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ALKYLATION AND CATALYST RECOVERY

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This invention relates to an alkylation process. More particularly, it relates to an alkylation process wherein an aromatic sulfonic acid catalyst is employed. In a preferred form, this invention relates to the alkylation of an alkylatable hydrocarbon with an olefinic hydrocarbon in the presence of a substantially anhydrous toluene sulfonic acid.

In processes for the alkylation of an alkylatable hydrocarbon employing an olefin as an alkylating agent and an aromatic sulfonic acid catalyst, the alkylation reaction mixture is worked up by treatment with an aqueous or alcoholic alkali, e. g., NaOH, to remove free aromatic sulfonic acids and the alkali-treated reaction mixture is then subjected to fractional distillation to separate products and unreacted materials. Catalyst losses, for a reason not hitherto appreciated, were excessive, and the employment of aromatic sulfonic acids was not considered practical except for the alkylation of small amounts of difficultly alkylatable compounds such as certain nitrogen-containing organic compounds having a very high market value. In the fractional distillation equipment employed in these processes, excessive corrosion has been encountered and, at times, plugging of the condensers, run-down lines and the like. Thus, in processes wherein anhydrous toluene sulfonic acid catalysts are employed for alkylation of aromatics with olefins, excessive catalyst losses, corrosion of distillation equipment and plugging of condenser lines resulted upon working up the reaction mixture in the manner described above.

It is an object of this invention to provide an improved process for the alkylation of alkylatable hydrocarbons wherein aromatic sulfonic acid catalysts are employed. Another object of this invention is to provide an improved process for the alkylation of aromatic hydrocarbons with substantially anhydrous toluene sulfonic acid catalysts wherein over-alkylation of the aromatic hydrocarbon is substantially avoided. An additional object is to provide an improved continuous alkylation process wherein aromatic sulfonic acid catalysts are employed. Still another object of this invention is to provide an improved method of working up the alkylation products and recovering and re-using catalyst in alkylation processes employing aromatic sulfonic acids as catalysts. A further object of this invention is to prevent plugging of condensers on product fractionators used in processes wherein alkylatable hydrocarbons are alkylated with olefins in the presence of aromatic sulfonic acids. Still other objects will become apparent from the following description of this invention.

In accordance with this invention, the above-enumerated difficulties encountered in alkylation processes employing substantially anhydrous aromatic sulfonic acid catalysts can be obviated by subjecting the alkylation reaction mixture, after discontinuing the injection of olefin hydrocarbons into said reaction mixture, to a suitable temperature for a period of time sufficient to result in substantial regeneration of free aromatic sulfonic acids from aromatic sulfonic esters which are formed in the course of the alkylation operations. The treatment of aromatic sulfonic esters to produce free aromatic sulfonic acids will hereinafter be described as aromatic sulfonic ester conversion. The regenerated aromatic sulfonic acids can then be readily removed from the alkylation products, e. g., by washing with an alkaline material such as caustic. After the regeneration and removal of aromatic sulfonic acid, the alkylation products may be readily distilled or fractionated without encountering excessive corrosion in the distillation equipment or plugging or fouling of condensers used in conjunction with the distillation equipment. The sulfonic acid catalyst may be regenerated from the alkali washing liquor and may be recycled to the alkylation reactor after a dehydration treatment. The process of the present invention renders possible substantially complete catalyst recovery for re-use in alkylation.

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Other methods of separating regenerated aromatic sulfonic acids from the reaction mixture can also be used. A particularly desirable method of separation comprises diluting the alkylation reaction mixture with a saturated aliphatic hydrocarbon in quantity sufficient to effect a substantial reduction in the solubility of the aromatic sulfonic acid in the alkylation reaction mixture, thereby yielding a distinct stratum of aromatic sulfonic acid which can be separated from the alkylation products and re-used. Ordinarily, the addition of about 0.25 to about 3 volumes of saturated aliphatic hydrocarbon such as hexanes, cyclohexane, pentanes, butanes, or their homologs or mixtures, e. g., naphtha, kerosene, gas oil, or the like, per volume of the alkylation reaction mixture is sufficient, although it will be understood that in some instances even greater dilution of the alkylation reaction mixture may be necessary. Temperatures between about 50 and about 150° F. may be conveniently maintained during the separation of the aromatic sulfonic acid phase from the alkylation products phase. The small proportion, e.g., 1–3%, of regenerated aromatic sulfonic acid which remains in solution in the alkylate can be removed by washing with water or alkalies prior to fractionating the alkylate.

