This invention relates to new methods for the manufacture of naphthalene from petroleum fractions, and more specifically from the heavy ends of naphtha reformate.

In broad aspect, the process comprises subjecting the reformate fraction to hydrodealkylation in the presence of steam and a hydrodealkylation catalyst more particularly described hereinafter. More specifically, the process envisages a novel system wherein selected fractions of the fresh feed are dealkylated together with a selected fraction of the reformate feed in a first distillation step, and a mother liquor recovered from the final crystallization of naphthalene from the product stream.

The overall result is that about 80 to 90% of the feedstock is converted to naphthalene and high-octane gasoline having an end point of about 400°F or lower. The remaining 10 to 20% of feed is recovered as fuel oil, and light fuel gases.

In the preferred modification of the process, the fresh reformate feedstock is first blended with the total effluent from the hydrodealkylation reactor, thereby effecting an immediate partial quench of the hot products to below cracking temperatures. The mixture of fresh feed and reactor product is then subjected to fractional distillation to separate four different liquid fractions. The lightest fraction is the gasoline which was synthesized in the hydrodealkylation step. The next lightest fraction is a cut which contains most of the naphthalene, both that synthesized in the dealkylation and that which was present as such in the fresh feed. This fraction is then subjected to fractional crystallization to recover the naphthalene, and the mother liquor therefrom, boiling for example from 400° to 450° F., is recycled to the hydrodealkylation zone for conversion to 400° F. end point gasoline. The third fraction is removed from the distillation step and is a cut which consists of methyl naphthalenes, both those present in the fresh feed and those which were unconverted in the hydrodealkylation step. This fraction is also recycled to the hydrodealkylation step. The bottoms fraction boils above about 500° F., and contains refractory materials which would tend to cause increased coking of the catalyst if not removed. It is hence not recycled but is used for fuel oil, or any other desired purpose.

Another preferred feature of the process consists of a novel technique for carrying out the above described four-way fractionation step. It has been found that for purposes of this invention, adequate separation of the fractions may be accomplished in a single fractionating column. The column is operated with the gasoline fraction going overhead, and with the heavy ends being taken off as bottoms. The naphthalene fraction (400° to 450° F. preferred boiling range) is taken off as a side-cut at about the 450° to 470° F. temperature level in the column. If desired it may be transferred to a stripping vessel (also serving as a surge drum) where light ends carried over as a result of relatively rough fractionation are stripped off and returned with the steam to the column at a point slightly above the level at which the naphthalene fraction was removed. The next to the naphthalene fraction (450° to 550° F. preferred boiling range) is removed from the column as a second side-cut at about the 510° to 530° F. temperature level in the column. This methyl naphthalene fraction may likewise contain some lighter ends, and if desired may be stripped with steam in a second stripping vessel, and the stripping gases returned to the column at a point slightly above the level at which it was removed. All of the steam which is returned to the column is fractionated upwardly and separates in the overhead reflux drum, from which it is removed. The bottoms from the fractionating column, boiling above 700° F., and preferably above about 550° F., is withdrawn from the system. According to this novel fractionation scheme, adequate separation is obtained in a single column where ordinarily two or three columns would be used.

From the foregoing it will be apparent that the principal object of the invention is to provide economical means for converting heavy reformate fractions almost entirely to naphthalene and high-octane gasoline of 400° F. end point or lower. Another object is to provide hydrodealkylation catalysts and conditions adapted to achieve this purpose. Still another object is to provide novel and economical means for isolating naphthalene from both the fresh feed and the hydrodealkylation products with a minimum of equipment and processing. Another object is to provide a novel and advantageous entry point for the fresh feed into the hydrodealkylation product recovery and recycle system. Other objects will be apparent from the description which follows.

In the reforming of naphthas, it is known that naphthalene and methyl naphthalenes are often present in the product, even though the feedstock may have contained no naphthalene components. It is believed that naphthalene and methyl naphthalenes are synthesized during the reforming step by reactions of dehydrogenation and/or dehydrocyclization. As a result of these and other reactions, the effluent from most reforming processes is found to comprise from about 1% to 10% of material boiling in excess of about 400°F, even in cases where the end point of the feed was as low as 385°F.

