AROMATIC RECOVERY USING HYDROGEN FLUORIDE AND COPPER FLUORIDE

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Application June 23, 1958, Serial No. 743,557

17 Claims. (Cl. 260—674)

This is a continuation-in-part of our copending application Serial Number 572,948, filed March 21, 1956 and now abandoned.

This invention relates to the separation of aromatic hydrocarbons from non-aromatic hydrocarbons. An object of the invention is a separation of aromatic hydrocarbons from admixture with non-aromatic hydrocarbons. Another object of the invention is the separation of polycyclic aromatic hydrocarbons from non-aromatic hydrocarbons. A particular object of the invention is the removal of aromatic hydrocarbons from petroleum distillates, such as catalytic reformates, naphthas and light gas oils. Another object is the separation of aromatic hydrocarbons from admixture with non-aromatic hydrocarbons, which extracted hydrocarbons contain only small amounts of non-aromatic hydrocarbons. Other objects will become apparent in the course of the detailed description.

It has been found that liquid HF in combination with copper fluoride is an extremely effective agent for the separation of aromatic hydrocarbons from admixture with non-aromatic hydrocarbons. The aromatic hydrocarbons appear to form a HF-soluble complex with the copper fluoride, in the presence of liquid HF, and are dissolved into the liquid HF acid phase.

The copper fluorides, namely, cuprous fluoride and cupric fluoride do not appear to react with aromatic hydrocarbons when the two are contacted. In the presence of liquid hydrogen fluoride, in an amount exceeding the solubility of the HF in the aromatic hydrocarbon, copper fluorides form a complex containing copper fluoride and aromatic hydrocarbon. Copper fluoride is essentially insoluble in liquid HF alone. When solid copper fluoride, sufficient liquid HF, and an aromatic hydrocarbon are contacted, the solid copper fluoride disappears completely, when sufficient aromatic hydrocarbon is present. By controlling the amount of aromatic hydrocarbon and using sufficient liquid HF, it is possible to have the three materials merge into a single homogeneous solution. That some chemical reaction has occurred is evidenced by the change in color of the liquid HF with particular aromatic hydrocarbons. For example, a solution formed from liquid HF, cuprous fluoride and methyl(naphthalene is a brilliant red in color. When the aromatic hydrocarbon is in admixture with non-aromatic hydrocarbons, a separate HF-insoluble phase, i.e., raffinate phase, is then present in the system.

This raffinate phase, when analyzed, contains less aromatic hydrocarbon than did the original mixture. By the use of sufficient copper fluoride and liquid HF, it is possible to produce a raffinate phase which is substantially free of aromatic hydrocarbons, i.e., will contain not more than 5% or 6% of aromatic hydrocarbons. The degree of aromatic hydrocarbon removal is dependent in part on the effectiveness of the contacting of the liquid HF, the copper fluoride, and the feed mixture.

An outstanding characteristic of the liquid HF-copper fluoride extracting agent is the fact that the extract recovered from the acid phase is substantially free of non-aromatic hydrocarbons, even in a one-step contacting operation, i.e., the extract generally contains in excess of 93-94% percent of aromatic hydrocarbon.

The amount of aromatic hydrocarbon extracted is dependent on the amount of copper fluoride present in the contacting zone and also on the amount of liquid HF present therein. Providing sufficient liquid HF to form a distinct separate acid phase is present, even trace amounts of copper fluoride will markedly reduce the aromatic content of the raffinate phase. The two copper fluorides do not behave in the same manner with respect to extraction efficiency. Cuprous fluoride appears to form a complex which contains 2 moles of aromatic hydrocarbon per mole of cuprous fluoride; thus, theoretically, the use of 0.5 mole of cuprous fluoride per mole of aromatic hydrocarbon present in the feed mixture will remove all of the aromatic hydrocarbons into the acid phase. Cupric fluoride appears to form a complex which contains only 1 mole of aromatic hydrocarbon per mole of cupric fluoride.

More than the theoretical requirement for complete extraction of the aromatic hydrocarbons may be introduced into the contacting zone. There does not appear to be any considerable beneficial result from the use of amounts much in excess of the theoretical requirement. The excess copper fluoride, when in the form of a powder, tends to accumulate at the interface between the raffinate phase and the acid phase and may, under some conditions, interfere with phase separation, causing raffinate phase to be withdrawn along with acid phase. It is preferred to operate either with the amounts of copper fluoride theoretically needed to remove the amount of aromatic hydrocarbons wanted to be extracted, or with the amount theoretically needed to extract all the aromatic hydrocarbons present in the feed mixture. It appears that by the use of an efficient contacting of particularly multi-stage operation, it is possible to remove virtually all the aromatic hydrocarbons from the feed into the acid phase when using 0.5 mole of cuprous fluoride per mole of aromatic hydrocarbon in the feed mixture or 1 mole of cupric fluoride per mole of aromatic hydrocarbon in the feed mixture.