This invention is particularly applicable to continuous alkylation processes. In a continuous process, an aliquot portion of the alkylate reaction mixture is removed continuously or intermittently and treated in accordance with the process of the invention to recover aromatic sulfonic acid catalyst, which is preferably recycled to the alkylation reactor, and alkylation products which are fractionally distilled to recover desired alkylates and unalkylated and/or over-alkylated materials, which may also be recycled to the alkylation reactor.

In order to prevent alkylation of the alkylatable hydrocarbon feed stock beyond the desired ex-

tent it is desirable to effect conversion of the aromatic sulfonic ester in the presence of an alkylatable substance, which is not identical with the feed stock used in the alkylation process. In a desirable alkylation process, olefinic hydrocarbons are injected into an alkylation reactor containing the alkylatable hydrocarbon and aromatic sulfonic acid catalyst until the alkylatable hydrocarbon has been alkylated to the desired extent, the olefin injection is discontinued, an alkylatable substance is thereafter added to the alkylation reactor and the aromatic sulfonic ester formed during the course of the alkylation operation is converted to aromatic sulfonic acid and an alkylated substance. Alkylatable substances suitable for use in our process include phenols, aromatic hydrocarbons, various sulfur and nitrogen compounds containing hydrogen bonded thereto, etc.

The process of this invention can be practiced with a wide variety of alkylatable hydrocarbons. It is preferred particularly for the alkylation of aromatic hydrocarbons, e. g., benzene, toluene, xylenes, ethylbenzene, ethyltoluenes, cymene, cumene, n-propyl benzene, isopropyl benzene, naphthalene and alkyl naphthalenes, e. g., methyl naphthalenes, dimethyl naphthalenes, and trimethyl naphthalenes, diphenyl, alkyl diphenyls, anthracene, alkyl anthracenes, phenanthrenes, etc. The process of this invention can be applied to either pure aromatic hydrocarbons or to mixtures of aromatic hydrocarbons which may also contain paraffins and naphthenes of similar boiling range. It is particularly applicable to synthetic mixtures of aromatic hydrocarbons such as are produced from coal tar processing, by hydroforming naphthas (hydrocatalytic reforming) and other processes which produce aromatic hydrocarbons.

Specifically, the process of this invention has been applied with gratifying results to synthetic aromatic hydrocarbon fractions containing a high proportion of alkyl polycyclic aromatic hydrocarbons, particularly mono-, di-, and trimethyl naphthalenes. Suitable sources of alkyl polycyclic aromatic hydrocarbons for use in our process are synthetic hydrocarbon fractions obtained by the catalytic conversion of petroleum oils with catalysts comprising at least one metal oxide selected from groups 2 to 6, inclusive, of the periodic table.

A suitable process for the production of alkyl polycyclic aromatic hydrocarbons is the hydroforming process. In this process a petroleum naphtha, which may be a virgin or cracked naphtha or mixture of both, is converted to aromatic hydrocarbons by contact with a solid, porous dehydrogenation catalyst at a temperature in the range of about 850° F. to about 1050° F., preferably in the presence of hydrogen. Suitable catalysts are oxides of metals of groups 2 to 6 of the periodic system, particularly oxides of 6th group metals such as chromium and molybdenum, preferably supported by alumina or magnesia. Excellent catalysts can be prepared by depositing about 4 to about 10% of molybdenum oxide upon an activated alumina. Suitable space velocities for hydroforming fall within the range of about 0.2 to about 4 volumes of the liquid charge stock per hour per volume of catalyst space. About 0.5 to about 8 mols of hydrogen can be charged to the process with each mol of naphtha feed stock. In addition to a high octane number naphtha, the hydroforming process produces a fraction which boils above the naphtha range, for example, in the range of about 425 to about 650° F., which is known as hydroformer bottoms.