It is likewise known that these heavy ends from reformate fractions may be subjected to hydrodealkylation to synthesize and recover naphthalene. The process of this invention goes further and provides new and novel catalysts and conditions for carrying out the dealkylation, and provides a highly economical system for the recovery and recycle of the various products from both the naphtha feed and the hydrodealkylation products.
In order to obtain a reformate containing substantial amounts of naphthenic components, it is preferable to start with a reformer feedstock which is rich in naphthenes and/or aromatics and which has an end boiling point above about 350 °F. and preferably above about 375 °F. Such naphthas may comprise straight-run gasoline, cracked gasoline, reformate, or delayed coker distillates and the like. Where cracked gasolines are used, it is preferred to pre-hydrogenate the feed before it is subjected to reforming. A preferred catalyst for use in the prehydrogenation step is cobalt molybdate supported on activated alumina, or on activated alumina containing a small amount of silica.

In the dealkylation step, the preferred catalyst is made up of activated alumina upon which is disintegrated a minor amount of molybdenum oxide (e.g. 5 to 20 percent) and a smaller amount of cobalt oxide (e.g. 1 to 5 percent). It is further preferred that the catalyst contain a stabilizing amount of silica, e.g. about 3 to 15 percent by weight, which is preferably coprecipitated with the alumina. A further preference is that the catalyst should contain a minor amount, e.g. 0.1 to 3 percent by weight, of an alkali metal or an alkali earth metal. Such metals are preferably added in the form of a hydroxide, carbonate or other heat decomposable compound, whereby upon final calcining the alkali metal component becomes converted to a heat stable material, e.g. an oxide, hydroxide, silicate, aluminate or the like.

To prepare catalysts of the above described nature, a hydrogel of the carrier is first prepared, as by precipitation or coprecipitation from aqueous solutions. The hydrogel is then dried and impregnated with soluble salts of molybdenum and cobalt, either simultaneously or alternately. The catalyzing component is preferably added by a final impregnation step, but may be added at any other desired stage of manufacture. For example, it may very conveniently be mixed with an ammonium molybdate solution and impregnated simultaneously with the molybdenum. Suitable alkali compounds for impregnation include, for example, sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, potassium sulfide, calcium hydroxide, etc.

It is found that the alkali component in the catalyst functions to reduce the undesirable cracking characteristics of the catalyst, thus reducing coude laydown and light gas make. The dealkylation process conditions are also designed to reduce detrimental cracking. For this purpose, steam is added to the feed mixture in proportions ranging between about 0.2 and 5 moles thereof per mole of feedstock. Operative temperatures for the dealkylation step range between about 800 °F and 1150 °F, and preferably between about 900 °F and 1100 °F. Hydrogen is used in ratios between about 1,000 and 10,000 s.c.f. per barrel of feed, and total pressures between about 500 and 2,000 p.s.i.g. may be used. Preferred pressures range between about 800 and 1,2000 p.s.i.g. Liquid hourly space velocities between about 0.4 and 5 may be used, preferably between about 0.5 and 2. Those skilled in the art will understand that the foregoing operative ranges of conditions should be properly correlated with each other to obtain optimum results.

Other catalysts which may be used herein include the oxides and sulfides of any of the group VI B and group VIII metals supported on an adsorbent oxide carrier. Suitable active components include for example the oxides or sulfides of tungsten, molybdenum, chromium, iron, cobalt, nickel, or mixtures thereof. These active components are supported in minor amounts (e.g. 1-20% by weight) upon carriers such as alumina, silica, titania, zirconia, activated clays, or the like, or mixtures thereof. In these cases also, it is preferable to add small amounts of an alkali component, as in the case of the preferred cobalt molybdate catalyst.

Reference is now made to the attached drawing which illustrates semi-diagrammatically a preferred adaptation of the process, but is not to be construed as limiting in scope. The hydrodealkylation reactor 2 is conventional in nature and is packed with a bed of 3/8" to 1/2" diameter. The feedstock, including recycle streams derived as hereinafter described, is brought in via line 4 and preheated to incipient dealkylation temperatures (e.g. 900 °F.) in heater 6. Since the reaction is exothermic, there will be a 20 to 100 °F. temperature rise through the reactor unless suitable quenching techniques are employed. The effluent from the reactor passes out via line 8 and, before any substantial cooling thereof, is admitted with all of the fresh dealkylation feedstock brought in via line 10. This fresh feed is preferably introduced at a relatively low temperature, e.g. to 200 °F., in order to effect a partial quench of the reactor effluent in line 8. This is to arrest noncatalytic cracking and to suppress coke deposition in the succeeding heat exchangers. The partially quenched mixture is then passed through a heat exchanger 12 to complete the cooling and condensation of liquid products, which are then transferred to high pressure separator drum 14. Fixed gases containing e.g. 50% or more of hydrogen are withdrawn via line 16 for recycle via line 18. A purge stream is withdrawn through line 20 to prevent the build-up of light gases in the system. Make-up hydrogen to replace the hydrogen chemically consumed and purged from the system is brought in via line 22. The combined recycle and make-up hydrogen is then mingled with the feed in line 4. Steam for the dealkylation reaction is admitted to line 4 via inlet line 24.

