FIG.-I

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RATE CONSTANT, K_t, FOR

WAX CRACKING vs. TEMPERATURE, t

FIG.-II

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FIG.-III

TEMPERATURE & CONVERSION vs. RESIDENCE TIME & DISTANCE

IN QUENCH LINE

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1

3,103,485
PROCESS FOR CRACKING PETROLEUM WAXES
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The present invention relates to an improved process
for the steam cracking of a petrolatum at low conversions
to produce straight chain olefins in the C_5—C_{18} range.
More particularly this invention relates to producing said
olefins as an additional product from a conventional
(high conversion) steam cracking of light naphtha to
produce predominantly C_2—C_5 unsaturates such as buta-
diene, isoprene, propylene, etc. Most particularly this
invention relates to feeding the stream of liquid petrola-
tum to be cracked at low conversions to the unquenched
1400–1500° F. effluent stream from the naphtha cracker.
Thereby, both the necessary rapid quench of the high
temperature steam cracker effluent and the desired low
conversion cracking of the petrolatum are obtained.

The cracking of petrolatum or waxes at low conver-
sion to produce straight chain olefins in the C_5—C_{18} range
is known at this time. Thus, according to this prior art
process, cracking is conducted at temperatures of about
1100° F., utilizing residence times to obtain conversions
to C_3^- of about 8 wt. percent. Likewise conventional
(high conversion) steam cracking of naphthas at tem-
peratures of 1400–1500° F. to obtain conversions to
C_3^- of about 45–80 wt. percent and thus produce mainly
C_2—C_5 diolefins and olefins is also known and widely
commercially utilized throughout the world. According
to this latter process residence times at these very high
temperatures must be closely controlled and a rapid
quench utilized to prevent additional cracking as well
as polymerization of the desired olefin and diolefin prod-
uct to undesirable materials such as methane, tars and
carbon. Thus, rapid quenching to temperatures below
about 1000° F. with water or a refractory oil has been
employed.

It has now been discovered that an efficient rapid
quench of this 1400–1500° F. effluent from conventional
high conversion steam cracking can be obtained utilizing
a petrolatum oil which is itself at the same time steam
cracked to yield desired C_8—C_{18} straight chain olefins.
It should be noted that the straight chain olefins of par-
ticular interest for detergents are in the C_{10}—C_{16} range.
Further, it has been discovered that the mixed product
obtained is highly compatible and can be easily sep-
arated by simple distillation. Thus, until the present
it might have been supposed that the polymer produced
in the conventional high conversion cracking process
would contaminate the C_{10}—C_{16} straight chain olefins
produced in the wax cracking operation. It has now
been found that the boiling range and extent of the
formation of this polymer is such that these C_{10}—C_{16}
olefins may be separated by simple distillation with little
contamination by polymeric materials formed in the light
naphtha cracking operation.

Thus it has now been found that the amount of the
polymeric materials formed from the light naphtha crack-
ing operation which boil in the same range as the
C_{10}—C_{16} straight chain olefins produced from wax crack-

2

ing, will be less than 20%, usually less than 10%, of the
amount of straight chain olefins in the same boiling
range. Since even the olefins produced by the prior art
low conversion steam cracking of petrolatum are con-
taminated by branched olefins, some diolefins and some
aromatics, some clean-up of these olefins by processes
such as solvent extraction, selective hydrogenation, etc.
is required to make them fit as detergent plant or oxo
plant feeds. Mixing in 10% or so of polymer, much of
which is olefinic, simply slightly increases the severity
of the necessary clean-up, and does not substantially
increase its cost.

Finally, in view of the fact that existing steam crack-
ing facilities can be utilized according to this invention
essentially without modification to do double duty and
thus additionally produce large amounts of C_8—C_{18}
linear olefins it is apparent that the present process will be
extremely economic. Thus, essentially the only major
new process investment items required are the fractiona-
tion facilities to recover the C_{10}—C_{14} cut from a side
stream off the steam cracker quench tower, and the
necessary treating facilities on the product stream to re-
move diolefins and aromatics.

