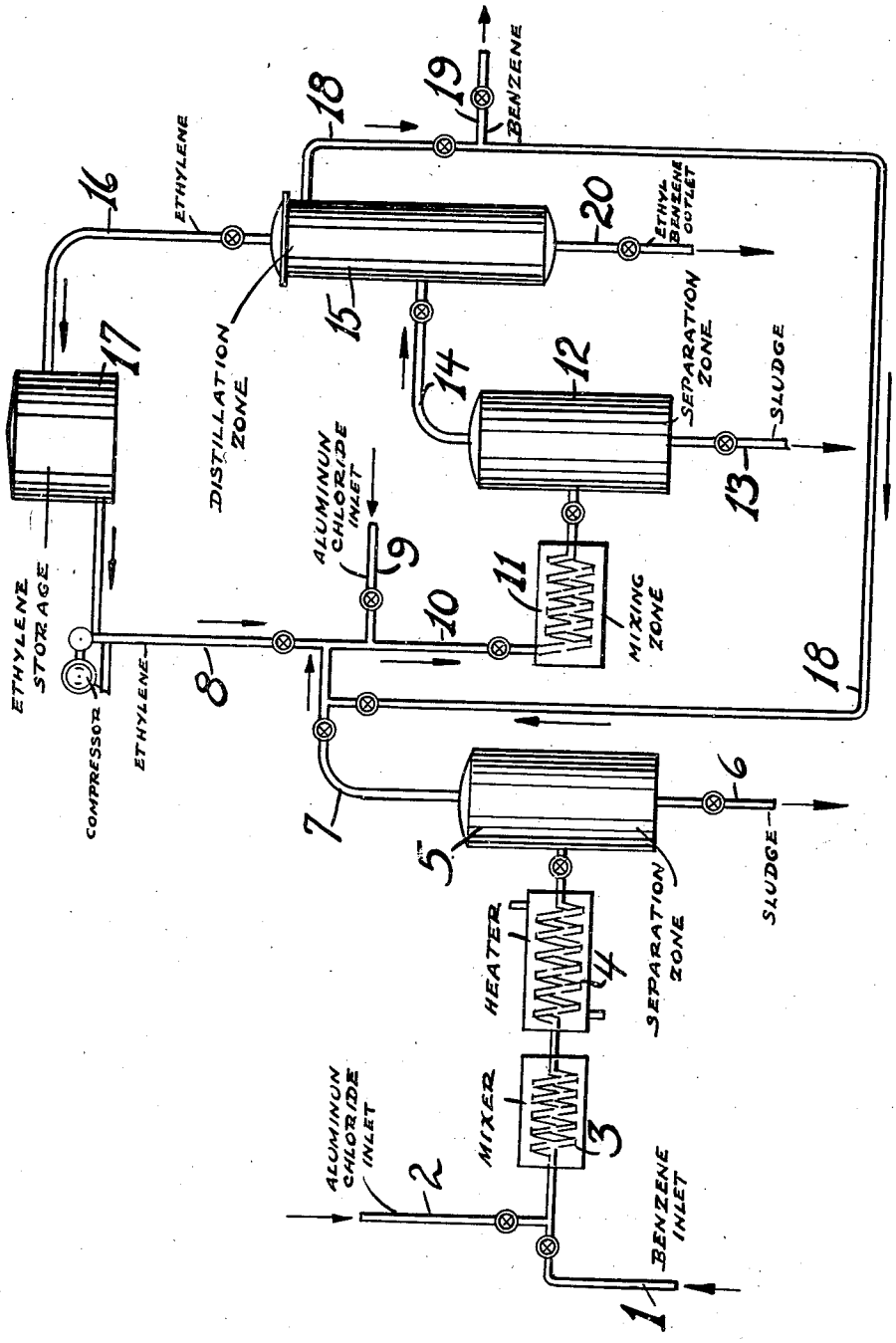
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ALKYLATED AROMATIC HYDROCARBONS

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ALKYLATED AROMATIC HYDROCARBONS

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The present invention is concerned with an improved process for the preparation of alkylated aromatic hydrocarbons, and particularly ethyl benzene. The invention is more particularly concerned with a process for the treatment of commercial or impure benzene by which it is possible to subsequently react the same with ethylene under conditions in which substantially improved yields of ethyl benzene are secured per volume of catalyst employed.

In accordance with the present process, ethyl benzene is prepared from commercial benzene by first pretreating the commercial benzene with a Friedel-Crafts halide catalyst, and particularly aluminum chloride or a similar reagent, followed by ethylating the treated benzene in a secondary stage with ethylene, also in the presence of a catalyst.