The liquid in high pressure separator drum 14 includes condensed water and hydrocarbons, as well as dissolved light gases. The water is withdrawn via line 26, and the hydrocarbon stream is transferred via line 28 and flashed into low pressure separator drum 30, which may be at atmospheric pressure or slightly above. Light gases including methane, ethane and the like are withdrawn via line 32 for use as fuel gas if desired. The liquid hydrocarbons in drum 30 are then transferred via line 34 and heater 36 to fractionating column 38 in which the mixture is split into the four fractions described above.

Fractionating column 38 should contain at least 25 plates and preferably about 40 plates to obtain the desired fractionation. It is unnecessary however to use more than about 60 plates. Such a fractionation column, designed for fractionating 1300 barrels per day of total feed thereof, may be for example 4.5 feet in diameter by 98 feet in height and would be operated spaced about 2 feet apart. The gasoline synthesized in reactor 2 is taken off as overhead, condensed, and transferred via line 40 to overhead reflux drum 42. A portion of the hydrocarbon condensate is returned to column 39 via line 44 as reflux, and the net gasoline product is withdrawn via line 46 and sent to storage facilities not shown. Suitable reflux ratios range between about 6/1 and 2/1, and preferably about 8/1 and 10/1.

The naphthalene fraction is withdrawn as a side-cut via line 48 at about the 12th plate down the column where the column temperature is about 460 °F. The optimum boiling range of this fraction will depend to some extent on the type of feedstock used, but in any event is cut so as to include at least about 65% of the naphthalene admitted in the column feed. Its boiling range is preferably about 400 °F to 450 °F, but to somewhat less advantage these initial and ending boiling points may be as much as 15 °F. above or below the stated values. It contains considerable amounts of high boiling distillate, e.g. 10-20% by volume, of monomethyl naphthalenes, but only small amounts of gasoline, and substantially no polymethyl naphthalenes. This naphthalene fraction is then transferred to a surge drum 59 which may also serve as a steam stripping vessel. Steam may be admitted near the bottom thereof via line 52 and the overhead vapor, comprising steam and light ends, is taken off via line 54 and returned to column 38 at a point somewhat above the out-
let into line 48. Steam from the stripping effluent rises through column 38 and is condensed via line 40 into reflux drum 42. The resulting aqueous phase is withdrawn via line 56. The methyl naphthalene fraction is withdrawn from column 38 as a second-cut effluent, which may be located about the 24th plate down the column where the column temperature is about 520°F. The boiling range of this fraction is preferably about 450° to 550°F, but to somewhat less advantage, these initial and end-boiling points may be as much as 25°F above or below the stated values. The overall purpose is to obtain a relatively rough but inexpensive fractionation so as to recover most of the methyl naphthalenes for recycle and to exclude from this fraction most of the naphthalene and substantially all of the high boiling, catalyst-deactivating components. If it is desired to remove light ends from the methyl naphthalene fraction, it is transferred to a second surge vessel 60 into which steam for stripping is introduced via line 62. The stripping effluent from vessel 60 is taken off via line 64 and returned to column 38 at a point somewhat above side-cut outlet line 58. The steam contained therein passes upwardly through column 38 as does the steam from line 54, and is condensed and exhausted via line 56. Naphthalene boiling range components returned via line 64 are fractionated upwardly and recovered via naphthalene side-cut line 48. The stripped product from stripping vessel 60 is taken off via line 4 and makes up the total feed to reactor 2. The bottoms product from column 38 is taken off via line 66 and removed from the system for use as fuel oil or any other desired purpose. A portion thereof may be returned as bottoms reflux via line 68 if sharper fractionation is desired.

The naphthalene fraction from surge vessel 50 is taken off via line 70, partially cooled in exchanger 72 and sent via line 74 to primary crystallizer 76, which is essentially a holding tank with a circulating stream of crystal slurry adapted to permit the building up of crystals of the desired size and purity. Pentane, or other lower paraffin hydrocarbon is added to crystallizer 76 via lines 78 and 80. This pentane serves to reduce the viscosity of the circulating slurry and facilitates the circulation thereof. It may be added in proportions ranging between about 0.1 and 3 volumes per volume of fresh naphthalene fraction admitted to crystallizer 76. In this primary crystallizing unit, the temperature is preferably maintained at about 90° to 110° F. by means of heat exchanger 77. A portion of the slurry from line 84 is recirculated via line 82 at a rate sufficient to provide about 1 to 20 volumes thereof per volume of undiluted liquid in line 74. This recirculating slurry provides crystal nuclei for the growth of crystals, and also permits high fluid velocities through exchanger 77, thereby preventing the deposition of crystals on the tube walls. The average holding time in crystallizer 76 may be about 0.2 to 3 hours.

