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REFINING WITH HF AND TaF_5

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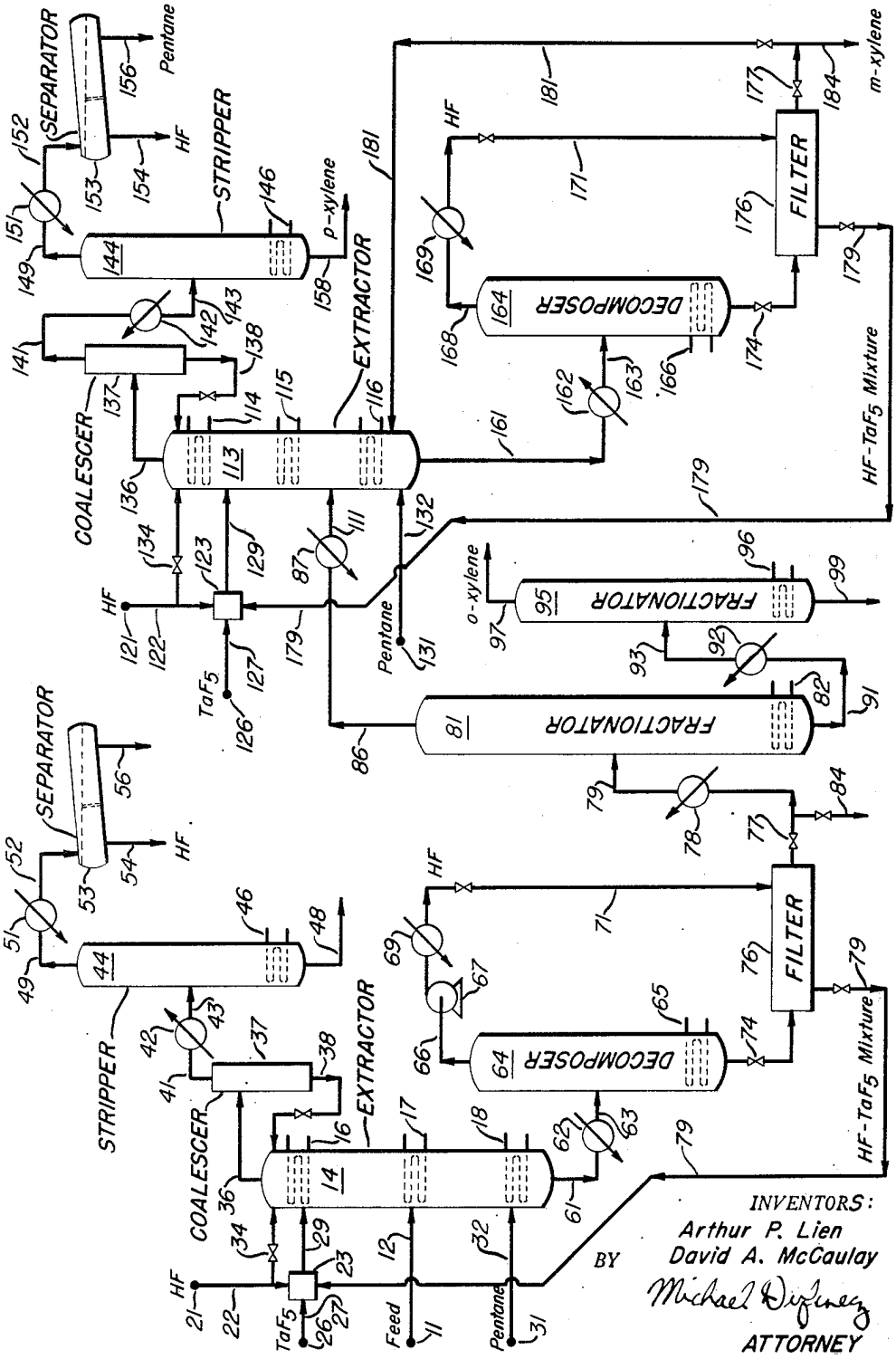

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REFINING WITH HF AND TaF_5

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This invention relates to the refining of mixed hydrocarbon oils. More particularly, it relates to the refining of hydrocarbon oils which contain, in addition to other hydrocarbon compounds, aromatics, organic sulfur compounds, oxygenated compounds and nitrogen compounds. Further, the invention relates to the treatment of isomeric dialkylbenzenes in order to effectuate the separation between isomers of groups of isomers thereof. The invention is of particular interest in the separation of the isomeric xylenes.

Naturally occurring hydrocarbon oils are mixtures of various classes of hydrocarbons and various organic compounds containing one or more of the elements sulfur, oxygen and nitrogen. For some uses many hydrocarbon oils contain an objectionable amount of aromatic hydrocarbons, e. g., diesel oils, kerosenes, domestic fuel oils and lubricating oils. For some uses hydrocarbon oils should not only be low in aromatics, but also low in organic sulfur compounds. In some cases such as coal tar distillate, the oil contains substantially only aromatics and some organic sulfur compounds, and it is desired to remove the sulfur compounds only. In the case of shale oil, it is desirable to remove not only sulfur compounds, but also nitrogen compounds and oxygen compounds. One of the better methods for refining of a mixed hydrocarbon oil containing objectionable amounts of aromatic hydrocarbons and organic sulfur compounds is to treat with liquid hydrogen fluoride containing boron trifluoride. The HF-BF_3 treating agent acts very much like a selective solvent. However, this process has the serious disadvantage of having to operate at high pressures when temperatures above ambient are used because the BF_3 is a very volatile gas. Another method for improving the quality of heavy hydrocarbon oils such as lubricating oils is by treatment with liquid HF and silver fluoride as disclosed in U. S. 2,531,723.

It is well known that the isomeric dialkylbenzenes cannot be resolved into high purity isomers by fractional distillation; particularly this is true when the mixture of isomers also contains close boiling non-aromatic hydrocarbons, e. g., a mixture of C_8 aromatic hydrocarbons and non-aromatic hydrocarbons can be at best resolved into an orthoxylene concentrate containing about 70% o-xylene and a lower boiling concentrate. In view of the commercial importance of the various xylene isomers, a considerable incentive exists for the recovery of high purity xylene isomers from mixtures thereof. To a lesser extent the high purity isomers of other dialkylbenzenes such as diethylbenzene, di-n-propylbenzene, etc. are of interest.

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It is an object of this invention to refine mixed hydrocarbon oils by an extraction method. Another object is the removal of aromatics hydrocarbons, organic sulfur compounds and phenolic compounds from hydrocarbon oils containing objectionable amounts of these materials. A further object is the refining of lubricating oil distillates to improve the viscosity index thereof.