It is necessary that the copper fluoride used be in the anhydrous form. The cuprous fluoride dihydrate available commercially does not form a complex with aromatic hydrocarbons in the presence of HF.

The presence of water has a deleterious effect on the extraction efficiency of the liquid HF-copper fluoride extracting agent. The process is carried out under essentially anhydrous conditions. The liquid hydrogen fluoride utilized in the process should be anhydrous or essentially so. The commercial grade anhydrous hydrofluoric acid which contains on the order of 1−2% weight percent of water is suitable for use in the process.

Some aromatic hydrocarbons can be extracted from a feed mixture by the use of copper fluoride in combination with just enough liquid HF to form a distinct separate acid phase. The separation efficiency of the agent, as measured by the moles of aromatic hydrocarbon extracted per mole of copper fluoride present, increases rapidly as the amounts of liquid HF present is increased, up to about 3 moles of HF per mole of aromatic hydrocarbon in the feed mixture. More than this amount is helpful in phase separation and in improving the contacting. It is preferred to operate with between about 5 and 15 moles of HF per mole of aromatic hydrocarbon in the feed. It is to be understood that more than this amount of HF may be used. Large amounts of HF are...
helpful when operating at low temperature with a viscous feed. Put in another way, the liquid HF usage may be between 30 and 150 volume percent, based on the total feed mixture. This usage of liquid HF is particularly suitable when the feed to the process is a petroleum distillate containing between 25 and 75 volume percent of aromatic hydrocarbons, for example, a catalytic reformate.

The copper fluoride may be introduced into the contacting zone either in the form of a solid powder or as a slurry in the liquid HF or even as a dispersion in the feed mixture. Or the solid powder may be introduced in the seed acid phase present in the contacting vessel. It is preferred to introduce the copper fluoride as a dispersion in the liquid HF portion of the agent. It appears that all aromatic hydrocarbons will form the complex with copper fluorides. The aromatic hydrocarbons may contain a single benzene ring or contain condensed benzene rings. The aromatic pyrocarbon may contain substituents on the ring or may be condensed rings wherein 1 or more of the rings is parafinic or olefinic in nature. Examples of suitable benzene hydrocarbons are benzene, toluene, xylene, such as m-xylene, the various other polyarylmethylbenzenes, such as mesitylene, isodurene and exemethylbenzene, ethylbenzene and the various polyethylenethanes, isopropybenzene, and the various polyisopropylbenzenes, also the various butyl and pentyl derivatives, such as t-butylbenzene, 2-phenylpenta- nene, etc.; in addition to these, the substituted benzenes containing 2 or more different substituents such as ethyl- toluene, isopropyltoluene, and ethylxylene. Examples of the naphthalene hydrocarbons which are suitable are naphthalene, the various methylidenaphthalenes, poly- methylidenaphthalenes, ethylnaphthalene and the various polyethylenenaphthalenes, also the naphthalenes containing propyl, isopropyl, butyl, t-butyl and pentyl substituents. The naphthalenes containing olefinc substituents are suitable, for example, ethenyl naphthalene, propenyl naphthalene, and pentenyl naphthalene. The various indanes are suitable. For example, methyl indanes, ethyl indanes, isopropyl indanes, etc. The various dicyanidnaphthalenes are suitable, such as the methyl, ethyl, propyl, and butyl substituted dicyanidnaphthalenes. The various trihy- drenaphthalenes are suitable, such as the methyl, ethyl, propyl, t-butyl and pentyl substituted tricyanidnaphthalenes.

It is preferred to utilize benzene, naphthalene, and the various alkylbenzenes and alkynaphthalenes whose alkyl groups contain not more than 5 carbon atoms. Examples of these are benzene, ethylbenzene, toluene, meta- xylene, naphthalene and a-methylnaphthalene. In addition to the aromatic complexes, the copper fluorides also form complexes with organo-sulfur compounds, such as mercaptans, thioethers, and disulfides. In gener- al, these organo-sulfur compound-copper fluoride complexes are much more stable than the aromatic hydrocarbon-copper fluoride complexes. It is difficult to recover the aromatic hydrocarbon from these organo- sulfur compound complexes. It is possible to separate a mixture of the aromatic hydrocarbon complex and the sulfur compound complex by decomposing the aromatic hydrocarbons and separating the decomposed aromatic hydrocarbons from the copper fluoride-organosulfur compound complex. In view of the difficulty of decom- plexation of the organo-sulfur compound complex, it is preferred to operate on a feed mixture of aromatic hydrocarbons and non-aromatic hydrocarbons which is substantially free of organo-sulfur compounds. Olefinic hydrocarbons in the presence of the liquid HF tend to alkylate the aromatic hydrocarbons. When it is desired to avoid degradation of aromatic hydrocarbons such as benzene, toluene, xylene, and ethylbenzene, it is preferred to use a feed which is essentially free of olefinic hydrocarbons. A suitable feed to the separation process of the invention is a petroleum distillate boiling below about 700° F. The distillate boiling between about 100° F. and 450° F., i.e., the gasoline range, derived from the product of the catalytic reforming in the presence of hydrogen, of petroleum naphthenes is particularly suitable as a source of aromatic hydrocarbons because of its very low sulfur content and olefinic hydrocarbon content. The entire naphtha boiling range material of the catalytic reformate may be used or any one of the narrower boiling range cuts closely boiling about a particular aromatic hydrocarbon, for example, the benzene fraction, the toluene fraction by the C8 aromatic hydrocarbon fraction. The HF, copper fluoride mixtures required to carry out a step may be carried out at a temperature between about - 40° C. and 150° C. In general, at temperatures above 150° C., many aromatic hydrocarbons, such as alkyl naphthenes, undergo cracking reactions with formation of tar and gases. Other aromatic hydrocarbons may be treated at temperatures well in excess of 150° C. Other sensitive aromatic hydrocarbons may need to be treated at temperatures below 150° C. The process operates very effectively at ambient temperatures and for this reason it is preferred to operate at temperatures between about 10° C. and 35° C.

