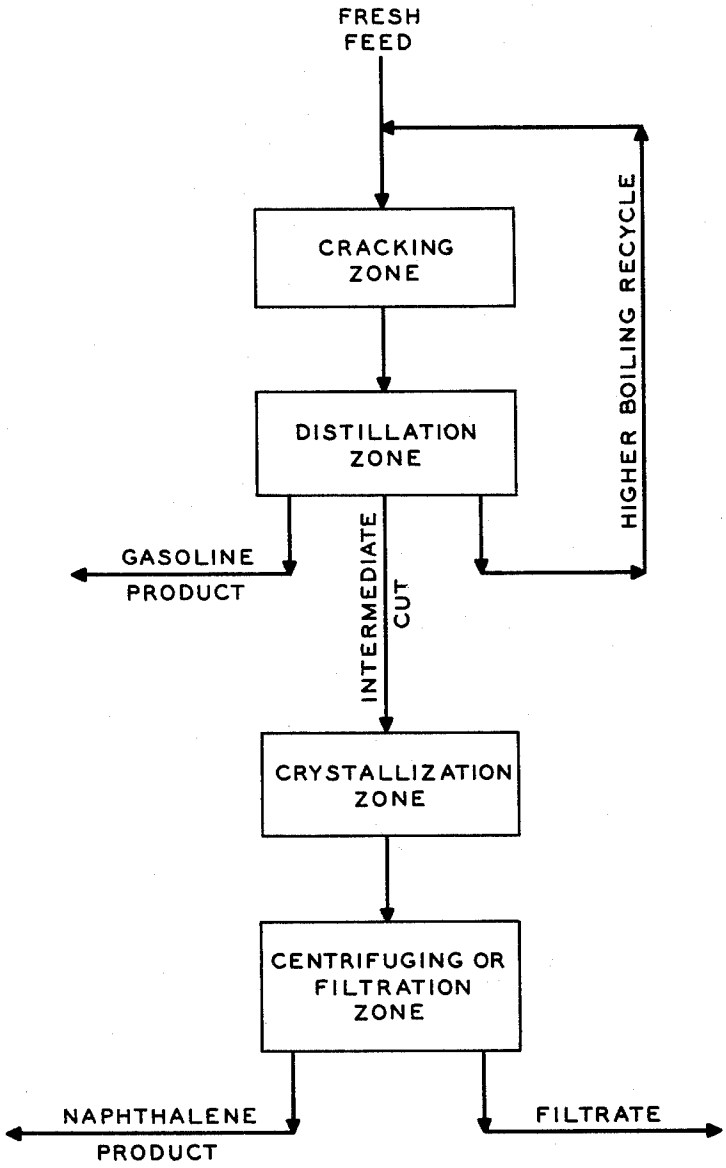
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PRODUCTION OF NAPHTHALENE

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PRODUCTION OF NAPHTHALENE

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This invention relates to a process for obtaining naphthalene as a by-product of catalytic cracking of petroleum for gasoline production.

Catalytic cracking of petroleum as generally practiced involves contacting a heavy gas oil or topped crude oil with a silica-alumina catalyst at a temperature about 925° F. and a liquid hourly space velocity about 3 weight units of oil per weight unit of catalyst per hour. Generally, conversion of fresh feed to 430 end point gasoline is about 45 volume percent and about 60 percent of the total feed to the cracking zone is fresh feed and the remainder is recycle stock. When the catalytic cracking unit is operated in this manner, the fraction of the effluent from the cracking zone boiling from about 400° to 450° F. has an appreciable naphthalene content of polynuclear aromatic hydrocarbons including naphthalene, but its naphthalene content is so small that economic recovery of naphthalene from such a stream is not feasible.

It is the object of the present invention to provide a method of operating a conventional catalytic cracking unit to produce a naphthalene-rich fraction in the effluent from which substantial quantities of naphthalene may be economically recovered as a by-product of the process.

Pursuant to the present invention, the catalytic cracking unit is operated under conditions sufficiently severe to cause a much higher conversion of fresh feed to gasoline than is typical of normal operation of the cracking unit and at a much higher ratio of recycle stock to fresh feed than is characteristic of conventional operation.

More particularly, in the practice of the present invention a fresh feed boiling in the range about 500° to 1050° F. is passed into a catalytic cracking zone and there contacted with a petroleum cracking catalyst at a temperature in the range about 850° to 1000° F. and at a liquid hourly space velocity in the range about 0.5 to 4.0 w./w./hr. The effluent from the cracking zone is fractionally distilled to separate a lower boiling gasoline fraction, an intermediate fraction boiling over a range of not exceeding 100 Fahrenheit degrees, and preferably about 75 Fahrenheit degrees, and including all of the 400–430 fraction of the effluent and a bottoms fraction. The major portion of the bottoms fraction including its lower boiling portion is returned to the cracking zone and a volume ratio of returned bottoms fraction to fresh feed above about 1.5 is maintained. The temperature and space velocity are adjusted within the ranges stated above so as to maintain conversion of fresh feed above 80%.

Percent conversion of fresh feed as used herein is obtained by expressing the fraction of the final liquid product boiling above 430° F. as volume percent of fresh feed and subtracting that value from 100. The intermediate fraction is rich in naphthalene and naphthalene is recovered from it.

The appended drawing is a block diagram showing the process flow employed in the practice of the invention.