Advantages of the present new process are:

(1) If the wax cracking were carried out separately,
a separate light ends system would be needed which
would be very uneconomic (the C_3^- yield from low con-
version wax cracking is 8% or less, and not particularly
olefinic at that).

(2) The wax, petrolatum or paraffinic stock which is
used as the quench oil fulfills a useful function in the
main steam cracking process.

(3) While wax and petrolatum are preferred feed-
stocks to the wax cracker, they are also of premium
value. A paraffinic crude refinery stream (virgin gas
oil, cat cycle stock raffinate) is cheaper, but the tolerable
percent conversions to produce high quality linear olefins
is lower than with wax. Thus, the cracker is more ex-
pensive since more feedstock has to be handled than with
pure wax or petrolatum. In the present invention proc-
ess the quench oil is only (in the most economical opera-
tion) cracked to the extent of a few percent (3–5) any-
way and thus the low conversions and large amounts of
oil required to be cracked in this mild gas oil cracking
may be extremely economically tolerated.

(4) Pour and cloud point of the quench material is
lowered 5–10° F. by this technique. Hence, by using a
gas oil or cycle stock raffinate for this quench we:

(a) Quench the light naphtha steam cracker effluent
(b) Make straight chain olefin out of the cheapest feed
stock.
(c) Lower the pour and cloud point of the middle
distillate products obtained from the quench oil.

The present invention will be more clearly understood
from a consideration of the accompanying diagram-
matic illustration of a steam cracking furnace and quench
system for carrying out the present invention.

Turning now to FIGURE 1, a naphtha, specifically a
light naphtha boiling in the range of 100 to 300° F.,
preferably 100 to 220° F., e.g. 160 to 220° F., is sup-
plied through line 1 with steam supplied through line 2
to a cracking furnace 3. This furnace is operated at

temperatures of 1300 to 1500° F., preferably 1380 to 1450° F., e.g. 1400° F., pressures of 0 to 50 p.s.i.g., preferably 5 to 25 p.s.i.g., e.g. 10 p.s.i.g., with residence times of 0.1 to 5, preferably 0.5 to 2, e.g. 1 second and with amounts of steam supplied being in the range of 0.1 to 1, preferably 0.2 to 0.5, e.g. 0.25 lb. of steam per lb. of oil. These conditions are preferably adjusted to obtain C_3^- conversions of above 40 wt. percent, preferably 45–80 wt. percent. A waxy distillate quench oil is supplied through line 6 to quench the effluent from the cracking zone which is passed through line 4 to quench zone 5. This quench zone may be an elongated tube with provision for multiple or alternate injection of the waxy distillate oil through lines 7, 8, 9, 10, 11, 12, 13, and 14 in addition to line 6, if desired, as the vapors pass through the tube. The quenched products from the cracking of the light naphtha feed and from the low conversion cracking of the waxy distillate are passed from the quench zone 5 through line 15 to further quench facilities and of course, fractionation facilities for separation of the products.

Suitable waxy distillate quench oils may be certain highly paraffinic crude oils containing less than 50 wt. percent aromatics and naphthenes, boiling in the range of 500 to 1200° F., preferably 600 to 1100° F., e.g. 650 to 800° F. These paraffinic oils may be obtained for example from Lirik, Bahia and San Joaquin crudes. Likewise, an excellent quench oil is a petrolatum boiling in the range of 650 to 1100° F., containing about 10 to 60% wax. Other suitable feedstocks are heavy gas oil fractions from less paraffinic crudes, such as a Middle East crude but the quality of the straight chain olefins produced is poorer. Other feedstocks are extracted gas oils (to remove some of the aromatics and naphthenes) and the raffinate from the extraction of catalytic cracking unit cycle stocks boiling in the range of 650 to 900° F. All of the materials above described will produce high yields of the desired C_8 to C_{18} linear olefins.