As the contacting step involves a reaction between solid copper fluoride, aromatic hydrocarbons, and probably some liquid HF, maximum extraction efficiency requires that the contacting be carried on for a sufficient time. The degree of agitation appears to be the controlling factor in the attainment of maximum yields. With efficient agitation, contacting times on the order of 5 minutes are sufficient. With inefficient agitation, times as much as 1 hour or more may be needed.

It is to be understood that the contacting operation requires the presence of liquid hydrogen fluoride. Therefore, the contacting zone must be maintained at a pressure sufficiently high to keep the HF in the liquid state. The aromatic hydrocarbons pass into the liquid HF to form a solution containing liquid HF and an HF-soluble complex containing copper fluoride and aromatic hydrocarbons. In addition to these, the solution will contain physically dissolved non-aromatic hydrocarbons. Also, the solution will contain organo-sulfur compounds which have reacted with copper fluoride to form an HF-soluble complex. The complex appears to decompose readily at moderate temperatures. By the time all the HF has been distilled from the distillation zone, there will remain behind precipitated solid copper fluoride, and possibly some aromatic hydrocarbons. In the case of the lower boiling aromatic hydrocarbons, all or substantially all of the aromatic hydrocarbons will also distill over during the recovery operation. The complex of organo-sulfur compounds and copper fluoride is much more stable than the complex of aromatic hydrocarbon and copper fluoride. This complex may still be present in the distillation zone after HF has ceased to distill over. For example, a solution containing HF, diethyl sulfide, and cuprous fluoride has to be heated to 400° C. at atmospheric pressure for some hours before all the HF has been distilled over and the cuprous fluoride recovered completely as such. It is not necessary to decant the non-aromatic rich raffinate phase from the liquid HF solution in order to obtain a separation between the two classes of hydrocarbons. In general, the feed mixture has been contacted with the liquid HF and copper fluoride for a period comprising liquid HF and dissolved complex, a non- aromatic hydrocarbon-rich fraction may be obtained by subjecting the feed-liquid HF-copper fluoride admixture to distillation. The first hydrocarbons distilled are the non-aromatic hydrocarbons (some aromatic hydrocarbons also appear obtained) and, with the separation of a liquid HF solution remains containing essentially pure complexed aromatic hydrocarbons. This liquid HF solu-
tion is then distilled to remove these aromatic hydrocarbons overhead. This distillative separation method is particularly applicable to aromatic concentrates, e.g., mixtures containing 90 weight percent or of aromatic hydrocarbons. In this method the copper fluoride is used in an amount of at least on the order of that theoretically needed to complex the aromatic hydrocarbons in the feed, e.g., usually from about 80% to 120% of the theoretical amount.

The distillative separation method may also be used to obtain very pure aromatic hydrocarbons from ordinary feed mixtures when it is not desired to use paraffin hydrocarbon countersolvent. Thus, a raffinate phase is decanted from a liquid HF solution phase containing the aromatic hydrocarbon phase is then subjected to distillative separation to remove as the first overhead fractions the non-aromatic hydrocarbons.

In general, the distillative removal of the HF from the solution may be carried out at temperatures between about 20° C. and 125° C. Pressure has an important bearing on the temperature which is needed to be used. At the lower temperatures, it is necessary to operate with a vacuum on the system. Thus, at 20° C. it is desirable to operate with a pressure of about 1 mm. Hg. As the temperature is increased, more pressure is tolerable on the distillation zone and at about 125° C. it is possible to operate with a pressure of about 1 atmosphere or even slightly more. Thus, there is a relationship between the temperature and pressure which may be set out as the lower the temperature the lower the pressure needed, or the lower pressures correspond to the lower temperatures. The distillation may be continued only for that time needed to remove all the HF present (disregarding the amount present in complex with organosulfur compounds), leaving in the distillation zone residue of solid copper fluoride and extract hydrocarbons. Or, the distillation may be continued until all of the extract hydrocarbons have been distilled away from the distillation vessel leaving solid copper fluoride remaining therein.