The fresh feed subjected to catalytic cracking may be a heavy gas oil or a topped crude oil generally boiling from about 500° to 1050° F. The fresh feed can be obtained from any of a variety of crude oils available for catalytic cracking. Naphthenic California crudes, moderately paraffinic Arabian crudes and the highly paraffinic Minas crude are all suitable as feed sources in the practice of the invention and are generally representative of the spectrum of crude oil types available to the refiner.

Conventional cracking catalysts are employed in the practice of the invention. Natural or activated clay catalysts, synthetic silica-alumina catalysts, silica-magnesia catalysts, silica-zirconia catalysts, and the like, are all suitable for use in the practice of the invention.

The feed is contacted with the catalyst at a temperature in the range about 850° to 1000° F. and at a liquid hourly space velocity in the range about 0.5 to 4.0 w./w./hr. (weight of feed per weight of catalyst per hour). The temperature and space velocity are adjusted within the ranges above specified to maintain a conversion of fresh feed of about 80%, and generally in the range of 80 to 95%. This severity of cracking may be obtained by going to the lower end of the space velocity range described or to the upper end of the temperature range described, or by reducing space velocity and raising temperature within the described ranges. Preferably, however, the desired degree of conversion is attained by raising the recycle rate relative to fresh feed to a value exceeding 1.5/1 and maintaining the space velocity based on total feed, and the cracking temperature close to values characteristic of conventional catalytic cracking.

The effluent from the catalytic cracking zone is fractionally distilled to separate a gasoline product fraction having an end point from 365° F. to about 400° F., an intermediate fraction boiling over a range less than 100 Fahrenheit degrees and including essentially all of the 400–430 fraction of the effluent and a bottoms fraction having an initial boiling point approximately the same as the end point of the intermediate fraction. At least the lower boiling portion of the bottoms fraction is returned to the catalytic cracking zone as recycle and generally all of the bottoms fraction except minor proportions of heavy ends are recycled to the cracking zone.

The intermediate fraction is controlled so that its boiling range does not exceed about 100 Fahrenheit degrees. Such a fraction containing essentially all of the 400–430° portion of the effluent is readily separated by the distillation equipment generally installed and in use in connection with catalytic cracking units and will have a naphthalene content above 20% by volume. Narrow boiling fractions much richer in naphthalene may be separated, but their separation requires installation of distillation equipment more elaborate than that normally available as an adjunct to an existing catalytic cracking unit.

The intermediate fraction is subjected to conventional treatment for naphthalene recovery. Naphthalene may be recovered simply by cooling the intermediate fraction to ambient temperature and allowing it to stand until naphthalene crystals form, usually from about 50 to 200 hours. If desired, the intermediate fraction can be cooled to 40° F., or lower, to cause more rapid deposition of the naphthalene crystals.

If desired, the intermediate fraction can be extracted with a solvent selective for aromatic hydrocarbons such as sulfur dioxide or an aqueous alkylene glycol to recover an extract very rich in naphthalene from which the naphthalene can then be separated by crystallization.

After the naphthalene crystals have formed, the slurry is filtered or centrifuged to recover a naphthalene filter cake and a filtrate of reduced aromatic content. The filter cake may be washed with a low boiling hydrocarbon such as pentane to remove interstitial mother liquor and final purification may be made by distillation or recrystallization. Alternatively, naphthalene can be recovered by selective adsorption on silica-gel or by azeotropic distillation as described in U.S. Patent 3,043,890.

Naphthalene was produced pursuant to the invention in the following run:

A fresh feed derived from blended Arabian and Minas crudes, boiling from 600° to 1050° F. was catalytically cracked used a silica-alumina cracking catalyst containing 32% alumina under the following conditions:

Cracking temperature, ° F.	878
Space rate, total feed, wt./hr./wt.	2.3
Recycle, ratio to fresh feed v./v.	2.0
Conversion, 430° F. TBP, vol. percent	89.5

Yields based on fresh feed of net liquids were as follows (approximate cut points):

	Vol. percent
90–300° F. gasoline	34.5
300–430° F. gasoline	24.0
430–600° F. light cycle oil	4.0
600° F.+ heavy cycle oil	6.5

Concentration of naphthalene in plant distilled streams was observed to be:

	Vol. percent
90–300° F. gasoline	0
300–430° F. gasoline	5.4
430–600° F.	6.0
600° F.+ heavy cycle oil	0

The naphthalene content of the 365–440° F. fraction specifically separated for treatment to recover naphthalene is 36% by volume. The naphthalene content of the 360°–460° F. fraction is 25% by volume. The naphthalene recovered by crystallization melted at 79.2° C.

I claim:

Process for obtaining naphthalene as a by-product of catalytic cracking of petroleum to produce gasoline, which comprises:

(1) passing a petroleum distillate feed boiling within the range about 500° to 1050° F. into a cracking zone and there contacting it with a petroleum cracking catalyst at a temperature in the range about 850° to 1000° F. and at a liquid hourly space velocity in the range about 0.5 to 4.0 w./w./hr.,

(2) fractionally distilling the effluent from the cracking zone to separate a lower boiling fraction having an end point about 400° F., an intermediate fraction boiling over a range not exceeding 100 Fahrenheit degrees and containing essentially all of the 400–430° F. fraction of the effluent and a bottoms fraction having an initial boiling point approximately the same as the end point of the intermediate fraction,

(3) returning at least the lower boiling portion of the bottoms fraction to the cracking zone and maintaining the volume ratio of the returned bottoms fraction to fresh feed above about 1.5,

(4) adjusting temperature and space velocity within the ranges set forth above to maintain conversion of fresh feed above 80%,

(5) and separating naphthalene from the intermediate fraction.

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