Dec. 7, 1943. J. HAPPEL 2,336,244

RECOVERY OF NAPHTHALENE

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Fig. 1

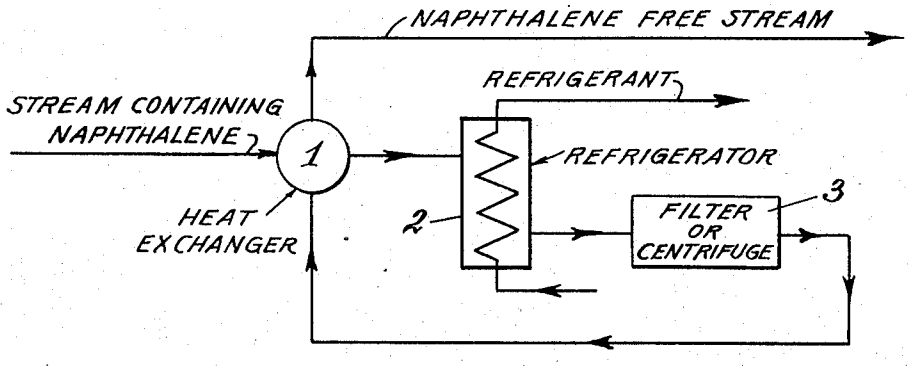
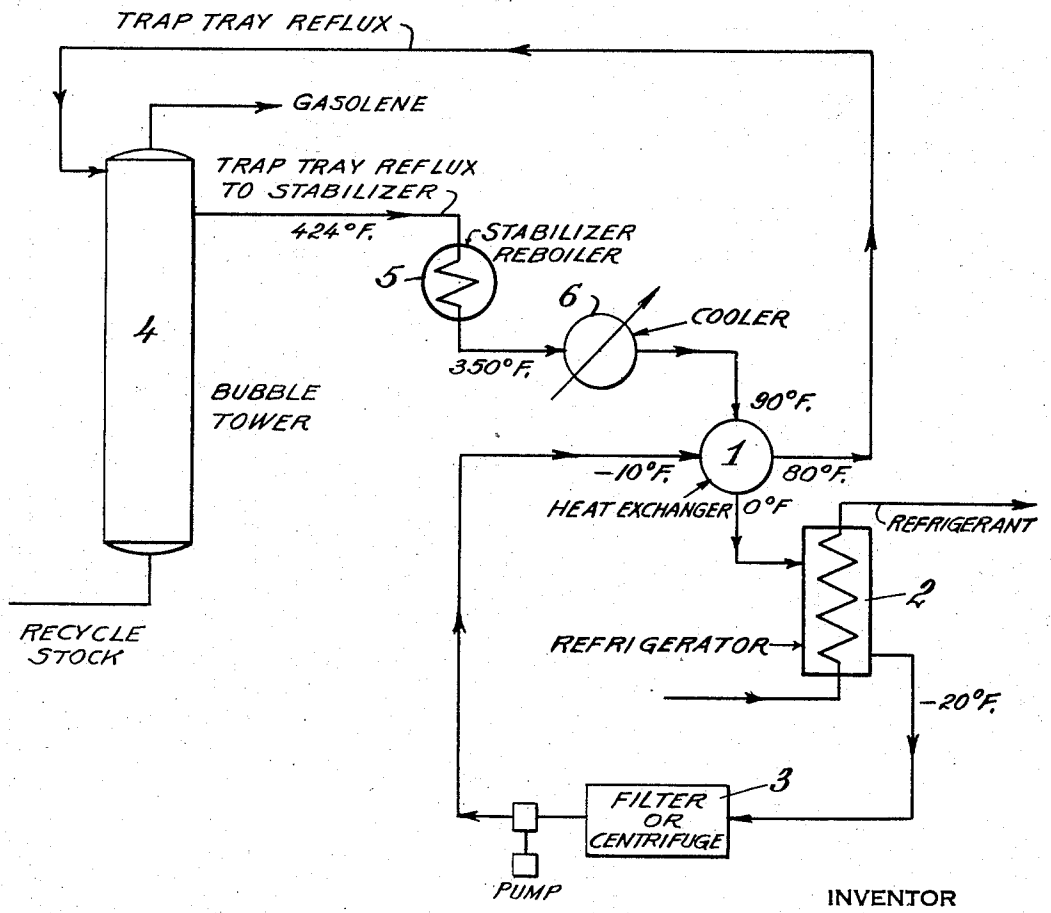


Fig. 2.



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RECOVERY OF NAPHTHALENE

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Application February 7, 1939, Serial No. 255,040

1 Claim. (Cl. 260—674)

The present invention relates to the recovery of naphthalene from cracked petroleum products. More particularly this invention relates to the recovery of naphthalene in gasoline cracking processes.

It is an object of my invention to recover a valuable by-product from gasoline cracking processes.