Hydroformer bottoms comprises a complex mixture of alkyl- and polyalkyl polycyclic aromatic hydrocarbons, including relatively large proportions of mono- and polymethyl naphthalenes.

The process of this invention can also be applied to alkyl polycyclic aromatic hydrocarbons derived from certain crude petroleum oils by extraction with selective solvents. Alkyl polycyclic aromatic hydrocarbons are also present to a considerable extent in cracked cycle stock produced by cracking high boiling petroleum oils such as gas oils, preferably with catalysts. Cracking with solid cracking catalysts comprising one or more oxides of metals selected from groups 2 to 6, inclusive, of the periodic table can be effected at temperatures of the order of about 850 to 1050° F. and pressures of atmospheric to 50 p. s. i. or even higher. A suitable cracking catalyst is active silica promoted with about 5 to about 30% of active alumina or magnesia. Also, activated clays can be used as catalysts. Alkyl polycyclic aromatic hydrocarbons can be concentrated from cracked cycle stocks by a variety of selective solvents. Suitable selective solvents include nitromethane, nitroethane, ethylene glycol monoethyl ether, diethylene glycol monoethyl ether, diethylene triamine, dipropylene glycol, methanol, ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, morpholine ethanol, triethylene tetramine, tetraethylene pentamine, etc.

A wide variety of olefinic hydrocarbons can be used as alkylating agents in our process, e. g., propylene, butene-1, butene-2, isobutene, pentenes, hexenes, heptenes, and the like.

Aromatic hydrocarbons can generally be alkylated by olefinic hydrocarbons in the presence of aromatic sulfonic acid catalysts at temperatures in the range of about 150 to about 400° F., providing that the highest temperature chosen for alkylation does not exceed the decomposition temperature of the particular sulfonic acid used as the catalyst. With substantially anhydrous toluene sulfonic acids, alkylation temperatures in the range of about 265 to about 300° F. are preferred. Alkylation pressures may be atmospheric or higher, e. g., 0 to 100 p. s. i. g. or even higher. The proportion of aromatic sulfonic acid catalyst may vary from about 1 to about 20 mol percent based on the aromatic hydrocarbon feed stock, or even more, the upper limit being in some instances, determined by the limiting solubility of the catalyst in the aromatic hydrocarbon feed stock. Ordinarily, increased rates of alkylation are obtained with increasing amounts of catalyst in the reactor. The specific feed stocks, catalysts, proportions of catalysts, and desired extent of alkylation will, naturally, affect the optimum duration of the reaction period. Normally, for mono-alkylation, reaction periods in the range of about 5 to about 25 hours may be used.

The specific aromatic sulfonic ester conversion temperatures employed in the process of this invention will depend upon the particular aromatic sulfonic ester formed in the process. In general, conversion of the ester may be effected at the temperatures used in the alkylation process. The rate of conversion may be increased by operating at a temperature above the alkylation temperature but not in excess of the decomposition temperature of the corresponding aromatic

sulfonic acid and/or under a pressure below that employed in the alkylation operation, particularly atmospheric or lower pressures such as pressures of 100, 25, 10, or even 1 mm. of mercury. Generally suitable aromatic sulfonic ester conversion temperatures fall within the range of about 150 to about 400° F. Suitable conversion temperatures for toluene sulfonic esters will generally fall within the range of about 200 to about 300° F. The time necessary to effect conversion will depend on the particular aromatic sulfonic ester, its amount, other conversion conditions, the desired extent of conversion, etc. Suitable times corresponding with the general conversion temperature range given above ordinarily exceed about 0.5 hour, and may fall within the range of about 1 to about 10 hours. With anhydrous toluene sulfonic esters, conversion times in excess of about 0.5 hour may be used, preferably about 2 to about 4 hours. It may be possible to increase the rate of conversion by the use of catalysts, such as hydrogen chloride gas, hydrogen fluoride, active clays, BF_3, etc.