When extract hydrocarbons and solid copper fluoride have been left in the distillation zone, the solid copper fluoride may be readily filtered away from the liquid hydrocarbons.

In the laboratory, the extract hydrocarbons may be readily separated from the acid phase by diluting the acid phase with cold water or dilute aqueous caustic solution. The extract forms an upper hydrocarbon phase above a lower aqueous phase. The extract may be then neutralized prior to further processing, such as distillation into close boiling fractions or even high purity aromatic hydrocarbons. The total extract contains substantially only aromatic hydrocarbons. Even in a one-step laboratory contacting, the extract will contain on the order of 94-95% of aromatic hydrocarbons.

The results obtained with the process of the invention are set out in the following illustrative examples.

With the exception of Runs 5 and 6, the runs were carried out in a Hestellog autoclave provided with a mechanical stirrer. In these runs, the solid copper fluoride and liquid HF were introduced into the autoclave followed by the particular feed mixture. The cuprous fluoride and cupric fluoride were anhydrous powders.

### TABLE I

<table>
<thead>
<tr>
<th>Run No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cuprous fluoride, g.</td>
<td>31</td>
<td>11</td>
<td>8</td>
<td>31</td>
<td>27.5</td>
<td>27.5</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>Feed</td>
<td>33</td>
<td>35</td>
<td>30</td>
<td>390</td>
<td>390</td>
<td>100</td>
<td>75</td>
<td>69</td>
</tr>
<tr>
<td>Toluene, ml.</td>
<td>61.7</td>
<td>88.0</td>
<td>34.1</td>
<td>83</td>
<td>83</td>
<td>83</td>
<td>83</td>
<td>83</td>
</tr>
<tr>
<td>n-Heptane, ml.</td>
<td>55.4</td>
<td>52.1</td>
<td>36.5</td>
<td>37.5</td>
<td>37.5</td>
<td>37.5</td>
<td>37.5</td>
<td>37.5</td>
</tr>
<tr>
<td>Vol. Percent Aromatic</td>
<td>52.6</td>
<td>62.6</td>
<td>39.1</td>
<td>32.4</td>
<td>24.5</td>
<td>24.5</td>
<td>24.5</td>
<td>24.5</td>
</tr>
<tr>
<td>Raffinate; Vol. Percent Aromatic</td>
<td>37.0</td>
<td>35.7</td>
<td>38.5</td>
<td>43.8</td>
<td>43.8</td>
<td>43.8</td>
<td>43.8</td>
<td>43.8</td>
</tr>
<tr>
<td>Feed, Vol. Percent</td>
<td>4.4</td>
<td>4.1</td>
<td>3.1</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Arom. Ext/CpF, moles</td>
<td>1.9</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>HF/Feed, Vol. Percent</td>
<td>21</td>
<td>32</td>
<td>90</td>
<td>74</td>
<td>50</td>
<td>55</td>
<td>55</td>
<td>55</td>
</tr>
</tbody>
</table>

1. Catalytically Reformate: Benzene, toluene, Cs and Cs, 48%; olefins, 1%, paraffins and naphthenes, 48%.
2. Feed, from Run 5.
4. Equimolar amounts of m-xylene and p-xylene.

In all cases, commercial grade anhydrous hydrofluoric acid containing about 1 weight percent of water was used. The toluene and n-heptane were cp grade material. In all cases, the contents of the autoclave were stirred for one hour at ambient temperature. The contents were then permitted to settle for 10 minutes. The lower acid phase was withdrawn into a polyethylene bucket containing crushed ice. The upper hydrocarbon, i.e., extract layer was decanted from the lower aqueous layer and neutralized with ammonium hydroxide solution. The neutral extract was analyzed by distillation and infrared spectrometry. The raffinate layer was neutralized and water-washed and then was analyzed by distillation and infrared spectrometry.

Table I sets out the data obtained utilizing cuprous fluoride as the copper fluoride. Runs 1, 2 and 3 were carried out under essentially the same conditions except for the amount of HF present. These runs show that over the range of HF to total feed volume ratio of .21 to .31 the amount of toluene extracted was 2 moles per mole for cuprous fluoride charged. In each of these runs, a considerable excess of toluene was present over that complexible by the cuprous fluoride charged. Run 4 was carried out using the theoretical amount of cuprous fluoride based on the toluene content of the feed. The toluene extracted per mole of cuprous fluoride charged was very close to the theoretical. In this run, the extract contained 92 mole percent of toluene and 8% of heptane. The raffinate contained only 4 mole percent of toluene.