As previously mentioned, quenching may be conducted by supplying quench oil at multiple points in stages through the quench zone or may be conducted by supplying the entire amount of the quench oil initially. It should be noted that it may be preferred to introduce the major portion of the quench oil initially so as to quickly reduce the temperature to say 1200 to 1300° F., e.g. 1250° F., to prevent deleterious cracking and polymerization of the high temperature light naphtha cracking effluent and also to obtain the major portion of the waxy distillate cracking at preferred temperatures of around 1100° F. Likewise, it is contemplated that water may be supplied through lines 6 to 14 for additional control of temperature and that steam may be supplied at the beginning of the zone through line 6 to control the proportion of steam to hydrocarbon in the quench zone if desired. The waxy distillate oil may be introduced at temperatures of 400 to 800° F., preferably 500 to 700° F., e.g. 600° F. and supplied in amounts based on the gaseous effluent (including H_2O) of 30 to 70 wt. percent, preferably 40 to 60 wt. percent, e.g. 55 wt. percent. Quenching times may be in the range of 0.2 to 2 seconds, preferably 0.2 to 1, e.g. 0.5 second (i.e. time to reduce the temperature to below about 1000° F.)

Following quenching, separation of the total cracked product may be obtained as follows:

The 1000° F. effluent is passed to a conventional steam cracker quench tower wherein the original steam cracker product and the additional product from the wax cracking are separated by conventional fractionation means. The light products (C_5 and lighter) are removed overhead as a gas to be processed further in a conventional light ends system. Steam cracked naphtha (300° F. End Point or so) is also removed overhead, as a liquid, and is sent to the same light ends system, and/or conventional naphtha fractionation and finally char treating. The desired straight chain olefins are removed as one

or several sidestreams from the quench tower and may be further processed by steam stripping to remove lighter materials and distillation to separate finer cuts. These steps may also be preceded or followed by extraction and/or selective hydrogenation, or similar treatments to remove or clean up undesirable diolefins and aromatics.

The heavier steam cracked products, as well as recycle quench oil are removed as sidestreams and bottoms streams from said quench tower.

The present invention will be more completely understood from a consideration of the following data and an example which further illustrate and define the present invention. Thus, it is shown below:

(1) that enough heat is available to carry out the desired cracking,

(2) that the kinetics are favorable for the reaction,

(3) that only small amounts (10 to 25 wt. percent) of contamination of the waxy cracked product with polymer in the same boiling range from the naphtha steam cracker are obtained,

(4) that conversions of the waxy distillate of up to 10 to 20 wt. percent per pass can be obtained (unconverted materials can of course be separated by distillation and recycled),

(5) that large amounts of straight chain C_{10} to C_{14} olefins can be extremely economically produced in this manner (e.g. 16,000 s.t./yr. C_{10} to C_{14} olefins in a 6000 barrel/day naphtha steam cracker, and

(6) that the pour and cloud point of a middle distillate cut quench oil is reduced by this process.

A commercial high conversion steam cracker is operated under conventional furnace effluent conditions. Instead of the conventional cat cycle stock, a waxy distillate, preheated to 600° F., is used as the quench material in a system as described in the drawing (FIG. 1). Sufficient waxy distillate is injected into the cracker effluent to cool it from 1400 to 1000° F. A residence time of e.g. 0.5 second is utilized in the quench line, with uniform addition of quench material to the flowing gas stream along the length of the line. The result obtained is similar to that obtained in a conventional quench utilizing a single injection point at the inlet.

To determine the extent of conversion of the quench oil obtained in the quench line both reaction rate constants and the temperature gradient through the quench line were determined. With respect to the former, data obtained in a laboratory steam cracker were used to determine the reaction rate constant for the cracking operation at a particular temperature and pressure as follows:

Wax feed temperature	800° F.
Coil outlet temperature	1100° F.
Residence time	1 sec.
C_3^- Conversion	8 wt. percent.

From this single run, the cracking rate constant, K_t, was calculated as follows:

$$\frac{dx}{d\theta} = K_t(100 - x)$$

x = wt. percent C_3^- Conversion
θ = time, sec.