During conversion of the aromatic sulfonic ester it is desirable to subject the mixture of alkylation reaction products to vigorous agitation. Mechanical agitation may be used alone, or may be supplemented with or supplanted by agitation with gases which serve also as a stripping medium. A refinery propane or butane stream may, for example, be used as a stripping and agitating gas.

The following examples are illustrative, but not limitative of my invention. The aromatic hydrocarbons to be alkylated were alkyl naphthalenes obtained from hydroformer bottoms. The examples describe the use of my preferred catalyst, a substantially anhydrous toluene sulfonic acid. The catalyst may be ortho-, meta-, or para-toluene sulfonic acid, but I prefer to use a "technical" toluene sulfonic acid which contains more than one isomer and may contain all three.

I have found that the substantially anhydrous toluene sulfonic acids are much more soluble in hydrocarbons than hydrous toluene sulfonic acids and can be used as homogeneous catalysts under conditions where hydrous toluene sulfonic acids are quite immiscible with hydrocarbon feed stocks. Furthermore, anhydrous toluene sulfonic acids appear to induce higher reaction rates than the hydrated acids. In fact, in many instances, hydrated toluene sulfonic acid has been found to be substantially devoid of catalytic alkylation activity. Typical toluene sulfonic acids which I have employed as catalysts for the alkylation of alkyl polycyclic aromatic hydrocarbon with olefins have the following properties:

TABLE I

Neutralization equiv. (theory: 172)	177.5
Density, grams/ml. at 84.9° F	1.3043
Refractive index:	
(a) Of 11.4% aqueous solution	1.352
(b) Calculated to 100% toluene sulfonic acid	1.507
Crystallizing point, °F. (approx.)	95
Water content, weight, percent (by refluxing with toluene, 3.5 hours)	1.05
Physical appearance	Viscous liquid or semi-crystalline mass depending on temperature; dark reddish brown color.
Assay (toluene sulfonic acids)	94.0% (min.)
Free H_2SO_4	1.0% (max.)
Toluene	0.2% (max.)
Water	2.0% (max.)
Sulfones	3.0% (max.)
Para toluene sulfonic acid	80% (approx.)
Ortho toluene sulfonic acid	20% (approx.)

Table II sets forth examples of the butylation and propylation of hydroformer bottoms fractions. In Table II, the hydroformer bottoms fraction boiling in the range of 437 to 554° F. comprised predominantly a mixture of mono-, di-, and trimethyl naphthalenes. The hydroformer bottoms fraction boiling at 482 to 527° F. comprised predominantly dimethyl naphthalenes. Specific operating procedures used in obtaining the data set forth in Table II will be described below.

TABLE II

Preparation and properties of butylated and propylated alkyl naphthalenes

Example	1	2	3
Product	mono and dibutyl	crude mono and dibutyl	dipropyl.
Reactor	5 liter glass	2 gallon steel	3 liter glass.
Alkylation Conditions:			
Mol per cent toluene sulfonic acid catalyst.	3	10	8.
Pressure	Atm	30 p. s. i. g	70 mm. Hg.
Temperature, °F	265–285	265–285	257–265.
Time	80 hrs	18 hrs	92 (in excess).
Mols olefin absorbed/mol hydroformer bottoms.	1.2	1.51	2.14.
Charge Stock:			
Olefin	Butene-1	Mixed B–B [1]	Refinery propylene.[3]
Hydroformer bottoms, boiling range (°F.) at 1 atm.	482–527	437–554	437–554.
Total Product Yields, Wt. per cent Based on Charge:			
Unreacted	26	21.2	7.6
Monoalkylated	38.7	97.7	17
Dialkylated	60.4		106.1
Polyalkylated and Bottoms	17.9	35.1	7.3
Total	143	154	138
Dialkylated Product, Wt. per cent of Theoretical Yield.	35.2	56.8	69.1.
Products	1	2	3.
Boiling Range, °F	{248–338/1 mm {563–680/760 mm	541–633/760 mm	{612–653/772 mm. {293–318/1 mm.
n_D^{25}	1.5630	1.5464	1.5592.
d_4^{25}	0.9489	0.921	0.9390.
Color	Light Yellow	Light Red (4½ ASTM).	Light Yellow (1½ ASTM).
Weight per cent Aromatics by sulfonation [2]	98.6		98.5.
Iodine No. (Wijs)	0.0	0.7	0.
Viscosity at 100° F., Centistokes	24.9	42.1	46.5.
Saybolt Viscosity, Universal (seconds/-100° F.).	118	195	215.