Still another object of this invention is a process for the separation of individual dialkylbenzene isomers from a mixture of isomers of said dialkylbenzene, e. g., xylene isomers. An additional object is a process for the recovery of a meta-xylene enriched fraction from mixtures of m-xylene with at least one other xylene isomer. A particular object is the treatment of a hydrocarbon fraction in the C_8 aromatic hydrocarbon-boiling range for the separation of the C_8 aromatic hydrocarbon therefrom and the further treatment of said C_8 aromatic hydrocarbons to obtain high purity m-xylene, o-xylene and p-xylene fractions. Other objects of the invention will be apparent in the detailed description thereof.

It has been discovered that several of the objects of this invention can be attained by treating hydrocarbon oils which contain appreciable amounts of aromatic hydrocarbons, and/or organic sulfur compounds, and/or phenolic compounds, and/or nitrogen compounds by treating said hydrocarbon oils with tantalum pentafluoride—TaF_5—in the presence of a sufficient amount of substantially anhydrous liquid HF to form a separate HF-rich phase.

It has further been discovered that a hydrocarbon oil which contains dialkylbenzenes and polyalkylbenzenes can be substantially completely freed of said dialkylbenzenes and polyalkylbenzenes by treatment with an amount of substantially anhydrous liquid HF to form a separate HF-rich phase and at least about 1 mol of TaF_5 per mol of said dialkylbenzenes and polyalkylbenzenes.

It has been discovered that by the treatment of a mixture of at least two isomeric dialkylbenzenes with sufficient liquid HF to form a separate HF-rich phase and less than about 1 mol of TaF_5 per mol of said dialkylbenzenes, a separation can be effected between said isomers. It has been found that the HF-rich (extract) phase will contain a mixture of said isomers wherein the molar ratio thereof is different from the ratio in the feed; and the raffinate phase will contain a mixture of said isomers wherein the molar ratio thereof is different from the ratio in the feed. The meta-isomer is preferentially extracted into the extract phase. When treating a

mixture of ortho and para-isomers the ortho-isomer is preferentially extracted into the extract phase.

The feed to our mixed hydrocarbon oil refining process can be: various fractions obtained from the distillation of crude oil, e. g., naphthas, kerosenes, heater oil, lube oils, etc., or the crude oil itself, or reduced crudes. Another class of materials suitable as a feed may be oils derived from the treatment of the above materials, e. g., raffinates and extracts from the solvent treatment of kerosenes or lube oils. Shale oil, and its various fractions, is a suitable feed to our process. The so-called light oil from the coking of coal is an exceptional feed to our process since the sulfur compounds in the benzene and toluene fractions are extremely refractory to conventional desulfurization methods. The liquid products from the hydrogenation of coal or the Fischer-Tropsch process are suitable feeds to our process. Liquid HF-TaF_5 is a powerful catlyst for alkylation purposes. Appreciable amounts of olefins can be eliminated from olefin-containing feeds by treatment with liquid HF-TaF_5; the alkylate may or may not be extracted into the extract phase. In general, oils containing large amounts of olefins are not a desirable feed to our process. In general, the most suitable feed stocks are petroleum distillates boiling in the heavier-than-gasoline range, i. e., above about 350° F. and below about 750° F., and particularly those distillates derived from high sulfur and high aromatic content crudes, such as, West Texas crude, Winkler crude, etc.

Tantalum pentafluoride is a crystalline solid having a melting point of about 202° F. and a boiling point of about 446° F. The solid is appreciably soluble in substantially anhydrous liquid HF. It has been discovered that the solubility of TaF_5 in substantially anhydrous liquid HF is greatly increased when a polyalkyl aromatic hydrocarbon, a polynuclear aromatic hydrocarbon, many types of organic sulfur compounds, or phenolic compound is brought into contact with TaF_5, in the presence of substantially anhydrous liquid HF. For example, a mixture of liquid HF and solid TaF_5 is readily changed to a clear liquid when the mixture is contacted with a sufficient amount of xylene (no significant change in properties is obtainable by the treatment of a mixed hydrocarbon oil with TaF_5 in the absence of substantially anhydrous liquid HF).

Tantalum pentafluoride is readily decomposed by water. The process of this invention should be carried out under substantially anhydrous conditions. The liquid HF used in the process should not contain more than about 1 or 2% of water, i. e., the liquid HF should be substantially anhydrous.

We have discovered that organic sulfur compounds and some aromatic compounds not amenable to removal by liquid HF treatment are removable from the raw oil by treating said oil with TaF_5 in the presence of sufficient liquid HF to form a separate HF-rich phase. The HF-rich phase, hereafter called the extract phase, contains liquid HF, aromatics, organic sulfur compounds, phenolic compounds, some non-aromatics and TaF_5, i. e., if all of these organic compounds are present in said oil. It is believed that the TaF_5 in the extract phase exists in the form of a coordination compound or adduct with the aromatics and organic sulfur and phenolic compounds. Benzene and toluene can exist in the extract phase in about the amount soluble in liquid HF alone, which amount is about 2–3 volume percent based on HF. By using a sufficient amount of TaF_5 and a sufficient amount of liquid HF, it is possible to produce a refined oil which contains substantially no compounds other than non-aromatics and benzene and/or toluene, if these aromatics are present in the raw oil.

Some improvement in quality of the oil can be obtained by using even a trace amount of TaF_5 and further improvements can be obtained by increasing the amount of TaF_5 until substantially all the materials removable by the liquid HF-TaF_5 treating agent have been removed. In general, the larger the amount of extractable materials present, the more TaF_5 needed in the treatment. The upper limit on TaF_5 usage is readily determined by the fact that when a solid TaF_5 phase appears, no further improvement is obtainable. By the time that this third phase of solid TaF_5 appears, a sufficiently refined oil has usually been attained. Thus we can use between a trace amount of TaF_5 and an amount of TaF_5 that will not dissolve completely into the extract phase. Expressing the TaF_5 usage in another way, we can use from 0.1 weight percent to about 25 weight percent and, in some cases to about 100 weight percent, based on the raw oil. The amount of TaF needed to obtain a particular degree of refinement is readily determinable by small scale treatment of samples of the raw oil.

