is sufficiently low to condense the steam therein but not so low as to effect precipitation or crystallization of waxy materials which may be present in the stream due to incomplete separation in flash tower 14. In general a temperature of about 75° to about 125° F., preferably about 100° F., is satisfactory. In addition to water, some of the heavier cracked products are also condensed in cooler 20. The cooled product is removed from cooler 20 by line 22 and passed to separator 24 which is operated at a temperature of about 100° to about 125° F. and a pressure of about 8 to about 12 pounds per square inch gauge. The water is removed from the base of separator 24 by line 26, while C₄ to C₆ and lighter cracked products,

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preferably C_5 and lighter, are removed overhead by line 28. The remainder of the cracked products are removed from the side of separator 24 by line 30.

From the base of flash tower 14, through line 32, is removed the remainder of the product which may not have been removed overhead by line 18, that is about C_{12} to about C_{20} and heavier, preferably about C_{16} to about C_{18} and heavier hydrocarbons. Since it is necessary to cool the cracked products entering flash tower 14, as previously pointed out, and since it is extremely desirable to effect such cooling without resorting to the addition to the system of extraneous material which would subsequently have to be removed from the product, if not from the system, often at great trouble and expense, a portion of the product in line 32 is recycled by line 15 34, and passed through cooler 35 wherein the product is cooled to a temperature of about 300° to about 500° F. The cooled product is then introduced into line 13 by line 16. The amount of recycle depends on many variables, for example, its temperature, the temperature of the cracked product in line 13, the temperature desired in flash tower 14, etc. In general, at least about 100, and preferably about 150 to about 300 percent, by weight of recycle, based on the cracked product in line 13, is sufficient to effect the desired cooling.

The remainder of the heavier product is passed by line 36 through valve 38 wherein the pressure is reduced to about 3 to about 8 pounds per square inch gauge, preferably to about atmospheric pressure. The product at a reduced pressure and at a somewhat reduced temperature, because of its movement through lines 36 and 40 and its reduction in pressure in passing through valve 38, is heated, if necessary, in heater 42 by any convenient means, to a temperature of about the same order as that existing in flash tower 14.

The product leaving heater 42 by way of line 44 is passed to tar stripper 46 wherein tar and other similar products present in the bottoms product are removed therefrom. This is effected by passing about 40 to about 70 pounds of steam per barrel of product in line 44, at a temperature of about 600° to about 800° F. into the base of tar stripper 46 by line 48. A temperature of about 600° to about 800° F. and a pressure of about 2 to about 6 pounds per square inch gauge is employed therein. As a result thereof, tar and heavier coke-forming products are removed from the base of tar stripper 46 by line 50.

Removed overhead by line 51 are the remainder of the cracked products entering tar stripper, not removed by line 50, and steam. The mixture in line 51 is then passed through cooler 52, which is operated at a temperature sufficiently low to condense the steam and some of the cracked products but not so low as to effect precipitation or crystallization of waxy materials which may be present in the stream due to incomplete separation in tar stripper 46 or flash tower 14. Generally a temperature of about 75° to about 125° F. is sufficient. The cooled product is removed from cooler 52 by line 54 and passed to separator 56 which is operated at a temperature of about 100° to about 125° F. and a pressure of about 0 to about 5 pounds per square inch gauge. Water which is condensed is removed from the base of separator 56 by line 58 and C_3 to about C_6 hydrocarbons, preferably about C_4 to about C_5 hydrocarbons are removed overhead by line 60. The remainder of the cracked product which has been liquefied is removed from the separator 56 by line 61 and is preferably pressured by pump 62 to a pressure of about 15 to about 25 pounds per square inch gauge. The product in line 61 is thereafter introduced into fractionator 64, which is maintained at a reboiler temperature of about 400° to about 700° F. and a pressure of about 2 to about 5 pounds per square inch gauge, wherein the product is separated into two fractions. The overhead, which is removed by line 66, comprises C_{12} to C_{20} and lighter hydrocarbons,

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preferably C_{14} to C_{16} and lighter hydrocarbons while the fraction removed from the base of fractionator 64 by line 4 comprises C_{12} to C_{20} and heavier hydrocarbons, preferably C_{14} to C_{16} and heavier hydrocarbons. The bottom fraction is preferably recycled and joins the fresh charge in line 2 as previously described. This recycle comprises about 100 to about 300 percent by weight, based on the fresh charge in line 2. In the event, however, operation is such, for example, that line 18 contains all or substantially all of the C_{16} and lighter hydrocarbons in the cracked product and C_{17} and heavier hydrocarbons are to be used as recycle of line 4, the overhead from tar stripper 46 need not be sent to fractionator 64 but can be passed directly to line 4 for recycle.