[1] Refinery butane-butylene stream containing 41% olefins.
[2] Method tends to give low values in the high ranges or aromatic content.
[3] Contains 47.9% propylene.

Example 1

A sample of butylated hydroformer bottoms was prepared by the alkylation of a three mol percent solution of technical (anhydrous) toluene sulfonic acid in dimethylnaphthalenes. The solution was placed in a 5 liter, 3 neck flask fitted with an efficient mechanical stirrer, a water condenser, and a gas distributor which introduced the gas through small holes beneath the surface of the liquid. The gas was metered in at a rate slightly faster than it was absorbed. The alkylation was continued until 1.2 mols of olefin per mol of hydroformer bottoms, calculated as dimethylnapthalene, had been absorbed. Beyond this point the absorption of olefins was slow. Alkylation was then stopped and when the flask contents had cooled the reaction mixture was washed carefully with dilute alkali and then with water in order to remove the catalyst. When vacuum distillation of the dired mixture was attempted, the presence of a white crystalline solid was noted in the distillate; some had also solidified in the condenser. This solid was a hydrated toluene sulfonic acid which had been liberated by the decomposition of toluene sulfonic esters at the distillation temperature. The solid was found to be very soluble in water and highly acidic. The distillation was continued, however, at total take-off allowing remaining esters to decompose until the temperature reached 410° F. at 3 to 4 mm. Hg pressure. The toluene sulfonic acid was washed out of the distillate with dilute alkali and nonalkylated and unreacted hydrocarbons were removed by topping this distillate through a 60 x 2.5 cm. column packed with ⅛ inch Fenske helices to an overhead temperature of 450° F. at 200 mm. pressure. The product was diluted with isopentane and decolorized by filtering through clap. After solvent removal the mixed mono- and di-butyl dimethylnaphthalene yield based on crude butylated product was 75 weight percent. Physical properties were determined and are listed in Table II under product 1.

Example 2

For this alkylation, a refinery stream of butylenes-butanes B-B) was used in place of pure butene-1, and found to be quite satisfactory. The B-B charge, containing 41% olefins, was dispersed well under the surface of the liquid through a distributor tube. The exhaust gas from which most of the olefins had been removed was allowed to escape from a pressure reducing valve located at the top of the reactor. Samples of the exhausted gas were taken from time to time and anaylzed for total unsaturates. As alkylation progressed the reaction became slower and the concentration of olefins in the exhausted gas increased until a constant value was reached. Toluene sulfonic esters formed in the course of alkylation were removed from alkylation products by allowing them to alkylate more naphthalenes after the addition of the olefin charge was discontinued. To this end, an "after-alkylation" period of 3–4 hours was allowed, followed by caustic washing to remove regenerated toluene sulfonic acid. The results were very satisfactory, as judged from the fact that no evidence of toluene sulfonic acid on final distillation could be found. After the initial alkylation product was treated with alkali, it was substantially neutral. However, after the "after-alkylation" operation the product was distinctly acidic, showing that toluene sulfonic acid was liberated. The color of the alkylation products was improved by filtering an isopentane solution thereof through an adsorptive clay.

