MANUFACTURE OF ALKYLATED AROMATIC HYDROCARBONS

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Application January 29, 1958, Serial No. 711,977

9 Claims. (Cl. 260—671)

This invention relates to the manufacture of chemicals. More particularly, this invention relates to the manufacture of alkylated aromatic hydrocarbons.

In accordance with one embodiment this invention relates to the recovery of straight chain olefinic hydrocarbons from gaseous streams containing the same and the utilization of the recovered straight chain olefinic hydrocarbons for the alkylation of aromatic hydrocarbons. In accordance with another embodiment this invention relates to a unitary process for the recovery of normally gaseous straight chain olefinic hydrocarbons and the manufacture of alkylated aromatic hydrocarbons wherein the recovery of the normally gaseous straight chain olefinic hydrocarbons and the manufacture of alkylated aromatic hydrocarbons is carried out substantially simultaneously. Accordingly, it is an object of this invention to provide a process for the manufacture of alkylated aromatic hydrocarbons.

Still another object of this invention is to provide an improved process for the manufacture of alkylated aromatic hydrocarbons such as ethylbenzene, cumene, isocumene, xylenes and the like.

Yet another object of this invention is to provide a process for the recovery of normally gaseous olefinic hydrocarbons such as ethylene and propylene and the n-butene, n-pentene and similar mixtures thereof, such as occur in petroleum refinery streams and the utilization of the recovered straight chain olefinic hydrocarbons in an alkylation operation for the alkylation of hydrocarbons, such as aromatic hydrocarbons.

How these and other objects of this invention are achieved will become apparent in the light of the accompanying disclosure made with reference to the accompanying drawings wherein Fig. 1 schematically illustrates one embodiment of the practice of this invention directed to the manufacture of an alkylated aromatic hydrocarbon and wherein Fig. 2 schematically illustrates another embodiment of the practice of this invention directed to the manufacture of an alkylated aromatic hydrocarbon. In accordance with this invention it has been discovered that alkylated hydrocarbons such as alkylated aromatic hydrocarbons are advantageously produced by employing an aromatic hydrocarbon as the desorbent or desorbing medium in the desorption of adsorbed straight chain olefinic or unsaturated hydrocarbons from an adsorbent containing the same, and then employing the resulting desorption effluent comprising desorbed (aromatic hydrocarbon) and the adsorbed straight chain olefinic hydrocarbon under conditions such that the straight chain olefinic or unsaturated hydrocarbon reacts with the desorbed (aromatic hydrocarbon) to form the corresponding alkylated aromatic hydrocarbon.

By straight chain olefinic hydrocarbon is meant any aliphatic or acyclic or open chain unsaturated hydrocarbon which does not possess side chain branching. Representative straight chain olefinic hydrocarbons are ethylene, propylene, the n-butene, the n-pentene, the n-hexene, the n-heptene, the n-octene and the like. Other straight chain olefinic hydrocarbons may also be suitably employed in the practice of this invention. These other unsaturated straight chain hydrocarbons include butadiene, pentadiene and the like as well as the straight chain acetylenic hydrocarbons.

The selective adsorbent employed in the practice of this invention for the adsorption of straight chain unsaturated or olefinic hydrocarbons include the natural or synthetic zeolites or alumino-silicates such as a calcium alumino-silicate which exhibit the property of a molecular sieve, that is, matter made up of porous crystals wherein the pores of the crystals are of molecular dimension and are of substantially uniform size. In general, the zeolites may be described as water-containing alumino-silicates having the general formula \( (R, R')_2 Al_2 O_3.n SiO_2.m H_2 O \) wherein \( R \) may be an alkaline earth metal, such as calcium, strontium, or barium, or magnesium, and wherein \( R' \) is an alkali metal such as sodium or potassium or lithium. These materials, after the removal of substantially all of the water therefrom, retain their crystalline structure.