Sufficient liquid HF must be present in the extraction zone to form a separate HF-rich phase, i. e., extract phase. The minimum amount of liquid HF needed will vary somewhat with the type of oil being treated and the extractable materials content of the raw oil. The viscosity of the raw oil affects phase separation and, in general, the more viscous the raw oil, the more HF needed to obtain good phase separation. The presence of extractable materials in the liquid HF increases the viscosity of the extract phase so that good phase separation may be difficult when treating raw oils containing large amounts of extractable materials with small amounts of HF. When treating naphthas and light gas oils the minimum HF usage may be as low as 5 volume percent, based on the raw oil. When treating lube stocks such as distillate for the production of S. A. E. 20 oil, as much as 20 volume percent of liquid HF may be needed to obtain good phase separation. We prefer to use more than the bare minimum amount of liquid HF. As much as 1500 volume percent liquid HF has been used without detrimental effect. However, little significant gain in refinement is obtained by using very large amounts of liquid HF. For most raw oils satisfactory phase separation and a satisfactory degree of refinement can be obtained by using from about 10 to about 500 volume percent of liquid HF. We prefer to use between about 30 and 300 volume percent.

Since viscosity does have an appreciable effect on the cleanness of the phase separation, the viscosity of the raw oil may be reduced by adding an inert diluent thereto. The diluent should be relatively inert to the solvent action of the treating agent and also to the catalytic action of the treating agent. Additionally, the diluent should be readily separable by distillation from the refined oil, although in some cases it may be desirable to leave the diluent in the refined oil. Suitable diluents are pentane, hexane, petroleum ether, cyclohexane, various naphtha fractions low in extractable materials, etc. Materials such

as heptane or octane can be used when the treating is about ambient temperatures. However, diluents containing about 6 or more carbon atoms are readily isomerized and even cracked by our treating agent at temperatures above about 250° F., so that their use at elevated temperatures is undesirable. In general, olefinic hydrocarbons are not suitable diluents. The amount of diluent used will be dependent upon the type of raw oil being charged, but in general will be between about 10 and 200 volume percent based on raw oil. When using a diluent it may be possible to reduce the amount of liquid HF ordinarily used and still obtain a satisfactory phase separation.

The temperature of treating is of considerable importance in our mixed hydrocarbon oil refining process because the liquid HF-TaF_5 treating agent is a very powerful catalyst for isomerization, alkylation, cracking and other reactions. In order to avoid side reactions due to catalytic effects, the temperature of contacting should be below about 200° F. Temperatures below 30° F. may be used where the properties of the feed oil do not interfere with phase separation and/or where very large amounts of HF are being used. The treating temperature should always be above the pour point of the (diluted) raw oil in order to avoid difficulty in phase separation. We prefer to operate at from about 50° to about 100° F.

We have found that in some cases a better produce can be obtained by taking advantage of the catalytic action of our treating agent at elevated temperatures. By contacting the oil at temperatures between about 200° and 400° F., and preferably between about 250° and 350° F. and then cooling to below about 100° F. before making the phase separation, it is possible to obtain a refined oil in greater yield and/or better quality.

Contacting time will be dependent on the type of raw oil, the amount of liquid HF-Ta_5 treating agent and the temperature of operation. In general times between about 5 minutes and 60 minutes in each extraction stage will be sufficient to obtain the desired degree of refining when operating between 50° and 100° F. The higher the temperature in the contacting zone, the shorter should be the contacting time. At 400° F. the contacting time should be between 1 and 10 minutes; prolonged contacting times may be harmful to product quality and/or yield.

It is to be understood that when the process is being carried out at temperatures above the boiling point of liquid HF, superatmospheric pressures must be maintained on the system in order to keep the HF in the liquid state.

Normally the raffinate from our hydrocarbon refining process will be the desired final product. However, the low sulfur, low aromatic content thereof makes the refined oil a very suitable feed to a catalytic cracking operation; thus our process may be used to treat cycle gas oils which are low quality catalytic cracking feeds in order to improve their suitability for catalytic cracking. These cycle oils may be derived from thermal cracking, coking or catalytic cracking.

We have found that the organic sulfur compounds present in the extract from the treatment of heavy naphtha and gas oils boiling between about 350° and 600° F. are very readily catalytically cracked to produce a high octane, low sulfur product. Particularly good results are obtained when the extract is fractionated and that portion boiling below about 450° F. is charged to the catalytic cracking operation.

We have also discovered that a mixture of at least two isomeric dialkylbenzenes can be separated into fractions having a different molal ratio than the feed mixture and different from each other when said mixture is contacted with liquid HF and TaF_5 under appropriately selected conditions. We have found that the isomeric dialkylbenzenes react with TaF and HF to form adducts or complexes which are extremely soluble in liquid HF. The stability of the complex appears to be dependent upon the configuration of the dialkylbenzene. The order of stability is, in decreasing rank, meta: ortho: para. The meta-isomer complex is several fold the most stable. Thus by treating a feed containing at least two different isomers of a dialkylbenzene with a sufficient amount of liquid HF to form an extract phase, and with less TaF_5 than is needed to bring substantially all of said dialkylbenzene isomers into the extract phase, it is possible to produce a dialkylbenzene containing raffinate phase and dialkylbenzene containing an extract phase. The raffinate phase contains both isomers in a ratio of the "less-stable-complex-forming isomer" to the "more-stable-complex-forming isomer" which ratio is greater than the ratio of said isomers in said feed; the extract phase contains both isomers in a ratio of the more stable to the less stable, which ratio is greater than the ratio of said isomer in said feed.

We believe that the complex formed by a dialkylbenzene, TaF_5 and liquid HF contains 1 mol of said dialkylbenzene, 1 mol of TaF_5 and (probably) 1 mol of HF. We believe the complex contains HF because no complex is formed by xylene and TaF_5 in the absence of liquid HF. At the temperatures for the operation of our dialkylbenzene-isomeric mixture separation process, benzene and monoalkylbenzenes do not form a detectable amount of complex.

We have also found that polyalkylbenzenes, such as, ethylxylene, isodurene, pentamethylbenzene and hexamethylbenzene form complexes with TaF_5 and liquid HF. It is believed that these polyalkylbenzene complexes contain 1 mol of TaF_5 per mol of polyalkylbenzene.

We have also discovered that ethylbenzene, which is usually associated with xylenes as produced in hydrocarbon conversion processes, undergoes disproportionation with surprising ease in the presence of liquid HF and TaF_5 to produce chiefly benzene and diethylbenzenes and, in the presence of xylenes, ethylxylenes. The disproportionation of ethylbenzene is of immense value in simplifying its separation from xylenes and makes it possible thereafter to separate selectively or to concentrate individual xylene isomers from each other by means of liquid HF and TaF_5, without interference by ethylbenzenes.

We have also found that isomeric xylenes may be substantially completely extracted from a mixture of xylenes and saturated hydrocarbons of the same boiling range by contacting said mixture with a molar excess of liquid hydrogen fluoride and with TaF_5 in at least a uni-molar ratio of TaF_5 to xylenes. Benzene and toluene are not particularly soluble in the liquid HF-TaF_5 treating agent, with the result that xylenes may be extracted from mixtures thereof with benzene and toluene (as well as saturated hydrocarbons) by the employment of liquid HF and TaF_5 in an amount which is at least uni-molar with respect to the xylenes present in said mixture.