As shown in Figure 1, the olefins produced are recovered and found in lines 28, 60 and 66. The recovery of the olefins in these lines into their individual components, or even combinations or fractions of olefins, can be effected in any desired manner. For example, in the event the olefins in lines 28 and 60 comprise C_2 , C_3 and C_4 olefins, they can be combined, as shown in Figure 2, in line 68, compressed, dried by conventional means (not shown) and passed to fractionator 70 which can be operated at a pressure of about 250 to about 400 pounds per square inch gauge and an overhead temperature of about 0° to about 5° F. Methane and any other lighter constituents which may be present, are removed overhead by line 72, while C_2 , C_3 and C_4 hydrocarbons are removed from the base of fractionator 70 by line 74. From line 74, the C_2 , C_3 and C_4 fraction is passed to fractionator 76 which is operated at a pressure of about 250 to about 350 pounds per square inch gauge and an overhead temperature of about -10° to about $+10^\circ$ F. Here the C_2 fraction is removed overhead by line 78 and the C_3 and C_4 fraction is removed from the base by line 80. The C_2 stream may be split into C_2H_4 and C_2H_6 by means of a column operating at about 270 pounds per square inch and an overhead temperature of about -20° to about -23° F. The C_3 and C_4 stream may be further separated by similar distillation in a column (not shown) operating at about 250 pounds per square inch and an overhead temperature of about 110° to about 115° F.

Similarly, the hydrocarbon fraction in line 66 can be separated into its individual components by any conventional means. Thus as shown in Figure 3, assuming the hydrocarbon fraction in line 66 contains C_{15} and lighter hydrocarbons, it is sent to fractionator 82 which is operated at a pressure of about 30 to about 100 pounds per square inch and an overhead vapor temperature of about 122° to about 212° F. C_5 and lighter hydrocarbons are removed overhead by line 84 and C_6 to C_{15} hydrocarbons are removed from the base by line 86. This latter fraction is passed to fractionator 88, operated at a pressure of about 15 to about 30 pounds per square inch and an overhead vapor temperature of about 150° to about 190° F., where C_8 fraction is removed overhead by line 90 and a C_7 to C_{15} fraction is removed from the base by line 92. This fractionation into the individual components is continued by passing the hydrocarbons to successive fractionation columns, operated at appropriate pressures and temperatures, wherein the lightest individual fraction is removed overhead and the remainder is removed from the base and passed to the next succeeding column, until the fraction containing C_{15} and higher hydrocarbons is passed by line 94 to fractionator 96, operated at a pressure of about 5 to about 50 millimeters mercury absolute and an overhead vapor temperature of about 240° to about 350° F., wherein the C_{15} fraction is removed overhead in line 98 and the C_{16} and heavier fraction is removed from the base thereof by line 100 to line 4 of Figure 1.

While it has been shown above that the hydrocarbon fraction can be separated into its individual components, this has been done merely for illustrative purposes, and

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it is within the scope of the present invention to separate the hydrocarbon fraction prepared in the cracking zone into fractions containing various numbers of individual components. Thus a C_{11} to C_{14} fraction can be removed and used as such in alkylation or sulfonation reactions. Since there is a spectrum of hydrocarbons obtained in the cracking operation in accordance with this process and C_2 , C_6 and C_{10} hydrocarbons predominate, fractionation can be effected to remove these as individual components therefrom and not the others.

The process of the present invention can be illustrated by the following example. In a processing period 2366 pounds of Gulf Process Wax A, a typical regular grade paraffin wax for this process having the following inspection:

Gravity, ° API	34.3
Viscosity, SUV, sec. 210° F.	52.1
Flash, P-M, ° F.	435
ASTM D 93-52	
Pour point, ° F.	>115
ASTM D 97-47	
Oil content, percent by wt.	22.4
ASTM D 721-53T	
Carbon residue, Conradson, percent.	0.12
ASTM D 189-52	
Aniline point, ° F.	251
ASTM D611-2-53T	