A particularly suitable solid adsorbent for straight chain unsaturated hydrocarbons, indeed for any straight chain hydrocarbons, is a calcium alumino-silicate, apparently actually a sodium calcium alumino-silicate, manufactured by Linde Air Products Company and designated Linde Type 5A Molecular Sieve. The crystals of this particular alumino-silicate have a pore size or opening of about 5 Ångstrom units or sufficiently large to admit straight chain hydrocarbons such as ethylene, propylene, the n-butene and the like, to the substantial exclusion of the non-straight chain hydrocarbons, e.g., naphthenic, aromatic, isoparaffinic and isoolefinic hydrocarbons. This particular selective adsorbent is available in various sizes, such as in the form of \( \frac{1}{8} " \) or \( \frac{3}{8} " \) diameter pellets, or as a finely divided powder having a particle size in the range 0.5—5.0 microns. Also suitable as a selective adsorbent for the selective adsorption of gaseous straight chain unsaturated hydrocarbons is an alumino-silicate, apparently actually a sodium alumino-silicate, manufactured by Linde Air Products Company and designated Linde Type 4A Molecular Sieve. The crystals of this particular alumino-silicate have a pore size of about 4 Ångstrom units, a pore size sufficiently large to admit relatively low molecular weight unsaturated hydrocarbons, such as ethylene and propylene, to the substantial exclusion of the higher molecular weight straight chain hydrocarbons, such as n-pentene, the n-pentenes and the like.

In the practice of this invention solid selective adsorbents such as zeolites which have a rigid three dimensional anionic network and interstitial dimensions sufficiently large to adsorb straight chain unsaturated or olefinic hydrocarbons but sufficiently small to exclude the non-straight chain hydrocarbons are suitable. The naturally occurring zeolite, chabazite, exhibits such desirable properties. Another suitable naturally occurring zeolite is analcitem NaAlSiO_4.H_2 O which, when dehydrated, and when all or part of the sodium is replaced by an alkaline earth metal such as calcium yields a material which may be represented by the formula \( (C_a, N_a)_2 Al_2 Si_2 O_7.2 H_2 O \) and which, after suitable combination with desorbing straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons. Other naturally occurring or synthetically prepared zeolites such as phacolite, gmelinite, harmotome and the like, or suitable base exchange modifications of these zeolites, may be employed in the practice of this invention.

Referring now to the drawings and particularly to Fig. 1 thereof which schematically illustrates one em-
bodiment of the practice of this invention directed to the manufacture of an alkylated aromatic hydrocarbon, a gaseous stream such as a petroleum refinery stream, containing straight chain unsaturated hydrocarbons such as ethylene and propylene is introduced via line 11 into adsorber 12 wherein it is contacted with a suitable adsorbent which preferentially adsorbs straight chain olefinic hydrocarbons over non-straight chain hydrocarbons. There issues from adsorber 12 via line 14 a gaseous effluent stream now having a reduced amount of straight chain olefinic hydrocarbons therein. When the adsorbent material within adsorber 12 has become substantially saturated with straight chain olefinic hydrocarbons the introduction of the gaseous stream containing straight chain olefinic hydrocarbons via line 11 is halted and there is introduced into the adsorber 12 via lines 15, 16 and 11 an aromatic hydrocarbon as a desorbing medium or desorbent. The thus-introduced aromatic hydrocarbon is employed to heat the selective adsorbent therein and to desorb the adsorbed straight chain olefinic hydrocarbons from the adsorbent material within adsorber 12. As a result of the above-indicated desorption operation there is recovered from adsorber 12 via line 18 a gaseous desorption effluent comprising the aromatic hydrocarbon (desorbent) and the resulting desorbed straight chain olefinic hydrocarbon (desorbate). The desorption effluent is then introduced via line 18 into alklylation reactor 19 wherein it contacts a suitable alklylation catalyst and wherein the unsaturated straight chain olefinic hydrocarbon serves to alkylate the aromatic hydrocarbons associated therewith.