When the feed stock to our process consists of a lower dialkylbenzene wherein the alkyl radical contains between 1 and 5 carbon atoms, such as xylene, in admixture with non-aromatic hydrocarbons and/or benzene or toluene, contacting of said feed stock with a sufficient amount of our liquid HF-TaF_5 treating agent results in a raffinate phase and an extract phase. The extract phase consists of liquid HF, complex and some physically dissolved hydrocarbons. The degree of removal of the xylene from the feed is dependent upon the amount of TaF_5 present in the treating agent. Substantially complete removal of the xylene can be achieved by using at least about 1 mol of TaF_5 per mol of xylene present in the feed. In some cases, particularly when the ratio of non-complexible hydrocarbon to xylene is quite high, more than 1 mol of TaF_5 per mol of xylene will be necessary to achieve substantially complete removal of xylene. The amount of TaF_5 should be limited to about that amount which will be completely complexed or brought into solution in the extract phase. We have found that solid TaF_5 present in the extract phase has a marked catalytic effect on the aromatic hydrocarbons in the extract phase and undesirable side reactions, such as, isomerization, disproportionation and even cracking may occur; this effect is especially apparent when operating at higher temperatures. In general, while we may use from as little as 0.1 mol of TaF_5 per mol of dialkylbenzene in the feed to as much as 3 mols, we prefer to use between about 0.3 and 1.5 mols of TaF_5 per mol of dialkylbenzene in the feed.

When monoalkylbenzenes, such as, ethylbenzene, propylbenzene, isopropylbenzene, butylbenzene, etc. are present in the feed stock, the liquid HF-TaF_5 treating agent catalyzes the rapid disproportionation of these compounds to dialkylbenzenes. The dialkylbenzenes form complexes with TaF_5 and pass into the extract phase. Therefore, when these monoalkylbenzenes are present in the feed stock, it is necessary to use sufficient TaF_5 to complex with the corresponding dialkylbenzene as well as with the other dialkylbenzenes present in the feed stock itself. When ethylbenzene and/or propylbenzene are present in the feed stock, we prefer to use 0.5 mol. of TaF_5 per mol of said compound in addition to that used for the dialkylbenzenes present in the feed.

The maximum degree of separation of a mixture of two isomeric xylenes is attainable by using about 1 mol of TaF_5 per mol of the more stable complex isomer present in the feed. While a high purity metaxylene, e. g., in excess of about 95%, cannot be separated from a mixture of xylenes in a single contacting stage, it is possible to achieve this result by using a multi-stage or countercurrent tower operation.

Sufficient liquid HF must be present to participate in the formation of the complex and to dissolve the complex. We prefer to use an excess over this amount in order to insure the formation of a separate extract phase. In general, when operating with mixed feeds containing xylene, the use of about 5 volume per cent of liquid HF based on the total feed will be sufficient to form a separate extract phase. As much as 500 volume per cent of liquid HF or more may be used. In general the use of larger amounts of liquid HF assists in phase separation and also, surprisingly enough, decreases the amount of non-aromatic hydrocarbons present in the extract phase. We prefer to use between about 100 and 300 volume percent of liquid HF, based on total mixed feed.

Temperature is an important factor in our aromatic separation process. When the contacting is carried out at temperatures in excess of about 125° F., side reactions take place, such as, isomerization of meta-xylene to the equilibrium mixture of the three isomers and disproportionation of the xylenes to higher alkylbenzenes. When operating at temperatures below about 30° F., longer contact times are necessary to achieve good separations and, at temperatures below about 0° F., the disproportionation of ethylbenzene, etc. is slowed down markedly, which is disadvantageous when treating ethylbenzene-containing feeds. Although we can operate at higher temperatures by using very short contact times and by quenching the reaction mixture at the end of the contacting, we prefer to operate below about 100° F. Under some conditions of temperature, TaF_5 usage and long contact time, ortho and/or para-xylene are isomerized to the meta-xylene isomer. When it is desired to minimize this isomerization, not only should temperature be held at less than about 90° F., but also contact times should be short and the amount of TaF_5 used should be such that a minimum amount of ortho and/or para-xylene are present in the extract phase.

Contacting times are dependent upon the temperature at which the contacting is carried out and upon the degree of agitation in the contacting zone. When using normal methods of agitation, contacting time may vary from as little as 1 minute to as much as 3 or more hours. In general when operating at between about 30° and 90° F. and with a feed from which it is desired to remove substantially all the xylene isomers contained therein, a suitable contacting time is between about 1 minute and 30 minutes.

We have found that the organic sulfur compounds normally present to some extent in virtually all hydrocarbon mixtures form complexes with TaF_5 and HF. In general these sulfur compound complexes are more stable than the dialkylbenzene complexes and are more difficult to decompose. However, heating the complex to temperatures on the order of 400° F. will drive off the HF and thus dissociate the complex. The alkylphenols which are normally present in cracked stocks also complex with TaF_5 and HF. These complexes tend to interfere with phase separation and also introduce undesired impurities into the extract oil. In order to eliminate this interference, feed stocks containing such alkylphenols should be dephenolized by a suitable treatment, e. g., washing with 25% aqueous caustic solution. We prefer a feed stock that is substantially free of alkylphenols and which is low in total sulfur content, i. e., on the order of about 0.02 weight per cent of sulfur, such as can be obtained by extraction with HF alone.

In order to eliminate insofar as possible the loss of the desired dialkylbenzenes to polyalkylbenzenes by alkylation with olefins present in a mixed feed stock, we prefer to operate on a feed stock that is low in olefin content, e. g., less than about 3 or 4%.

Our process may be applied to a mixture of hydrocarbons comprising aromatics, paraffins, naphthenes and olefins (along with associated phenolic and sulfur compounds) which boil in the approximate boiling range of the particular dialkylbenzenes to be recovered. We prefer to operate on a feed which is low in the interfering

phenolic compounds, sulfur compounds and olefins.

A particularly suitable feed for our dialkylbenzene separation process is the naphtha derived from the so-called hydroforming process, i. e., from the vapor phase treatment of a virgin naphtha at 850° to 1050° F. in the presence of hydrogen over a catalyst such as molybdena on an alumina support or a platinum-containing catalyst. The hydroformate from such a process is low enough in sulfur to permit operation without further desulfurization and is sufficiently low in olefin that little degradation of the desired xylene content results during the separation step.