Using the same variation of K_t with temperature ($t°$ F.) as for other gas oil cracking rate constants, a relationship well known in the art

$$\left(K_t = K_{1200}(3.18 \times 10^{12}) - \frac{47,000}{t + 460} \right)$$

a plot of such variations of the present K_t with temperature was obtained and is shown in FIG. II.

With respect to the temperature gradient through the quench line a heat balance (including allowing for the endothermic heat of reaction) was made utilizing 10 equal injections of quench oil at 0.05 second intervals. A graph of the variation in temperature along the length

of the quench line was plotted and is shown in attached FIG. III. In this figure the coordinates for each curve are indicated by the arrows shown, the x coordinate having a double scale which applies to both curves. Likewise from this temperature gradient and from the FIG. II plot of reaction constants vs. temperature, the extent of conversion of quench oil obtained at intervals through the quench line was calculated and is also presented in FIG. III. Thus from the figure it can be seen that after only 1/10 of a second, the temperature has already been reduced to 1200° F. and nearly 2/3 of the conversion has taken place, while only 20% of the quench oil has been introduced. At the 1/4 second point the temperature is below 1100° and 90% of the final conversion has occurred. It should be mentioned that since 90% of the final conversion is obtained at a point only half way through the quench line that if desired, a conventional (perhaps cheaper) quench oil can be substituted for the remaining one-half of the quench oil to be supplied to the quench line, if desired.

The yields of the C_{11}—C_{13} linear olefins obtained from various gas oil feed stocks were determined in a laboratory reactor and are listed together with C_3^- conversion. This table shows that for a highly paraffinic feed, the yield of C_{11}—C_{13} is of the order of 40–50% of the C_3^- conversion.

STEAM CRACKING YIELDS

Feed Stock	C_3^- Conv., Wt. Percent	C_{11-13} Yield, Wt. Percent	C_{11-13}/C_3^-	Olefins In C_{11-13}, Wt. Percent
Eicosane	7.6	3.5	0.46	95.6
Cetane	7.3	3.6	0.49	94.6
Lirik (Sumatra)	13.7	5.8	0.42	84.3
Bahia (Brazilian)	9.6	4.1	0.43	86.3
Tia Juana (Venezuela)	4.5	3.3	0.74	66.9
Middle East	8.8	5.0	0.57	67.2
Cat. Cracking Cycle Oil Raffinate After Phenol Extraction	13.6	5.3	0.39	77.5

To determine C_{10}—C_{14} from the C_{11}—C_{13} figures, the latter were multiplied by 5/3 reflecting the molecular weight range. This factor, incidentally, agrees very well with the corresponding yields of these fractions from petrolatum cracking.

With respect to the yield of steam cracker polymer in the C_{10}—C_{14} range, data were obtained from a commercially operating steam cracker. The unit was operating at high conversions to C_3^- on a mixed naphtha feed stock.

Feed:
    60 vol. percent 60/160° F.
    40 vol. percent 280/360° F.
Conversion:
    55 wt. percent
Yields of Naphtha:
    Initial/60° F. .... 19.1 wt. percent on feed.
    60/430° F. .... 23.3 wt. percent on feed.
    430/490° F. .... 0.6 wt. percent on feed.
    490° F.+ .... 1.9 wt. percent on feed.

The above data show that the polymer yield is of the order of 0.1 wt. percent on feed/10° F. boiling range, in the neighborhood of 400–500° F. However, when taking into account that other operating plants utilize a feed having a 220° F. end point, and that the conversion is 45 wt. percent, the polymer yield in C_{10}—C_{14} range for these units is probably only 0.05 wt. percent/10° F. boiling range. Based on these numbers it was assumed that the yield of polymer in the C_{10}—C_{14} boiling range is at the most 1 wt. percent on steam cracker feed.

Regarding pour point reduction by this quench technique, a 600 to 800° F. Aramco gas oil was cracked under conditions to obtain a C_3^- conversion of 8.3 to 9.2%. The following data were obtained.

Pour point of feed (600 to 800° F.), 65° F.
Pour point of 610+° F. product, 55° F.
The pour of the 600 to 800° F. product must be <55° F.
The 610+° F. product was 63–66% of feed.