It is well known in the art to produce ethyl benzene by various operations. For example, one conventional process employed is to condense ethylene with benzene in the presence of aluminum chloride or other similar catalyst, followed by removing the ethyl benzene by a distillation process. An operation of this character, while entirely satisfactory for producing the ethyl benzene, does have the disadvantage that relatively low yields of ethyl benzene are secured per unit volume of catalyst employed, particularly when the benzene is secured from commercial sources.

I have, however, now discovered that, providing the feed benzene be treated in an initial stage with a relatively small quantity of aluminum chloride and the sludge removed, followed by reacting the benzene in a secondary stage with ethylene and additional catalyst, a marked unexpected improvement in yield is secured. The process of my invention may be readily understood by reference to the attached drawing illustrating one embodiment of the same. For the purpose of description it is assumed that the benzene comprises one secured from coal tar. This benzene is introduced into the system by means of line 1. The benzene is mixed with a suitable catalyst which for the purpose of description is taken to be aluminum chloride, which is introduced into line 1 by means of line 2, passed through mixer 3, heating zone 4 and then introduced into separation zone 5. Temperature and pressure conditions are adjusted so as to secure the formation of a sludge which is removed by means of line 6 along with the added aluminum chloride. The pretreated benzene is withdrawn from separation zone 5 by means of line 7 and combined with ethylene which is introduced by means of line 8.

Additional aluminum chloride is introduced into the system by means of line 9, the mixture passed through mixing zone 10, heating zone 11, and introduced into separation zone 12. The spent aluminum chloride is removed by means of line 13 while the reaction product comprising ethyl benzene is removed by means of line 14 and passed into distillation zone 15 wherein the unreacted ethylene is removed overhead by means of line 16 and returned to ethylene storage 17 from where it may be recycled to the system by means of line 8. The unreacted benzene is removed as an intermediate side stream by means of line 18 and preferably recycled to the secondary stage. However, under certain conditions it may be desirable to withdraw this benzene from the system by means of line 19. The ethyl benzene is removed from distillation zone 15 by means of line 20.

The process of the present invention may be widely varied. The invention essentially comprises pretreating benzene in an initial zone with a catalyst, preferably with a small amount of aluminum chloride in order to remove objectionable constituents, followed by contacting the treated benzene in a secondary stage with additional catalyst, preferably aluminum chloride in the presence of ethylene, under conditions to form ethyl benzene. It is to be understood that the respective zones comprise any suitable number and arrangement of units.

The catalyst employed in the initial zone may comprise any suitable material which will tend to form a sludge of the objectionable constituents. Suitable catalysts are Friedel-Crafts type halides or mixtures thereof. However, the preferred substance comprises aluminum chloride. The amount of aluminum chloride employed may vary considerably depending upon the character of the benzene and the related operating conditions. However, in general I prefer to employ from 0.01 to 0.1 mol of aluminum chloride per mol of benzene. In accordance with the preferred modification of my invention, it is desirable to employ atmospheric pressure although higher pressures may be used if desired in the initial stage, and to contact the aluminum chloride and benzene at a temperature in the range from about 100 to 200° F., preferably 140 to 180° F. The benzene and aluminum chloride are held at this temperature for a sufficient time period which is in the range from about ½ to 2 hours.

The treated benzene removed from the initial stage is then contacted with a catalyst adapted to secure the ethylation of the benzene. Although catalysts such as Friedel-Crafts halides may be used, I prefer to employ aluminum chloride. In general, it is desirable to use from 0.5 to 1.5 mols of aluminum chloride per 6 to 10 mols of benzene. The ethylation reaction is generally conducted by employing approximately 3 mols of benzene per mol of ethylene. The temperature is conducted in the general range from about 130 to 180° F. and at atmospheric pressure, although higher pressures may be employed. The time of reaction will vary widely depending upon specific operating conditions but in general is about ½ to 1½ hours.

Under these conditions, the amount of ethyl benzene formed per unit volume of catalyst is appreciably high.

In order to illustrate the invention further, the following example is given which should not be construed as limiting the same in any manner whatsoever:

Example 1

Commercial benzene obtained from coal tar was refluxed with 0.01 mol fresh $AlCl_3$ per mol of benzene for one hour at 160° F. The mixture was settled and the thus treated benzene was alkylated with ethylene (3 mols benzene per mol ethylene) with a contact time of about one hour at 160° F. to obtain a yield of 16.7 lbs. of ethyl benzene per pound of catalyst. This compares with a yield of 10.7 lbs. with commercial untreated benzene, and 15.4 lbs. with a commercially purified benzene.