Any hydrocarbon oil which contains appreciable amounts of lower dialkylbenzenes can be charged to our process either directly or after suitable pretreatment to lower the sulfur and alkylphenol content. These feed stocks may be derived from the distillation of petroleum, from the thermal or catalytic cracking of naphthas from petroleum, from the hydroforming or hydrodesulfurization of virgin or cracked naphthas, or they may be derived from the coking of coal or from the drip oil produced in the production of carbureted water gas or producer gas. Other source of feed to our process are the highly aromatic extracts obtained by treating petroleum oils with selective solvents, such as, phenol, furfural, SO_2 and the like; usually these extracts will have to be desulfurized prior to treatment by our process. It should be understood that our process is applicable to the extraction of dialkylbenzenes and particularly the extraction of meta-dialkylbenzenes from isomeric dialkylbenzenes, regardless of the method by which the feed was prepared.

The more common feed stocks for our process are a mixture of dialkylbenzenes, non-aromatic hydrocarbons, benzene, toluene and ethylbenzene. The non-complexible materials, i. e., non-aromatic hydrocarbons, benzene and toluene usually form from 50 to 75 volume percent of the total feed. (Monalkylbenzenes other than toluene are not considered non-complexible materials because their disproportionation results in the formation of a complexible material, for example diethylbenzene.) Where xylene concentrates are available from superfractionation equipment, a feed stock containing 70 or 80% of xylene and ethylbenzene may be available. We have found that phase separation and selectivity are improved when the feed stock does not exceed about 50 volume percent of complexible hydrocarbons.

When operating on a substantially pure xylene and ethylbenzene mixture we prefer to add from about 50 to 200 volume percent of an inert hydrocarbon diluent. The diluent should be a paraffinic and/or naphthenic hydrocarbon or a mixture of hydrocarbons that is low in materials that would interfere with phase separation and that will be readily separable by simple fractional distillation from the individual aromatic hydrocarbons. We prefer to use as diluents paraffinic and naphthenic hydrocarbons of low boiling point since these materials are not isomerized or cracked by the liquid HF at the preferred operating temperatures. Suitable hydrocarbons are butane, pentane, hexane, heptane, petroleum ether, etc. When operating at low temperatures such as 30° F. the diluents might be higher boiling paraffinic or naphthenic hydrocarbons containing 10 or 11 carbon atoms. In general when treating a mixed feed stock to remove substantially all the dialkylbenzenes, sufficient non-complexible hydrocarbons will be present in the feed so that no additional diluent is needed. We prefer to operate with an amount of non-complexible hydrocarbons, i. e., present either as diluent or naturally; which amount is about equal in amount to the extractable hydrocarbons present.

The non-aromatic hydrocarbons extracted from the feed by the treating agent boil in about the same range as the aromatic hydrocarbons. Their presence decreases the purity of the aromatic hydrocarbons and they must be removed in order to obtain substantially pure aromatics as the final product. We have found that these non-aromatic hydrocarbons can be readily displaced from the extract phase by washing the extract phase with an inert diluent non-aromatic type hydrocarbon such as pentane, hexane or a 10- or 11-carbon atom paraffin. A single stage washing operation is usually sufficient to reduce the non-aromatic content of the extract phase to a point where substantially pure aromatics can be obtained by simple fractional distillation of the recovered aromatic hydrocarbons.

The raffinate phase from our process will usually contain some dissolved liquid HF and also some entrained HF; small amounts of solid TaF_5 may also be entrained. The TaF_5 can be recovered by filtration, by a coalescing operation or in some cases by distilling the raffinate oil. The liquid HF is readily removed from the raffinate phase by distillation at temperatures of about 100° F., at atmospheric pressure. In some cases the raffinate may contain minor amounts of alkyl fluorides; these can be readily removed by percolation through bauxite.

The extract phase is readily decomposed by treatment with water, preferably cold water or ice; the upper layer of extract oil can be decanted from the lower aqueous layer. The extract oil contains the extracted materials, i. e., hydrocarbons and/or organic sulfur compounds. The lower aqueous layer consists of a mixture of hydrofluoric acid and TaF_5 decomposition product. The extract oil can be freed of traces of HF by treatment with dilute caustic. This method is particularly suitable for laboratory operations.

We prefer to decompose the extract phase as follows: The extract phase is placed in a vessel, usually provided with a few fractionation trays, wherein the temperature of the extract phase is raised until the HF vaporizes and passes out of the vessel. The top temperature in the decomposing vessel is held at about the boiling point of HF in order to prevent the removal of extract materials along with the HF. In the bottom of the decomposer after the removal of HF, there exists a slurry of extract materials and solid finely divided TaF_5 This slurry is passed to a filter which retains the solid TaF_5. The TaF_5 can be reused in the process. In the case of lower boiling extract materials, the extract materials may be distilled leaving behind the solid TaF_5. By operating under vacuum, the HF may be removed at low temperatures. We may operate at temperatures up to about 400° F.; the lowest possible temperature is preferred because of the side-reactions resulting from the catalytic action of the treating agent. Where it is desired to avoid side-reactions in the extract phase, the decomposer may be operated under vacuum in order to remove a major part of the liquid HF at

temperatures below about 100° F.; and then the partially denuded extract phase is heated to from about 200° to 400° F. to remove the remainder of the HF.

The results obtainable with our isomeric dialkylbenzenes separation process are illustrated by the following example: In this test the contacting was carried out in a carbon steel reactor equipped with a 1725 R. P. M. stirrer. The TaF_5 was prepared by the reaction of $TaCl_5$ and liquid HF. A considerable excess of liquid HF over the theoretical amount and 0.4 mol of $TaCl_5$ were agitated in the reactor at ambient temperature until the reaction was complete as indicated by a substantially constant pressure of about 285 p. s. i. g. The HCl and excess HF were evacuated from the reactor leaving therein the TaF_5 product.

The feed to this test consisted of a synthetic blend of 60 volume percent n-heptane, 20 volume percent m-xylene and 20 volume percent of p-xylene; the feed blend contained 0.8 mol of xylene. Substantially anhydrous liquid HF equal to 160 volume percent, based on total feed, was introduced into the reactor and then the feed was introduced therein. The contents of the reactor were agitated at about 68° F. for 60 minutes. The contents of the reactor were then permitted to settle for about 10 minutes before being withdrawn.

The lower extract phase was withdrawn into a vessel containing crushed ice; the hydrocarbons from the decomposed extract phase were decanted away from the aqueous layer and contacted with dilute aqueous caustic solution to remove traces of treating agent. The raffinate and the extract were analyzed by combination of infrared analysis, specific gravity and refractive index methods.