Run No. 7 was carried out using as the feed a mixture of methylbenzene and n-heptane. Slightly more than the expected 2 moles of methylbenzene per mole of cuprous fluoride charged was taken into the acid phase. Also, the purity of the extract was greater than working with toluene or xylene, as the extract was virtually free of heptane.

Run No. 8 was carried out on a mixture of meta-xylene and para-xylene. The run shows that the cuprous fluoride is almost as effective under these conditions as with toluene.

Runs 5 and 6 were carried out on a catalytic reformate obtained from platinum reforming of a virgin naphtha. This catalytic reformate was taken as that material including all of the benzene, toluene, xylene, ethylbenzene...
and trimethylbenzenes present in the total reformate. This catalytic reformate contained essentially no organo sulfur compounds and only 1 volume percent of olefin hydrocarbons. In each run, the theoretical amount of cuprous fluoride was used. In Run No. 5, the extract contained 95% of aromatic hydrocarbons and the reformate 6% of aromatic hydrocarbons. The acid phase from Run 5 was pumped at ambient temperature for 3 hours at a pressure of about 2 mm. Hg. All of the hydrocarbons in the HF were taken overhead leaving solid cuprous fluoride in the flask. This recovered solid cuprous fluoride was used in Run No. 6. The results show that it was fully as effective as the fresh cuprous fluoride used in Run No. 5.

Another run under the conditions of Run 6 was carried out. The acid phase was separated from the reformate phase and the acid phase was then washed with isopentane. The hydrocarbon layer was separated from the washed acid phase. The washed acid phase was then maintained at ambient temperature at about 2 mm. Hg. pressure until all the HF and hydrocarbons had been distilled away from the solid cuprous fluoride. The hydrocarbons were then fractionated into close boiling fractions. Analysis of the close boiling fractions showed that the aromatic hydrocarbon fractions were, within the error or infrared spectrometry, free of non-aromatic hydrocarbons.

### TABLE II

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6</td>
<td>6</td>
<td>80</td>
<td>22</td>
<td>44</td>
<td>35</td>
<td>22</td>
<td>36</td>
<td>3.6</td>
<td>3.1</td>
<td>121</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

In Table II, there are set out runs utilizing cupric fluoride as the copper fluoride. These runs show that cupric fluoride gives results on recovery of toluene from admixture with n-heptane essentially identical with those obtained using cuprous fluoride. The big difference between the fluorides lies in the fact that cupric fluoride removes only 1 mole of toluene per mole of cupric fluoride charged.

**Run No. 11**

The feed mixture to this run was an aromatic-rich mixture having a bromine number of 3.5 and a sulfur content, Lamp Method, of 0.004 weight percent. By gas chromatography the mixture contained, on a weight basis, 0.7% of hydrocarbons boiling below benzene, 78.7% of benzene, 0.1% of hydrocarbons boiling above benzene and below toluene, and 20.5% of toluene. Fractional distillation of this mixture permitted the recovery of only two-thirds of the benzene present as naphtha.

The contacting-distillation was carried out in an autoclave provided with a mechanical stirrer. Feed was charged in an amount of 40 cc. (36 g.)—0.5 moles of aromatic hydrocarbon. Liquid HF was charged in an amount of 100 cc. (2.5 moles). Cuprous fluoride was charged in an amount of 0.25 mole—theoretical amount needed to complex all the aromatic hydrocarbon present.

The contents of the autoclave were stirred at about 25° C. for 1 hour. A vacuum was then pulled on the autoclave and fractions consisting of HF and hydrocarbons were gradually distilled overhead and collected in a receiver. The HF was removed from the hydrocarbons in each fraction and the recovered hydrocarbons in each fraction analysed by gas chromatography. The individual fractions distilled and the hydrocarbon analysis are given below:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>HF Content, g.</th>
<th>Hydrocarbon Content, g.</th>
<th>Hydrocarbon Analyses (Wt. Percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Benzene</td>
</tr>
<tr>
<td>1</td>
<td>18.6</td>
<td>0.7</td>
<td>68.4</td>
</tr>
<tr>
<td>2</td>
<td>12.5</td>
<td>0.4</td>
<td>82.4</td>
</tr>
<tr>
<td>3</td>
<td>11.1</td>
<td>0.3</td>
<td>68.1</td>
</tr>
<tr>
<td>4</td>
<td>15.8</td>
<td>0.7</td>
<td>85.7</td>
</tr>
<tr>
<td>5</td>
<td>31.6</td>
<td>31.8</td>
<td>85.3</td>
</tr>
<tr>
<td>6</td>
<td>31.6</td>
<td>31.8</td>
<td>85.3</td>
</tr>
<tr>
<td>7</td>
<td>120.4</td>
<td>86.3</td>
<td></td>
</tr>
</tbody>
</table>

Fractions 5 and 6 were combined and the benzene separated, by fractional distillation, from the toluene. The freezing point of the benzene product was determined in duplicate runs as 5.45° C. and 5.51° C., which indicates a purity of at least 99.9%.