Example 3

Propylene from a refinery stream was used, under conditions similar to those employed in butylene alkylation (see Example 2) to alkylate a mixture of mono-, di-, and tri-methylnaphthalene to produce dipropyl derivatives. Upon completion of alkylation, propylene injection was discontinued and the alkylation reaction mixture was maintained, with stirring, at the reaction temperature for four hours to convert toluene sulfonic propyl esters to free toluene sulfonic acid and additional alkylate. Regenerated toluene sulfonic acid was removed from the alkylate by washing with aqueous caustic and the alkylate was then fractionated.

It will be evident that the above examples merely describe a preferred embodiment of my novel alkylation and catalyst recovery process. My invention is to be limited only by the following claims.

I claim:

1. In a process for the alkylation of an alkylatable hydrocarbon wherein said hydrocarbon is contacted in an alkylation zone with an added olefin stream and a substantially anhydrous aromatic sulfonic acid, whereby said alkylatable hydrocarbon is alkylated and a substantial proportion of said aromatic sulfonic acid is converted to an ester derived from said olefin and aromatic sulfonic acid, the steps which comprise discontinuing the addition of said olefin stream upon completion of the desired alkylation reaction, subjecting the alkylation reaction mixture to a temperature and for a time sufficient to effect substantial conversion of said ester, whereby aromatic sulfonic acid is regenerated, diluting the alkylation reaction mixture with a saturated hydrocarbon in quantity sufficient substantially to reduce the solubility of the aromatic sulfonic acid in the alkylation reaction mixture, whereby the aromatic sulfonic acid separates as a distinct stratum from the alkylation reaction products, and recovering aromatic sulfonic acids so produced.

2. The process of claim 1 wherein at least a portion of the aromatic sulfonic acid which is regenerated and recovered from the reaction mixture is recycled to the alkylation zone.

3. In a process for the alkylation of an alkyl polycyclic aromatic hydrocarbon wherein said hydrocarbon is contacted with an added olefin stream and a small, catalytic quantity of a substantially anhydrous aromatic sulfonic acid, whereby said alkyl polycyclic aromatic hydrocarbon is alkylated and a substantial proportion of said aromatic sulfonic acid is converted to an ester derived from said olefin and aromatic sulfonic acid, the steps which comprise discontinuing the addition of said olefin stream upon completion of the desired alkylation reaction, subjecting the alkylation reaction mixture under conditions precluding substantial distillation thereof to a temperature in the range of about 150° F. to about 400° F. for a period of time between about 0.5 and about 10 hours to effect substantial conversion of said ester, whereby aromatic sulfonic acid is regenerated, diluting the alkylation reaction mixture with a saturated hydrocarbon in quantity sufficient substantially to reduce the solubility of the aromatic sulfonic acid in the alkylation reaction mixture, whereby the aromatic sulfonic acid separates as a distinct stratum from the alkylation reaction products and recycling at

least a portion of regenerated, substantially anhydrous aromatic sulfonic acid thus recovered to the alkylation operation.

4. The process of claim 1 wherein the conversion of the aromatic sulfonic ester is effected at a temperature between about 150° F. and about 400° F. for a period of time between about 0.5 and about 10 hours.

5. The process of claim 1 wherein the aromatic sulfonic acid is substantially anhydrous toluene sulfonic acid.

6. The process of claim 1 wherein the alkylatable hydrocarbon is an alkyl polycyclic aromatic hydrocarbon.

7. The process of claim 1 wherein the alkylatable hydrocarbon is contained in a fraction comprising a substantial proportion of methylnaphthalenes, said fraction boiling between about 437° F. and about 554° F. at one atmosphere.

8. The process of claim 1 wherein the aromatic sulfonic acid is substantially anhydrous toluene sulfonic acid and wherein the alkylatable hydrocarbon is contained in a fraction comprising a substantial proportion of methylnaphthalenes, said fraction boiling between about 437° F. and about 554° F. at one atmosphere.

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