The net product from crystallizer 76 is then transferred via line 84 and, at a high velocity through cooler 86 (to prevent crystal deposition on the tube surfaces), to the second crystallizing unit 88 which may be similar in construction to crystallizer 76. The temperature in crystallizer 88 is maintained between about 10° and 40° F., preferably about 30° F., by means of cooler 86. Here again, a circulating stream of slurry is maintained via line 90 in order to provide adequate nuclei for crystal growth. If desired, additional pentane may be added via line 92 to keep the viscosity sufficiently low for convenient handling. The pentane added at this point may, for example, be wash liquor derived from the final washing of naphthalene to be subsequently described.

The net effluent from crystallizer 88 is transferred via line 94 to a conventional centrifugation unit where the mother liquor is separated from the naphthalene by centrifugation. The solid naphthalene which separates in centrifuge 99 may be washed near the discharge end thereof with additional pentane added via line 98, and the resulting wash liquor used as previously described in crystallizer 88. The washing step serves to remove adhering mother liquor. The washed naphthalene is then transferred via line 100 to a steam heated holding tank 101, in which the remaining solvent is vaporized, together with a small amount of naphthalene. These solvent and naphthalene vapors are conveniently recovered by recycling them to crystallizer 88 via lines 103 and 92. By using a low-boiling solvent in this manner we entirely avoid air drying with its attendant loss of naphthalene by vaporization. The solvent-free naphthalene in holding tank 101 is withdrawn via line 105 and sent to storage facilities not shown. Naphthalene recovered in this manner is normally 99.5% pure, and may be rendered substantially 100% pure with an additional pentane wash.

The mother liquor from centrifuge 96 is taken off via line 102 and transferred to depanterizer column 104 in which the pentane is distilled overhead via line 106 and returned to the process via line 78. Fresh make-up pentane may be added via line 108.

The bottoms from column 104 is composed largely of monocyclic aromatic hydrocarbons and monomethyl naphthalenes, and can ultimately be converted to high quality gasoline and naphthalene by dealkylation. It is hence transferred via line 110 to surge vessel 60 where it mixes with the methyl naphthalene fraction from column 38, the resulting mixture constituting the equilibrium feed to the dealkylation step. This feed mixture is passed via line 4 and preheater 6 to reactor 2 as previously described.

It will be apparent that the naphthalene recovered via line 105 is derived both from fresh feed and from the dealkylation product. It has been found distinctly desirable to recover the fresh feed naphthalene in this manner in order to avoid unnecessary decomposition thereof during dealkylation. It is highly desirable to provide a reactor feed containing as little naphthalene as is consistent with economical removal thereof. The process of this invention provides a distinctly advantageous and economical method for recovering naphthalene from both the fresh feed and the recycle oil whenever the fresh feed contains as much as 3% by weight of naphthalene, and preferably more than about 6%. Where the fresh feed contains less than 3% naphthalene, it is normally disadvantageous to blend it with the dealkylation product because it will then act as a more solvent in the crystallization stage and will tend to lower ultimate naphthalene yields.

The following example is cited to illustrate the results obtainable in a specific adaptation of the foregoing process, but is not to be construed as limiting the scope of the invention:

EXEMPLARY

**Fresh dealkylation feed,**—522 b.d. (barrels/stream day) of a 356°F. reformate fraction, the reformate being obtained by reforming a pre-hydrogenated 385°F. end-point blend of straight-run naphtha, cracked naphtha and coker distillate. The reforming conditions are:

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt. percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monocyclic aromatics</td>
<td>35.3</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>15.2</td>
</tr>
<tr>
<td>Monomethyl naphthalene</td>
<td>31.0</td>
</tr>
<tr>
<td>Dimethyl naphthalenes</td>
<td>10.4</td>
</tr>
<tr>
<td>C13+ components</td>
<td>7.3</td>
</tr>
</tbody>
</table>

The fresh dealkylation feed has the following analysis.

**Catalyst,**—0.35% pt. on activated alumina.

**Temperature,**—950° F.

**Pressure,**—500 p.s.i.g.

**LHSV,**—2.5

**H2/Feed,**—9,000 s.c.f./b.
Dealkylation conditions:
 Catalyst  
 9/ MoO₃, 3% Co₂O₃, 1% NaOH impregnated on a 95% Al₂O₃-5% SiO₂ carrier. (½" pellets).