The raffinate was found to contain 25.3 volume percent of xylenes and the extract was found to contain 97% of xylenes. The mol ratio of TaF_5 to xylenes in the extract was 1.0. The molar composition of the xylenes present in the feed, raffinate and extract are tabulated below:

	Feed	Raffinate	Extract
m-Xylene	50	33.6	86.6
p-Xylene	50	66.4	13.4

The above test shows that a high purity meta-xylene product, i. e., about 95% meta-xylene and a high purity para-xylene product can be obtained by the use of about 4 theoretical extraction stages.

The figure shows an illustrative embodiment of our process. This figure demonstrates the treatment of a narrow boiling fraction in the xylene boiling range, i. e., 270° to 300° F. which has been derivel from the hydroforming of a virgin naphtha. The aromatic hydrocarbon content of this feed stock is ethylbenzene, 12 mol per cent; ortho-xylene, 21; meta-xylene, 48; and para-xylene, 19. The non-aromatic hydrocarbons of this feed amount to 55 volume percent of the total feed. The process described in this preferred embodiment of our process removes all the xylenes from the feed and converts much of the ethylbenzene into benzene and meta-diethylbenzene in a first step, and in a second step separates the xylenes into separate high purity isomeric fractions. In this example high purity means in excess of 95 mol per cent of the particular isomer.

In the first step of this process we show a tower-type of continuous countercurrent operation for the removal of substantially all the xylenes from the mixed feed. This tower can be packed with HF-resistant materials, such as, Raschig rings, Berl saddles, alumina balls, etc. Although we show a tower operation, we are not limited to the use of a tower and can use a series of batch countercurrent extraction zones. The separation factor for the removal of xylenes from non-complexible hydrocarbons is so great that in many cases a satisfactory degree of extraction can be obtained by a single stage contacting, i. e., only a single contractor and a settler are needed in the extraction zone. We prefer to use at least two stages when removing substantially all the xylenes from a feed stock of this type.

The mixed feed from source 11 is passed by way of line 12 into about the vertical midpoint of extraction tower 14. The exact point of feed entry will vary somewhat with the feed and the conditions of operation, e. g., in some cases the point of feed entry can be near the bottom of the tower. The complex formation is exothermic and to permit the maintenance of a substantially constant temperature in tower 14, heat exchangers 16, 17 and 18 are placed therein. These heat exchangers permit operation in the range of 30° to 80° F. throughout the tower. The tower may be operated with a temperature gradient from bottom to top, in some types of operation.

Substantially anhydrous liquid HF from source 21 is passed through line 22 into vessel 23, which vessel 23 is provided with agitating means not shown. Finely divided TaF_5 from storage 26 is passed by way of line 27 into vessel 23. Many methods are known for introducing a finely divided solid into a line and conveying the material into a closed vessel, e. g., storage 26 may be equipped with a star valve at the exit thereof and line 27 may be equipped with conveying flights for moving the solid. In vessel 23, the liquid HF and hte TaF_5 form a slurry—when, as is usually the case, more TaF_5 is used than is soluble in the liquid HF—which slurry is passed through line 29 into an upper part of tower 14. In this illustration the TaF_5 is added to the tower along with the liquid HF. However, the TaF_5 could be added along with the feed or could be injected into the tower directly; the treating agent may be added to the tower at one point as shown here, or at several points along the height of the tower between the point of feed entry and the top of the tower. Another method of introducing the TaF_5 into the system is to add $TaCl_5$ into vessel 23 where the chloride reacts with HF to produce TaF_5. Additional liquid HF must be added to vessel 23 to participate the reaction and leave the desired amount of liquid HF for use in the extraction zone. When adding $TaCl_5$, means for venting HCl should be provided on vessel 23.

In this illustration we use 200 volume percent of liquid HF based on the mixed feed and 1.3 mols of TaF_5 per mol of xylenes present in the mixed feed and 0.6 mol of TaF per mole of ethylbenzene present in the mixed feed. We have found that a slight excess of TaF_5 over the theoretical requirement is necessary in order to obtain substantially complete removal of xylenes from a mixed feed. However, we keep the excess addition as low as possible in order to reduce the amount of solid TaF_5 present in the extractor, and subsequently in the extract phase. This is done in order to reduce side reactions and decrease the problem of handling a mixed liquid-solid system. We contact at a uniform tempera-

ture of 60° F. and at a pressure of about 10 p. s. i. g. for a total time of about 10 minutes in tower 14.

In order to improve phase separation, selectivity of the extraction and elimination of close boiling non-aromatic hydrocarbons from the extract phase, an inert diluent, pentane, from source 31 is added to tower 14 by way of valved line 32 at a point near the bottom of the tower. The amount of pentane added is dependent on the feed, the temperature of the extraction and the amount of liquid HF and TaF_5 and may vary from about 10 to 200 volume percent. In this illustration we use 25 volume percent of pentane based on the C_8 aromatics in said feed.

Under some conditions of operation, liquid HF and TaF_5 are entrained in the raffinate phase and pass out of the tower. In order to retain most of this entrained material, a stream of liquid HF can be introduced into the tower below the exit point of the raffinate phase. This wash liquid HF is introduced into tower 14 by way of valved line 34. The amount of liquid HF from lines 29 and 34 should be adjusted to equal the amount of liquid HF desired to be present in extractor 14.

The raffinate phase, which includes some HF and TaF_5, is passed out of tower 14 by way of line 36 into coalescer 37. Coalescer 37 may be equipped with baffles, or may be packed with steel wool, etc. The entrained HF and TaF_5 agglomerate and drain to the bottom of coalescer 37. This recovered material is returned to tower 14 by way of valved line 38. The raffinate phase is passed out of coalescer 37 through line 41, heater 42 and line 43 into stripper 44, which is equipped with internal heater 46. The temperature in stripper 44 is maintained high enough to remove dissolved HF and, if desired, pentane. When removing both HF and pentane, a vapor outlet temperature of about 110° F. at atmospheric pressure is suitable. The raffinate oil which contains the non-aromatic hydrocarbons from the feed, some ethylbenzene and also benzene from the disproportionation of ethylbenzene, is withdrawn from stripper 44 by way of line 48 to storage not shown. This raffinate oil is an excellent blending stock for aviation gasoline by reason of its high octane number or the benzene can be readily recovered therefrom by distillative fractionation.

The vapors of HF and pentane are passed through line 49, cooler 51 and line 52 into separator 53. The liquid HF and pentane form two layers in separator 53. The lower HF layer is withdrawn by way of line 54 and is recycled to line 22 by lines not shown, for reuse in the process. The pentane is withdrawn by way of line 56 and is recycled to line 32 by lines not shown, for reuse in the process.