Example 2

In one operation, commercial benzene was treated with 5 pounds of 98% sulfuric acid per barrel. The benzene was then treated with caustic, followed by washing with water and then drying. The acid treating loss was less than about 1%. The benzene was then ethylated, employing an aluminum chloride catalyst at a temperature of about 160° F. and atmospheric pressure. Under these conditions, the yield of ethyl benzene was 10.7 lbs. per pound of aluminum chloride.

In another operation, the commercial benzene was employed directly for the ethylation of benzene under identical conditions using aluminum chloride as the catalyst.

In a third operation, the commercial benzene was treated under the same conditions in an initial stage with spent aluminum chloride catalyst secured from the secondary stage of the alkylation reaction.

The results of the respective operations were as follows:

Operation	Yield using operation 1 as 100%
	Percent
1	100
2	100
3	144

From the above, it is apparent that unexpected high yields are secured in accordance with the present process.

This invention, although especially valuable in the preparation of ethyl benzene is also applicable to the alkylation of other aromatics with other olefins, e. g. propylene, butylene, etc. with naphthalene, anthracene, etc.

What I claim as new and wish to protect by Letters Patent is:

1. Process for obtaining improved yields of alkylated aromatic hydrocarbons from olefins and impure aromatic hydrocarbons comprising treating said aromatic hydrocarbons with about 0.01 to 0.1 mol of a Friedel-Crafts catalyst per mol of aromatic hydrocarbon separating the treated aromatic hydrocarbons from the resulting catalyst sludge, and then alkylating the thus treated aromatic hydrocarbons with an olefin in the presence of a Friedel-Crafts type catalyst.

2. Process for obtaining improved yields of ethyl benzene from benzene of commercial purity, comprising treating said benzene with about 0.01 to 0.1 mol of aluminum chloride per mol of benzene separating the treated benzene from the resulting aluminum chloride sludge and then alkylating the thus treated benzene with ethylene in the presence of a Friedel-Crafts type catalyst.

3. Process according to claim 2 in which the benzene is a coal tar derivative.

4. Process according to claim 2 in which the treatment prior to alkylation is conducted at approximately 120 to 180° F.

5. Process according to claim 2 in which the treatment prior to alkylation is conducted for a time of about ½ to 1½ hours.

6. Process for obtaining improved yields of alkylated aromatic hydrocarbons from olefins and impure aromatic hydrocarbons comprising treating said aromatic hydrocarbons with a spent aluminum chloride catalyst already used in an alkylation reaction, separating the treated aromatic hydrocarbons from the resulting aluminum chloride sludge, then alkylating the separated aromatic hydrocarbons with an olefin in the presence of fresh aluminum chloride catalyst.

7. Process for obtaining improved yields of ethyl benzene by alkylating benzene with ethylene in the presence of an aluminum chloride alkylation catalyst comprising treating benzene of commercial purity with a spent aluminum chloride catalyst already used in an alkylation reaction, separating the treated benzene from the resulting aluminum chloride sludge, then alkylating said separated benzene with ethylene in the presence of fresh aluminum chloride.

8. Process for obtaining improved yields of alkylated aromatic hydrocarbon from an olefin and an impure aromatic hydrocarbon comprising treating said aromatic hydrocarbon with about 0.01 to 0.1 mol of aluminum chloride per mol of aromatic hydrocarbon, separating the resulting aluminum chloride sludge from the treated aromatic hydrocarbon, then passing the treated aromatic hydrocarbon in a mixture with an olefin and fresh aluminum chloride through an alkylation zone in which said aromatic hydrocarbon is maintained in a proportion substantially in excess of alkylation requirements, separating aluminum chloride sludge from the alkylation products, separately withdrawing alkylated aromatic hydrocarbon product and returning unalkylated aromatic hydrocarbon to said alkylation zone.

9. Process for obtaining improved yields of ethyl benzene comprising treating benzene of commercial purity with about 0.01 to 0.1 mol of aluminum chloride per mol of benzene, separating the resulting aluminum chloride sludge from the treated benzene and passing the latter in admixture with ethylene and fresh aluminum

chloride through an alkylation zone in a proportion of about 3 moles of benzene per mol of ethylene, separating aluminum chloride sludge from the alkylation products, also separating unalkylated benzene therefrom and returning said separated benzene, with an additional amount of said treated benzene, ethylene and fresh aluminum chloride, to said alkylation zone.

10. Process according to claim 9 in which the said aluminum chloride used in the said first mentioned treatment of benzene of commercial purity is spent aluminum chloride withdrawn from the said alkylation products.

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