The annexed figure, which forms a part of this specification, shows a preferred illustrative embodiment of the use of cuprous fluoride in conjunction with liquid HF for the separation of aromatic hydrocarbons from a catalytic reformate. It is to be understood that the illustrative embodiment set out is schematic in nature and many items of process equipment have been deliberately omitted as these may be readily added by those skilled in this art.

In this embodiment, the feed is a catalytic reforming boiler between about 150° F. and 370° F, which has been derived from the catalytic reforming of a virgin naphtha. Many catalytic reforming processes are now in commercial use in the petroleum industry, for example, Ultraforming, California, Hydroforming, Corresponding, and Platforming. This catalytic reformate feed contains about 50 volume percent of aromatic hydrocarbons. In addition to benzene, toluene, xylene and ethylbenzene, a small amount of C<sub>9</sub> aromatic hydrocarbons is present. This catalytic reformate contains less than 1% of olefinic hydrocarbons and on the order of 0.05 weight percent of sulfur. Feed from source 11 is passed by way of line 12 through drier 13. In drier 13, the water contained in the feed is removed essentially completely. Drier 13 may consist of a well-known alumina drier followed by chemical drying through lime to remove last traces of water. Any of the well-known techniques for removing dissolved water from hydrocarbons may be used herein. The dried feed is passed from drier 13 by way of line 14 into extractor 16 at a lower point thereof.

Extractor 16 is a vessel adapted for the continuous countercurrent contacting of two immiscible liquids. Instead of using a countercurrent tower, a number of individual stages providing countercurrent flow may be used. Extractor 16, in this embodiment, provides three theoretical separation stages.

Extracting agent is passed into extractor 16 at various points through valved lines 18, 18a, 18b, and 18c. Extractor 16 is divided into contacting zones as shown. Each of these contacting zones is agitated by means of a turbine-type stirrer 19, 19a, 19b, and 19c. The stirrers are driven by motor 20.

The agent utilized herein contains commercial grade anhydrous hydrofluoric acid in an amount corresponding to 55 volume percent, based on feed from line 14. Solid cuprous fluoride is present to the extent of 0.55 mole per mole of aromatic hydrocarbons in the feed from line 14. The agent is in effect a slurry of solid cuprous fluoride in the liquid HF.

In this embodiment, extractor 16 is operated at a constant temperature, over its entire height, of 20° C. and at a pressure of 5 p.s.i.g. in order to keep the HF in the liquid state. Sufficient contacting time is provided.
so that essentially all the aromatic hydrocarbon is extracted by the agent as the feed flows up extractor 16. From the top of extractor 16, there is withdrawn by way of line 21 a raffinate phase which contains a small amount of occluded agent. The raffinate phase is passed into coalescer 22, wherein the occluded agent is separated. The recovered agent is withdrawn from coalescer 22 by way of valved line 23 and may be recycled to line 18 for reuse in the process or withdrawn from the system by way of valved line 24. Coalescer 22 may be any vessel adapted to facilitate separation of dispersed immiscible liquid from another liquid, for example, coalescer 22 may be filled with steel wool. From coalescer 22, the raffinate is passed by way of line 26 into HF stripper 27 which is provided with internal heat exchanger coils 28.

Normally, the extract phase produced in extractor 16 contains only a very small amount of non-aromatic hydrocarbons. When it is desired to produce an aromatic hydrocarbon product which is free of close boiling non-aromatic hydrocarbons, a low boiling paraffin hydrocarbon may be introduced into the bottom of extractor 16 to wash from the extract phase these close boiling non-aromatic hydrocarbons. In this embodiment, isopentane from source 31 is passed by way of valved line 32 into line 33 and thence into extractor 16. The amount of wash liquid introduced is dependent upon the effectiveness of extractor 16, but in general, will be between about 0.1 and 0.5 volumes of isopentane per volume of total hydrocarbons in the extract phase. In this embodiment, 0.25 volumes of isopentane per volume of total hydrocarbons in the extract phase are introduced.

The isopentane introduced into extractor 16 passes out of extractor 16 along with the raffinate phase. Stripper 27 is operated to remove overhead from the raffinate phase dissolved HF and isopentane. Raffinate hydrocarbons containing less than on the order of 1% of aromatic hydrocarbons are withdrawn from the bottom of stripper 27 and passed to storage not shown by way of line 36.

The HF-isopentane vapors are removed from stripper 27 by way of line 37 and are condensed in cooler 38. The total stream may be passed by way of valved line 39 and line 41 to line 33 for reuse in extractor 16. Or, cooler 38 may be designed to act as a separator and a low pressure phase of HF withdrawn by way of valved line 42. If it is not desired to recycle the isopentane from line 39, it may be withdrawn from the system by way of valved line 43.