This shows that this method of cracking is a pour point reduction method for the quench oil. Actual reduction was therefore >10° F.

A design case based on the above discussion is presented below.

Example

In a system as described in FIGURE I a light naphtha boiling in the range of 160–220° F. is cracked under the following conditions:

(a) Furnace Outlet Conditions:
    Hydrocarbon .... 62,770 lb./hr.
    Steam .... 17,550 lb./hr.
    Temperature .... 1400° F.
(b) Quench Conditions (Uniform Additions):
    Waxy quench oil added .... 43,800 lb./hr.
    Quench outlet temperature .... 976° F.
    Quench oil inlet temperature .... 600° F.
    Total quench time .... 0.5 sec.
(c) Results:
    C_3^- Conversion of quench oil/pass   12.5 wt. percent.
    Yield of C_{10}—C_{14} ---- { 8.7 wt. percent on wax.
    3,810 lb./hr.
    15,900 s.t./yr.

    Naphtha Steam Cracker ploymer in C_{10}—C_{14} range - { 1.0 wt. percent on steam cracker feed.
    628 lb./hr.
    2,600 s.t./yr.

    Total C_{10}—C_{14} yield .... 18,500 s.t./yr.

It should be noted that in the above discussion percent C_3^- conversion refers to the percent by weight of C_3^- gases obtained per weight of naphtha cracked.

The foregoing description contains a limited number of embodiments of the present invention. It will be understood that this invention is not limited thereto since numerous variations are possible without departing from the scope of the following claims.

What is claimed is:

1. An improved process for preparing predominantly straight chain olefins in the C_8 to C_{18} range along with olefins and diolefins boiling in the C_2 to C_7 range, which comprises cracking a light naphtha in a cracking zone in the presence of steam at temperatures in the range of 1300 to 1500° F. and under conditions to obtain conversions to C_3 of above 40 wt. percent, withdrawing the product vapors from said cracking zone, immediately contacting the withdrawn product vapors, with 30 to 70 wt. percent of a waxy distillate based on the product vapors thereby quenching said product vapors to below about 1000° F. in from 0.2 to 2 seconds and also obtaining the major proportion of the waxy distillate cracking at about 1100° F. and separating a cut high in C_8 to C_{18} olefins and a cut high in C_2 to C_5 olefins and diolefins from the resultant mixture.

2. The process of claim 1 wherein the waxy distillate is a virgin gas oil boiling in the range of 500 to 1200° F.

3. The process of claim 1 wherein the waxy distillate is a petrolatum boiling in the range of 650 to 1100° F.

4. The process of claim 1 wherein the light naphtha is a naphtha boiling in the range of 100 to 300° F.

5. The process of claim 1 wherein quenching is conducted by supplying the quench oil at multiple points through a staged quench zone.

6. The process of claim 1 wherein the entire amount of the waxy distillate used as a quench oil is supplied at a single point in a quench zone.

7

7. An improved process for preparing a fraction containing a high proportion of straight chain and minimum branched chain olefins in the C_8 to C^{18} range along with olefins and diolefins boiling in the C_2 to C_7 range, which comprises cracking a light naphtha in a cracking zone in the presence of steam at temperatures in the range of 1300 to 1500° F. under conditions to obtain C_3^- conversions of above 40 wt. percent and utilizing amounts of steam supplied in the range of 0.2 to 0.5 lb. of steam per lb. of oil and residence times of 0.5 to 2 seconds, immediately quenching in a quench zone the product vapors from said cracking zone with 40 to 60 wt. percent based on the product vapors of a petrolatum boiling in the range of 650 to 1100° F. maintaining temperatures in the quench zone in the range of 1400 to 1000° F. and residence times in said quench zone in the range of 0.2 to 2 seconds and separating a C_8 to C_{18} fraction containing a high propor-

8

tion of straight chain olefins, and a C_2 to C_7 fraction containing olefins and diolefins from the quenched product vapors.

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