was introduced in line 2 at a temperature of 300° F. and mixed with 4435 pounds of recycle in line 4. The mixture was admixed with 834 pounds of steam at a temperature of 1000° F. and a pressure of 28 pounds per square inch gauge from line 8 and the resulting mixture was introduced in cracking chamber 12 which was maintained at a temperature of 1040° F. and a pressure of 25 pounds per square inch gauge. The mixture was permitted to remain in the cracking coil 5 seconds and then removed and cooled to a temperature of 675° F. in 0.10 second by admixing therewith 20,240 pounds of recycle from line 16. The cooled mixture was then passed to flash tower 14, maintained at a temperature of 610° F. and a pressure of 15 pounds per square inch gauge, where 32,270 cubic feet of gaseous material comprising 17,970 cubic feet of steam and 14,300 cubic feet of C_{12} and lighter hydrocarbons were removed overhead by line 18. This mixture was passed through cooler 20, where the temperature was reduced to 100° F., and then to separator 24. Water was removed from the base of separator 24 by line 26, 6970 cubic feet of C_5 and lighter hydrocarbons were removed by line 28 and 1030 pounds of C_6 to C_{12} liquid hydrocarbons were removed by line 30.

Removed from the base of flash tower 14 were 25,152 pounds of C_{12} and heavier hydrocarbons. 20,240 pounds of this mixture were passed through cooler 35, cooled therein to a temperature of 490° F. and passed by line 16 to line 13 to cool the product therein to 675° F. The remainder of the product in line 32 was passed through valve 38 where the pressure was reduced to 5 pounds per square inch gauge and thereafter to heater 42 wherein the temperature thereof was raised to 600° F. From heater 42, heated mixture was led to tar stripper 46. 810 pounds of steam at 700° F. were led into the stripper, wherein the temperature was 650° F. and the pressure 4 pounds per square inch gauge. 870 pounds of tar and similar products were removed from the base of tar stripper 46 by line 50 and 8660 cubic feet of cracked products were removed overhead by line 51. After cooling in cooler 52 to a temperature of 100° F., the cracked products were passed to separator 56 wherein the water which was condensed at the lower temperature was removed by line 58. There was a negligible amount of hydrocarbon gas to be removed overhead in line 60 so that the total hydrocarbon stream comprising 4042 pounds of C_{12} and heavier materials was removed by line 61. The cracked

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products in lines 28, 60 and 61 were thereafter separated into the individual components in the manner previously described. The results obtained are tabulated below in columns "A" of Table I.

In another example a premium feed stock, for example, Gulfwax having a gravity of 42.2° API and an oil content of 0.33 percent by weight was cracked under conditions similar to those used above on Gulf Process Wax A. The α -olefin yields and concentrations obtained from this operation are shown in the "B" columns of Table I.

Table I

Olefin	Alpha-Olefin Yield, Percent by Weight of Feed		Alpha-Olefin Concentration, Percent by Weight of Olefins in Carbon Fraction	
	A Regular Feed	B Premium Feed	A Regular Feed	B Premium Feed
C_2H_4	8.6	12.2	100	100
C_3H_6	7.0	10.0	100	100
C_4H_8	5.0	5.0	90	94
C_5H_{10}	4.4	3.5		
C_6H_{12}	6.0	7.8	91	97
C_7H_{14}	7.0	7.1	82	96
C_8H_{16}	5.5	6.8	78	95
C_9H_{18}	5.3	6.0	76	93
$C_{10}H_{20}$	5.5	6.7	77	97
$C_{11}H_{22}$	3.6	3.9	74	92
$C_{12}H_{24}$	4.6	0.4	71	89
$C_{13}H_{26}$	2.8	4.0	69	84
$C_{14}H_{28}$	1.7	4.2	66	89
$C_{15}H_{30}$	0.5	4.4	70	92
Total	67.5	82.0		

The high yields of total α -olefins from both the "regular" and the "premium" feed stocks and the high concentrations of the α -olefin components in the various carbon fractions are illustrative of the effects of rapid heat-up time, rapid quench rate and short residence time in the cracking zone.

Obviously many modifications and variations of the invention, as hereinabove set forth, can be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A method for producing normal alpha-olefins which comprises vaporizing a waxy charge by admixing therewith at least about 2 percent by weight of steam at a temperature of about 900° to about 1200° F., heating the resulting mixture at a temperature of about 1000° to about 1250° F. and a pressure of about one to about three atmospheres for about 0.2 to about 6.0 seconds, whereby the wax charge is cracked and a mixture predominating in normal alpha-olefins is produced, cooling said latter mixture to a temperature of about 600° to about 800° F. in less than about 3 seconds, passing said cooled mixture into a flash tower, separating and removing a light hydrocarbon fraction from said flash tower, removing the remainder of said cooled mixture from said tower, cooling and recycling a portion of the said remainder to constitute the sole means whereby the cracked products are cooled prior to their entry into said flash tower, and thereafter separating the cracked product into selected olefinic fractions.