Temperature, av. bed 1025°F.  
Pressure  
1,000 p.s.i.g.  
H₂/oil ratio  
6,540 s.c.f./lb.  
Steam/oil mole ratio 1.63.  
LHSV 1.0.

Fractionation of Fresh Feed Plus Dealkylation Effluent

Column conditions:  
No. of plates 40.  
Reflex ratio 8.6.  
Temperature gradient...  
Naphthalene side-cut 350–620°F.  
withdrawal Plate No. 12.  
Methyl naphthalene side-cut withdrawal Plate No. 24.

Products from column:  
Overhead 200 b/d. of 400°F. end point gasoline. (Octane No., 104–105 F-I., clear).  
Naphthalene side-cut 774 b/d. 400–450°F. boiling range, about 65 wt. percent naphthalene.  
Methyl naphthalene side-cut 373 b/d. 450–550°F. boiling range.  
Bottoms 30 b/d. boiling range 550°F.+

Crystallization of Naphthalene from Naphthalene Side-Cut

Primary crystallizer:  
Temperature 100°F.  
Ratio pentane/fresh side-cut feed 0.7 v/v.  
Average residence time 65 minutes.

Secondary crystallizer:  
Temperature 30°F.  
Ratio pentane/fresh side-cut feed 0.9 v/v.  
Average residence time 60 minutes.

Naphthalene recovery (78° C. M.P.):  
Wt. percent of fresh reformate feed... 49  
Wt. percent of naphthalene in naphthalene side-cut 85  
Overall yield based on mole-percent of naphthalene components in reformate feed 90  
Mother liquor recovery (solvent-free) b/d. 527

Total equilibrium feed to dealkylation:  
Solvent-free mother liquor b/d. 527  
Methyl naphthalene side-cut b/d. 373  
Total b/d. 900

It will thus be apparent that the fresh feed is converted to the following products:

Wt. percent of feed  
Light gases, mainly methane 10  
Gasoline (400°F. end-point, 104–105 F-1 clear octane No.) 35  
Naphthalene (79° C. M.P.) 49  
Fuel oil (550°F. + fraction) 6

As a result of using a 356°F. + reformate feed in the foregoing example, the yield of gasoline is somewhat higher than would normally be obtained. In using the preferred feedstocks with an initial boiling point between 380° and 410°F., the typical gasoline recovery is about 20–30%, while the naphthalene recovery is about 50–60% by weight.  

Obviously, the details of the foregoing example may be varied considerably as to feeds, catalysts, dealkylation conditions, product recovery and recycle stream recovery without departing from the invention. The true scope of the invention is intended to be defined by the following claims.

We claim:

1. A method for fractionating a hydrocarbon mixture made up essentially of (1) aromatic gasoline-boiling range hydrocarbons, (2) naphthalene, (3) methyl naphthalenes, and (4) heavy aromatic hydrocarbons boiling above the methyl naphthalene range to obtain each of said components in maximum purity, which comprises admitting said mixture to a fractionating column containing 25 to 60 plates, adding heat in the lower section to effect boil-up in the column and to develop a temperature gradient therein, removing a liquid naphthalene fraction from said column at about the 450–470°F. temperature level therein, subjecting said naphthalene fraction to steam stripping to strip out light ends and form a first stripping effluent, returning said first stripping effluent to the column at a point slightly above the point of removal of said naphthalene fraction, removing a methyl naphthalene fraction from said column at about the 510–530°F. temperature level therein, subjecting said methyl naphthalene fraction to steam stripping to strip out light ends and form a second stripping effluent, returning said second stripping effluent to the column at a point slightly above the point of removal of said methyl naphthalene fraction, removing overhead from said column a vapor mixture of steam and gasoline-boiling-range hydrocarbons at a temperature of about 340–360°F., condensing said gasoline-boiling-range hydrocarbons and separating water therefrom, returning about 6 to 12 volumes/hour of said gasoline condensate to the upper section of said column as reflux, withdrawing about one volume/hour thereof as not gasoline product, and removing a liquid bottoms product from said column about 610–630°F.

2. A method as defined in claim 1 wherein said hydrocarbon mixture is a blend of (1) a naphtha reformate fraction boiling above about 380°F., and (2) a dealkylation effluent obtained by the catalytic dealkylation of (a) said methyl naphthalene fraction and (b) said naphthalene fraction after removal therefrom of naphthalene.

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