The extract phase from tower 14 consisting of liquid HF, TaF_5, complex and pentane, as the predominant non-aromatic hydrocarbon, is withdrawn through line 61, and is passed through heat exchanger 62 and line 63 into decomposer 64, which is provided with internal heater 65. Decomposer 64 is operated at low temperature in order to decompose the complex without the introduction of side reactions, such as, interaction between the meta-diethylbenzene and xylenes to form ethylxylenes. A decomposition temperature of about 50° F. is suitable. The liquid HF is removed from the extract phase and the complex by operating decomposer 64 under vacuum. The conditions of operation of the decomposer are such that only HF passes out of the top of decomposer 64 through line 66, and vacuum pump 67. The HF vapors from vacuum pump 67 are condensed in cooler 69 and are passed into valved line 71.

Instead of operating decomposer 64 under vacuum, the extract phase may be heated very rapidly to an elevated temperature of about 125° F. and decomposer 64 operated as a flash drum. Under these conditions, the extract phase and complex can be decomposed with only a slight formation of side reaction products.

After the removal of the HF, the bottom of decomposer 64 contains the extract hydrocarbons and solid, finely divided TaF_5 precipitate. The bottoms are withdrawn through valved line 74 and are passed into filter 76. Filter 76 may be any type of HF-resistant and HF-vapor tight filter, such as a plate and frame filter, a rotary filter, or a centrifuge may be used. We prefer to use a Sweetland-type filter. The TaF_5 is retained in the filter and the extract hydrocarbons are passed into valved line 77. It is to be understood that even though we show only one filter, for continuous operation two or more filters would be used.

The TaF_5 is removed from filter 76 by means of a backwashing operation with liquid HF from line 71. The slurry of liquid HF and TaF_5 is passed from filter 76 through valved line 79 to vessel 23 for reuse in the process.

The extract hydrocarbons which consist of xylenes, other polyalkylbenzenes and a very small percentage of non-aromatic hydrocarbons, predominantly pentane, are passed through valved line 77, heater 78 and line 79 into superfractionater 81 which is provided with an internal heater 82. When desired, extract hydrocarbons may be withdrawn from line 77 through valved line 84. Superfractionater 81 is operated to produce an overhead of pentane, meta-xylene and para-xylene, which pass out of fractionater 81 by way of line 86 and are condensed in cooler 87. The bottom produce of fractionater 81, mainly ortho-xylene, is withdrawn through line 91 and is passed through heater 92 and line 93 into fractionator 95, which fractionator is provided with internal heater 96. A substantially pure ortho-xylene fraction is taken overhead from fractionator 95 by way of line 97 and is sent to storage not shown. The bottoms fraction of other polyalkylbenzenes is withdrawn through line 99 and sent to storage not shown. This bottoms fraction has a very high octane number and makes a very suitable blending stock for aviation safety fuel.

The mixture of meta-xylene, para-xylene and pentane from cooler 87 is passed through line 111 into a lower portion of extraction tower 113. Extractor 113 is provided with heat exchangers 114, 115 and 116. Extractor 113 is very smiliar in construction to extractor 14. In order to obtain high purity meta-xylene and high purity para-xylene, extractor 113 must provide at least 3, and preferable 4, theoretical extraction stages.

Liquid HF from source 121 is passed through line 122 into vessel 123, which vessel 123 is provided with agitating means not shown. Finely divided TaF_5 from storage 126 is passed by way of line 127 into vessel 123. The slurry of HF and TaF_5 in vessel 123 is passed by way of line 129 into an upper part of tower 113. The remarks made in connection with the operation of extractor 14 are also applicable to the operation of extractor 113.

In order to obtain a degree of separation such that will produce high purity meta-xylene and para-xylene, the amount of TaF_5 present should be at least about 1 mol per mol of meta-xylene present in the feed from line 111. The amount of liquid HF used in extractor 113 is about 300 volume percent based on xylenes in the feed. The temperature of contacting in extractor 113 is maintained uniformly at 70° F. for a contacting time of about 15 minutes; pressure in tower 113 is about 15 p. s. i. g. We prefer to operate on a mixture of xylenes and inert hydrocarbons. We attain this condition in extractor 113 by introducing pentane from source 131 and line 132 at a point near the bottom of extractor 113. The amount of pentane added is about 100 volume percent based on xylenes charged to the tower from line 113. By introducing the pentane into the tower in this way, we obtain the desired dilution of the xylene feed and also obtain the advantages of good phase separation.

Liquid HF from line 122 is passed through valved line 134 into the top of tower 113 in order to wash out some of the entrained TaF_5 in the raffinate phase. The raffinate phase and entrained HF and TaF_5 is passed out of extractor 113 through line 136 into coalescer 137. The recovered HF and TaF_5 is returned to the extractor from the bottom of the coalescer through line 138. The raffinate phase from coalescer 137 is passed through line 141, heater 142 and line 143 into stripper 144, which stripper is provided with internal heater 146.

Stripper 144 is operated to remove overhead the HF and pentane present in the raffinate phase. The HF and pentane vapors pass overhead through line 149, are condensed in cooler 151 and pass through line 152 into separator 153. Liquid HF from separator 153 is withdrawn by line 154 and is recycled by lines not shown to line 122, for reuse in the process. Pentane is withdrawn from separator 153 by line 156 and is recycled to line 132 by lines not shown for reuse in the process. A high purity para-xylene product is withdrawn from stripper 144 by way of line 158 and is sent to storage not shown.

The extract phase consisting of liquid HF, complex and pentane is withdrawn from extractor 113 through line 161 and is passed through heater 162 and line 163 into decomposer 164. Decomposer 164 is provided with an internal heater 166. Decomposer 164 may be operated at temperatures somewhat above the boiling point of liquid HF in order to reduce the size of vessel. Appreciable isomerization of the meta-xylene to an equilibrium mixture of xylene isomers takes place at temperatures much in excess of about 125° F., so we prefer to operate decomposer 164 at temperatures below about 100° F. HF vapors are taken overhead through line 168, are condensed in cooler 169 and are passed to valved line 171.

The bottoms in decomposer 164 consist of solid, finely divided TaF_5 precipitate and high purity meta-xylene. These bottoms are withdrawn through valved line 174 and are passed into filter 176. Filter 176 is similar in construction and operation to filter 76. The meta-xylene product passes out of the filter by way of valved line 177. The solid TaF_5 retained in filter 76 is removed by backwashing with liquid HF from line 171. The slurry of HF and TaF_5 from filter 176 is passed through valved line 179 into vessel 123 for reuse in the process.

In order to improve the efficiency of operation in extractor 113, a reflux of meta-xylene is introduced near the bottom of the extractor. This reflux may be obtained from line 177 and is introduced into the extractor by way of valved line 181. When operating with a reflux, it is necessary to add an additional amount of TaF_5 into the tower over that needed to complex the meta-xylene present in the feed. We add 1 mol of TaF_5 to extractor 113 for each mol of meta-xylene introduced in to the extractor by way of line 181.