2. A method for producing normal alpha-olefins which comprises vaporizing a waxy charge by admixing therewith at least about 2 percent by weight of steam at a temperature of about 900° to about 1200° F., heating the resulting mixture at a temperature of about 1000° to about 1250° F. and a pressure of about one to about three atmospheres for about 0.2 to about 6.0 seconds whereby the wax charge is cracked and a mixture predominating in normal alpha-olefins is produced, cooling said latter mixture to a temperature of about 600° to about 800° F. in less than about 3 seconds, passing

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said cooled mixture into a flash tower, separating and removing C_{12} to C_{20} and lighter hydrocarbons from said flash tower, removing the remainder of said cooled mixture from said tower, cooling a portion of said remainder to a temperature of about 300° to about 500° F. and recycling said portion of said remainder to constitute the sole means whereby the cracked products are cooled prior to their entry into said flash tower, and thereafter separating the cracked product into selected olefinic fractions.

3. A method for producing normal alpha-olefins which comprises vaporizing a waxy charge by admixing therewith at least about 2 percent by weight of steam at a temperature of about 900° to about 1200° F., heating the resulting mixture at a temperature of about 1000° to about 1250° F. and a pressure of about one to about three atmospheres for about 0.2 to about 6.0 seconds, whereby the wax charge is cracked and a mixture predominating in normal alpha-olefins is produced, cooling said latter mixture to a temperature of about 600° to about 800° F. in less than about 3 seconds, passing said cooled mixture into a flash tower, separating and removing a mixture of C_{12} to C_{20} and lighter hydrocarbons and steam from said flash tower, cooling said latter mixture to condense said steam, removing water condensate from said latter mixture, removing the remainder of said cooled mixture from said tower, cooling a portion of said remainder to a temperature of about 300° to about 500° F., admixing with the cracked products said portion of said cooled remainder to constitute the sole means by which the cracked products are cooled prior to their entry into said flash tower, and thereafter separating the cracked product into selected olefinic fractions.

4. A method for producing normal alpha-olefins which comprises vaporizing a waxy charge by admixing therewith at least about 2 percent by weight of steam at a temperature of about 900° to about 1200° F., heating the resulting mixture at a temperature of about 1000° to about 1250° F. and a pressure of about one to about three atmospheres for about 0.2 to about 6.0 seconds, whereby the wax charge is cracked and a mixture predominating in normal alpha-olefins is produced, cooling said latter mixture to a temperature of about 600° to about 800° F. in less than about 3 seconds, passing said

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cooled mixture into a flash tower, separating and removing a mixture of C_{12} to C_{10} and lighter hydrocarbons and steam from said flash tower, cooling said latter mixture to condense said steam, removing water condensate from said latter mixture, removing the remainder of said cooled mixture from said tower, cooling a first portion of said remainder to a temperature of about 300° to about 500° F., admixing with the cracked products said first portion of said cooled remainder to constitute the sole means by which the cracked products are cooled prior to their entry into said flash tower, removing tar from a second portion of said remainder, and thereafter separating the cracked product into selected olefinic fractions.

5. A method for producing normal alpha-olefins which comprises vaporizing a waxy charge by admixing therewith at least about 2 percent by weight of steam at a temperature of about 900° to about 1200° F., heating the resulting mixture at a temperature of about 1000° to about 1250° F. and a pressure of about one to about three atmospheres for about 0.2 to about 6.0 seconds, whereby the wax charge is cracked and a mixture predominating in normal alpha-olefins is produced, cooling said latter mixture to a temperature of about 600° to about 800° F. in less than about 3 seconds, passing said cooled mixture into a flash tower, separating and removing a mixture of C_{12} to C_{20} and lighter hydrocarbons and steam from said flash tower, cooling said latter mixture to condense said steam, removing water condensate from said latter mixture, removing the remainder of said cooled mixture from said tower, cooling a first portion of said remainder to a temperature of about 300° F. to about 500° F., admixing with the cracked products said first portion of said cooled remainder to constitute the sole means by which the cracked products are cooled prior to their entry into said flash tower, removing tar from a second portion of said remainder by admixing steam therewith, and thereafter separating the cracked product into selected olefinic fractions.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,945,076

July 12, 1960

William A. Pardee

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 2, for "C₁₂ to C₁₀" read -- C₁₂ to C₂₀ --.

Signed and sealed this 4th day of April 1961.

(SEAL)

Attest: ERNEST W. SWIDER

~~XXXXXXXXXX~~

Attesting Officer

ARTHUR W. CROCKER
Acting Commissioner of Patents