An extract phase consisting of liquid HF, cuprous fluoride-aromatic hydrocarbon complex and dissolved isopentane is withdrawn from extractor 16 and passed by way of line 46 into decomposer 47 which is provided with an internal heater 48. In this embodiment, decomposer 47 is operated at a temperature of 300° C, at a pressure of about 10 mm. Hg, for a time of about 1 hour.

Under these conditions, HF and some aromatic hydrocarbons and isopentane pass overhead through line 51. These vapors are condensed in cooler 52 and pass by way of line 53 into separator 54. Separator 54 is adapted for the gravity separation of two immiscible liquids. A lower phase of liquid HF is withdrawn from separator 53 by way of line 56. An upper phase of aromatic hydrocarbons and isopentane is withdrawn from separator 54 by way of line 58.

From the bottom of decomposer 47, a slurry consisting of aromatic hydrocarbons and solid CuF is passed by way of line 61 into washer 62. Washer 62 is a vessel adapted for fluidized contacting of an immiscible liquid-solid with a wash liquid. In this instance, isopentane from line 63 is introduced into washer 62 by way of distributor 66. The amount of isopentane introduced into washer 63 is sufficient to dissolve all the decomposed aromatic hydrocarbons and remove adsorbed aromatic hydrocarbon from the surface of solid CuF. The amount of low boilling paraffinic hydrocarbon used in washer 62, in general, is between about 0.25 and 1 volume of low boiling paraffinic hydrocarbon such as isopentane per volume of slurry charged to washer 62 by way of line 61. Herein isopentane is introduced by way of line 364 per volume of slurry in line 61. Washer 62 is operated at about ambient temperature and pressure.

A liquid stream of isopentane and aromatic hydrocarbons is withdrawn from the top of washer 62 and is passed by way of line 68 into filter 69. Filter 69 is adapted to remove solid CuF which has been entrained by the emerging stream. Preferably, two filters are used in parallel so that one filter may be cleaned to recover CuF without interrupting the continuous operation. The filtered material is passed by way of line 71 into fractionator 72. The hydrocarbons from line 58 are passed by way of line 71 into fractionator 72. Fractionator 72 is shown schematically. There is taken overhead isopentane vapors and these are passed by way of line 73 and line 64 back to washer 62. Makeup isopentane from source 74 is passed by way of valved line 76 into line 64.

Aromatic hydrocarbon stream consisting of benzene, toluene, C8 aromatic hydrocarbons and some C9 aromatic hydrocarbons is withdrawn from zone 72 by way of line 84 and is passed to further processing for the preparation of essentially pure close boiling aromatic product.

A slurry of CuF in isopentane is withdrawn from washer 62 by way of line 86. Liquid HF from line 87 is passed by way of line 82 through an eductor not shown, to pick up the slurry from line 81. The slurry of CuF, isopentane and liquid HF is passed by way of line 83 back to manifolded line 18 for reuse in extractor 16.

Makeup liquid HF in the form of commercial grade anhydrous hydrofluoric acid is introduced from source 84 by way of valved line 85 into line 57.

Makeup cuprous fluoride is introduced from source 87 by way of line 86 into washer 62. Instead of using the procedure set out in the illustrative embodiment, another form of operation is to use a batch system wherein the contacting is carried out in one vessel, the raffinate phase separated and treated to remove dissolved HF and occluded agent. The acid phase may be washed with a low boiling paraffin hydrocarbon in the contacting vessel and the hydrocarbon phase separated and treated for the recovery of the wash hydrocarbon. The acid phase remaining in the contacting vessel is then decomposed by heating at suitable conditions to remove overhead not only the HF but also the hydrocarbons.

The HF and hydrocarbons are separated and processed as shown in the illustrative embodiment. The solid copper fluoride remains in the contacting vessel and is ready for extraction of another batch of mixed feed. By the use of two or more contacting vessels, it is possible to carry out a continuous operation with respect to all parts of the system except the contacting vessels themselves.

Other embodiments may be readily devised and these are intended to be included within the scope of the invention.

Thus having described the invention, what is claimed is:

1. A process which comprises contacting, under essentially anhydrous conditions, a feed mixture comprising essentially aromatic hydrocarbons and non-aromatic hydrocarbons, with copper fluoride and liquid HF, said HF being present in an amount of at least about 3 moles per mole of said aromatic hydrocarbon and said copper fluoride being present in an amount of at least on the order of that theoretically needed to form a complex with said aromatic hydrocarbons and non-aromatic hydrocarbons, where said HF and said copper fluoride amounts are calculated as the minimum of that amount needed to form a complex with complexible organo-sulfur compounds present in said feed, to form an HF solution of a complex containing aromatic hydrocarbon and copper fluoride, separating a fraction com-
prising non-aromatic hydrocarbons from a fraction comprising liquid HF and dissolved complex, and recovering aromatic hydrocarbons from said liquid HF fraction.