Another object of my invention is to afford a process for recovery of naphthalene from a suitable cracked petroleum fraction of a gasoline liquid phase cracking process.

It is well known that light aromatic hydrocarbons such as benzene and naphthalene may be formed by subjecting petroleum oils to thermal cracking at very high temperatures. For instance, Ellis in Chemistry of Petroleum Derivatives (1934) pages 161 and 162, outlined the prior art on this subject by stating that in general "(1) Temperatures from 500° to about 600° C. yield principally mixtures of olefine and paraffin hydrocarbons; (2) at about 650° C. and above diolefines are formed; and (3) at 700° C. and slightly above, aromatic hydrocarbons are produced in quantity." It has been the prevailing opinion throughout the art that in order to produce aromatics such as benzene or naphthalene, temperatures around 600° to 700° C. must be used, and at temperatures of conventional liquid phase cracking for gasoline, i. e., temperatures below 1000° F. (538° C.) such aromatic compounds are not formed at all.

My invention is based upon the discovery that naphthalene is produced in appreciable quantities under certain conditions during the cracking of petroleum oils to gasoline at temperatures below 1000° F. Thus contrary to the prior knowledge of the art, I have found that in the conventional gasoline liquid phase cracking of petroleum oils free of naphthalene at temperatures below 1000° F., e. g., 800° F., to 1000° F., an appreciable quantity of naphthalene is formed and as a result of its boiling point normally tends to accumulate in the recycle stock. According to my invention a suitable fraction of the cracked product, e. g., the recycle stock for the cracking operation or a trap tray reflux from the bubble tower, which would contain the naphthalene is subjected to a recovery process for the naphthalene.

The recovery of the naphthalene from the stream containing it may be effected continuously or intermittently since the naphthalene merely accumulates in the cycle stocks if not removed at once, thereby causing the concentration to increase as the cracking progresses. The reason for this is because the pressure still tar does not contain large percentages of fractions boiling as low as naphthalene (424° F.) and, if proper fractionation is applied to the separation of the gasoline, all naphthalene will remain in the cycle stocks and its concentration increase since naphthalene is more refractory than the bulk of cycle stock. The amount of naphthalene that is recovered varies with the charging stock, cracking conditions, length of run, etc. In a cycle stock from cracking Mid-Continent gas oil at 960°–967° F. transfer line temperature and 790 lbs./sq. in pressure, the concentration of naphthalene was 0.36 lb./bbl. of cycle stock after three days of operation.

Accordingly, my invention based upon my discovery that naphthalene occurs in the cycle stocks of gasoline cracking processes affords a valuable new by-product for such processes that may be easily recovered. The recovery is preferably accomplished by suitable cooling to precipitate the naphthalene and then removing the precipitated naphthalene by filtering or centrifuging. It is desirable of course to utilize as much heat as possible in cooling by suitable heat exchange. The temperature to which the stream must be cooled in order to precipitate the naphthalene will vary depending upon the composition of the stream. Temperatures as low as —20° C. or lower may have to be used in some cases, while in other instances precipitating temperatures considerably higher, e. g., +32° F. may be adequate.

The invention will be further described with reference to the accompanying drawing wherein

Figure 1 is a flow diagram of a typical recovery system for the naphthalene that may be applied to any naphthalene-containing stream, and

Figure 2 is a flow diagram showing a preferred manner of recovering the naphthalene from the trap tray reflux leaving the bubble tower of a cracking unit.

Referring to Figure 1, a suitable stream of the refinery such as the recycle stock or bubble tower trap tray reflux containing naphthalene is cooled by passing through heat exchanger 1 in indirect heat exchange with the cool stream after removal of naphthalene. From exchanger 1 the stream containing naphthalene passes to refrigerator 2 wherein it is cooled sufficiently to precipitate the naphthalene and then the stream is passed to filter or centrifuge 3 wherein the precipitated naphthalene is separated. The cool naphthalene-free stream is then sent through exchanger 1 to whatever use it is to be put.

In Figure 2 the trap tray reflux is drawn off

from bubble tower 4 at about 424° F., and is used to heat the reboiler 5 of a stabilizer tower (not shown). From the reboiler 5 the reflux passes through a suitable water cooler 6. On leaving cooler 6 the reflux passes through a naphthalene recovery system similar to that shown in Figure 1, comprising heat exchanger 1, refrigerator 2, and filter or centrifuge 3. The cool naphthalene-free reflux leaving filter 3 is pumped back through heat exchanger 1 to the top of bubble tower 4.

I claim:

The process of producing naphthalene which comprises cracking a charging stock consisting only of Mid-Continent gas oil in liquid phase to gasoline under cracking conditions in the absence of added hydrogen at a temperature between about 800 and 1000° F., separating cracked product into gasoline, recycle, and residuum fractions, cooling the recycle stock fraction until naphthalene contained therein is precipitated, and then recovering said precipitated naphthalene prior to recharging the recycle fraction to the cracking operation.

JOHN HAPPEL.