The product meta-xylene is sent to storage by way of line 184. The product meta-xylene contains about 95 mol percent of meta-xylene, between about 0.5 and 1% of pentane, and the remainder para-xylene. When it is desired to have a substantially pure aromatic hydrocarbon product, this pentane impurity can be removed by a simple distillation.

We do not wish to be bound by the above embodiment as the only way of carrying out our process. Many other variations are possible and we include these within the scope of the invention. For example, instead of decomposing the extract phase from extractor 14, the extract phase may be introduced into a second extractor and sufficient meta-xylene in the presence of a suitable amount of diluent hydrocarbon introduced into the second extractor to spring the ortho and para-xylenes from their complex. Other methods of recovering the TaF_5 from the decomposed extract phase can be used, such as, decantation followed by recycle of a thick slurry of TaF_5 and aromatic hydrocarbons. Of course additional TaF_5 is needed in this method of operation in order to recover the recycled aromatic hydrocarbons.

We claim:

1. A process for treating a mixture of isomeric lower dialkylbenzenes, which process comprises contacting said mixture at a temperature below about 125° F. with an amount of liquid HF sufficient to form a separate acid phase, and an amount of TaF_5 which is not sufficient to cause all of said isomeric lower dialkylbenzenes to pass into said acid phase, and separating a raffinate phase from said acid phase and wherein the relative ratio of isomeric lower dialkylbenzenes in said acid phase is different from the relative ratio in said raffinate phase and the ratio in both of said phases are different from the ratio in said mixture.

2. The process of claim 1 wherein the amount of TaF_5 is less than about 1 mol per mol of dialkylbenzene present in said mixture and the amount of liquid HF is between about 5 and 500 volume percent based on said mixture.

3. The process of claim 1 wherein the alkyl substituents of said lower dialkylbenzenes contain between 1 and 5 carbon atoms.

4. A process for separating a mixture of at least two xylene isomers, which process comprises contacting said mixture at a temperature between about 0° and 125° F., with between about 5 and 500 volume percent of liquid HF based on said mixture and TaF_5 in an amount less than about 1 mol per mol of xylenes in said mixture, separating a raffinate phase from an extract phase, which extract phase comprises liquid HF, TaF_5 and xylenes and wherein the ratio between the xylene isomers in said extract phase is different from the ratio in said raffinate phase and the ratios in said extract phase and said raffinate phase are different from the ratio in said mixture.

5. The process of claim 4 wherein said mixture comprises essentially meta-xylene and para-xylene.

6. A process for separating meta-xylene from admixture with at least one other xylene isomer, which process comprises contacting said mixture at a temperature below about 90° F. with between about 100 and 300 volume percent, based on said mixture, of liquid HF and between about 0.3 and 1.5 mols of TaF_5 per mol of meta-xylene in said mixture, separating a raffinate phase from an extract phase wherein said raffinate phase has a molal ratio of meta-xylene to the other xylene isomers therein lower than the ratio in said mixture, and wherein the molal ratio of meta-xylene to other xylenes in said extract phase is higher than the ratio in said mixture, and recovering xylene isomers from said extract phase.

7. The process of claim 6 wherein said contacting is carried out in a continuous countercurrent apparatus and wherein the amount of TaF_5 is about 1 mol per mol of meta-xylene in said mixture and wherein the mixture of xylene isomers in said extract phase contains about 95% meta-xylene.

8. A process for recovering xylenes from a mixture of C_8 aromatic hydrocarbons, which process comprises contacting said mixture at a temperature below about 90° F. with between about 5 and 500 volume percent of liquid HF based on said mixture, and between about 0.3 and 1.5 mols of TaF_5 per mol of xylene in said mixture, and about 0.5 mol of TaF_5 per mol of ethylbenzene in said mixture and recovering xylene isomers from the products of said contacting.

9. The process of separating a mixture of xylene isomers, which process comprises contacting said mixture at a temperature below about 125° F., in the presence of an inert hydrocarbon diluent, with between about 5 and 500 volume percent of liquid HF based on xylenes and less than about 1 mol of TaF_5 per mol of xylenes, separating a raffinate phase, comprising essentially said diluent and xylenes, from an extract phase, comprising essentially liquid HF, xylenes, TaF_5 and a minor amount of said diluent, and wherein the relative ratio of the xylenes in said extract phase is different from the relative ratio of xylenes in said raffinate phase, and wherein both of said ratios are different from the ratio of xylenes in said mixture of xylene isomers, and recovering the xylenes from said extract phase and from said raffinate phase.

10. The process of claim 9 wherein said inert hydrocarbon diluent is present in an amount between about 50 and 500 volume percent based on said xylene.

11. The process of claim 9 wherein said inert hydrocarbon diluent is selected from the group consisting of paraffinic hydrocarbons containing between 3 and 6 carbon atoms.

12. A process of recovering meta-xylene from admixture with at least one other xylene isomer and ethylbenzene, which process comprises contacting said mixture at a temperature below about 90° F., in the presence of an inert hydrocarbon diluent, with between about 100 and 300 volume percent of liquid HF based on C_8 aromatic hydrocarbons and TaF_5 in an amount of about 1 mol per mol of meta-xylene in said mixture, and about 0.5 mol per mol of ethylbenzene in said mixture, separating a raffinate phase comprising essentially inert hydrocarbon diluent, benzene and C_8 aromatic hydrocarbons from an extract phase comprising essentially liquid HF, TaF_5, xylenes and C_{10} aromatic hydrocarbons and recovering from said extract phase a mixture of xylene isomers consisting predominately of meta-xylene.

13. A process for refining a hydrocarbon oil containing polyalkylbenzenes, which process comprises contacting said oil at a temperature below about 200° F. with from about 0.1 and 100 weight percent of TaF_5 in the presence of from about 10 to 500 volume percent of liquid HF, both based on said oil, and separating a raffinate phase from an extract phase.

14. The process of claim 13 wherein the usage of TaF_5 is between about 0.1 and 25 weight percent.

15. The process of claim 13 wherein the usage of liquid HF is between about 30 and 300 volume percent.

16. The process of claim 13 wherein said temperature is between about 50° and 100° F.

17. A process for removing polyalkylbenzenes from a naphtha which contains substantially no other extractable materials, which process comprises contacting said naphtha with about 1 mol of TaF_5 per mol of polyalkylbenzene to be removed in the presence of about 10 to 500 volume percent, based on said naphtha, of liquid HF at a temperature below about 100° F., and separating a raffinate phase from an extract phase, which extract phase contains extracted polyalkylbenzenes.

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