2. A separation process which comprises contacting, under essentially anhydrous conditions, a feed comprising aromatic hydrocarbons and saturated non-aromatic hydrocarbons, in the substantial absence of olefinic hydrocarbons, with a fluoride of the class consisting of cuprous fluoride and cupric fluoride and liquid HF, said HF being present in an amount of at least 3 moles per mole of aromatic hydrocarbons in said feed, at a temperature between about —40° C. and 150° C., at a pressure sufficient to keep said HF in the liquid state, separating a raffinate phase substantially free of aromatic hydrocarbons from an acid phase comprising liquid HF and an HF-soluble complex containing said fluoride and aromatic hydrocarbons, and recovering from said acid phase an extract consisting substantially of aromatic hydrocarbons and wherein the usage of said fluoride in moles per mole of aromatic hydrocarbon in said feed is at least about that set out in the following schedule:

<table>
<thead>
<tr>
<th>Fluoride</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cuprous fluoride</td>
<td>0.5</td>
</tr>
<tr>
<td>Cupric fluoride</td>
<td>1.0</td>
</tr>
</tbody>
</table>

where said usage of the defined fluoride and said HF are calculated in excess of the amount needed to complex complexible organo-sulfur compounds present in said feed.

3. The process of claim 2 wherein said copper fluoride is cuprous fluoride.

4. The process of claim 2 wherein said copper fluoride is cupric fluoride.

5. The process of claim 2 wherein said feed is a petroleum distillate boiling below about 700° F.

6. The process of claim 2 wherein said feed is a catalytic reformate.

7. The process of claim 2 wherein said temperature is between about 10° C. and 35° C.

8. The process of claim 2 wherein said HF is present in an amount between about 5 and 15 moles per mole of aromatic hydrocarbon in said feed.

9. The process of claim 2 wherein said feed is substantially free of organo-sulfur compounds.

10. The process of claim 9 wherein said acid phase is maintained at a temperature between about 20° C. and 125° C. at a pressure between about 1 mm. Hg. and about 1 atmosphere, the lower pressures corresponding to the lower temperatures, until all of the HF has been distilled away, leaving said fluoride in the solid state in the distillation zone.

11. A process for separating aromatic hydrocarbons from non-aromatic hydrocarbons, which process comprises (1) under essentially anhydrous conditions, contacting a mixture of aromatic hydrocarbons and saturated non-aromatic hydrocarbons, said mixture being substantially free of olefinic hydrocarbons and organo-sulfur compounds, with liquid HF, in an amount between about 20 and 150 volume percent based on said mixture, and a fluoride selected from the class consisting of cuprous fluoride and cupric fluoride, wherein when cuprous fluoride is said fluoride about 0.5 mole of cuprous fluoride are present per mole of aromatic hydrocarbon in said mixture and when cupric fluoride is said fluoride, about 1 mole of cupric fluoride is present per mole of aromatic hydrocarbon in said feed, at a temperature between about 10° C. and 35° C. and a pressure at least sufficient to keep said HF in the liquid state, (2) separating a raffinate phase from an acid phase which comprises liquid HF and a complex containing said fluoride and aromatic hydrocarbons, (3) and distilling HF from said acid phase at a temperature between about 20° C. and 125° C. at a pressure between about 1 mm. Hg. and about 1 atmosphere, the lower pressures corresponding to the lower temperatures to recover said fluoride and a hydrocarbon product consisting substantially of aromatic hydrocarbons.

12. The process of claim 11 wherein said distillation is continued until essentially all of the hydrocarbons in said acid phase have distilled, leaving solid fluoride in said distillation zone.

13. The process of claim 11 wherein said mixture is a catalytic reformate boiling in the gasoline range.

14. An aromatic hydrocarbon recovery process which comprises, under essentially anhydrous conditions, contacting a feed comprising essentially aromatic hydrocarbons and non-aromatic hydrocarbons with at least about 3 moles of liquid HF per mole of aromatic hydrocarbons in said feed and at least about the amount of copper fluoride theoretically needed to form a complex with the aromatic hydrocarbons in said feed, where said HF and said copper fluoride amounts are calculated in excess of that amount needed to form a complex with complexible organo-sulfur compounds present in said feed, to form a solution comprising liquid HF and a complex containing copper fluoride and aromatic hydrocarbon, distilling a fraction comprising non-aromatic hydrocarbons and HF from a fraction comprising liquid HF and dissolved complex and distilling HF and aromatic hydrocarbons from said liquid HF fraction.

15. The process of claim 14 wherein said feed contains at least about 90 volume percent of aromatic hydrocarbons.

16. The process of claim 14 wherein said HF usage is between about 5 and 15 moles per mole of aromatic hydrocarbon.

17. The process of claim 14 wherein said distillation is carried out at between about 25° and 100° C.

No references cited.