From reactor 19 there is recovered via line 20 an alklylation reaction effluent comprising unreacted aromatic hydrocarbon and the resulting alkylated aromatic hydrocarbon. This alklylation effluent is introduced via line 20 into fractionator 21 wherein it is fractionated into an overhead stream via line 16 containing the unreacted aromatic hydrocarbon which is recycled to adsorber 12 via lines 16 and 11 to effect the desorption of additional straight chain olefinic hydrocarbons. There is also recovered from fractionator 21 as product a bottoms fraction, via line 22 comprising the resulting alkylated aromatic hydrocarbons.

Referring now to Fig. 2 of the drawing which schematically illustrates another embodiment of the practice of this invention and wherein the same reference numerals employed in connection with Fig. 1 are employed to designate similar pieces of equipment, a gaseous stream comprising the straight chain unsaturated or olefinic hydrocarbon is introduced via line 11 into combination adsorber-reactor 12. Adsorber-reactor 12 contains the adsorbent which preferentially or selectively adsorbs the non-straight chain olefinic hydrocarbon and also contains a suitable alkylation catalyst. The special adsorbent and alkylation catalyst may be admixed together to form a substantially homogeneous admixture in the form of a fixed bed or a fluidized bed or a falling bed, or the adsorbent may be maintained separately from the alklylation catalyst within the adsorber-reactor as two separate beds.

When the gaseous effluent removed via line 14 from the adsorber-reactor indicates that the adsorbent therein is substantially saturated with straight chain olefinic hydrocarbons a suitable aromatic hydrocarbon is introduced thereinto via lines 15, 16 and 11 and the conditions in adsorber-reactor 12 adjusted so as to effect substantially simultaneous desorption of the desorbed straight chain olefinic hydrocarbons from the adsorbent therein and alklylation of the thus-introduced aromatic hydrocarbon by the resulting desorbed straight chain olefinic hydrocarbon. The resulting alklylation reaction effluent is recovered via line 18 and introduced into fractionator 21. From fractionator 21 a bottoms fraction comprising an overhead fraction via line 16 comprising unreacted aromatic hydrocarbon which is recycled to adsorber-reactor 12 via lines 16 and 11 to effect desorption of additional straight chain olefinic hydrocarbons. Also, there is recovered from fractionator 21 via line 22 as product a bottoms fraction comprising the resulting alkylated aromatic hydrocarbon.

The adsorptive separation of the straight chain unsaturated hydrocarbons from the hydrocarbon fraction or petroleum refinery stream containing the same may be carried out in the liquid or gaseous phase and at any suitable temperature and pressure. It is desirable, however, to coordinate the adsorptive separation conditions, e.g., temperature and pressure, with the desorptive separation conditions, more fully described hereinafter, so as to effect the most economical use of the materials employed and for ease of control.

The adsorptive separation or desorption of the straight chain olefinic or unsaturated hydrocarbons by the solid selective adsorbent may be carried out at any suitable temperature, such as a temperature in the range 50° to 750°F., and at any suitable pressure, such as in the range 0 to 10,000 p.s.i.g. and higher, the temperature and pressure being adjusted with respect to the hydrocarbon fraction undergoing treatment depending upon whether or not it is desired to maintain the hydrocarbon fraction undergoing separation in the liquid phase or in the vapor phase. The adsorptive separation may be carried out by stilling slurrying or contacting the solid selective adsorbent with the hydrocarbon fraction being treated, followed by separation or decantation of the treated hydrocarbon effluent, now substantially free of or having a reduced straight chain hydrocarbon content. Liquid phase adsorption may also be carried out by percolating the liquid hydrocarbon fraction to be treated through a bed of solid adsorbent material.

It is the usual practice, however, to carry out the adsorptive separation operation in the gaseous phase, that is, to maintain the hydrocarbon fraction undergoing treatment in the vapor phase during the adsorption operation. In such an operation any suitable method for effecting gas-solid contact may be employed, for example, a fixed bed, a moving bed or a fluidized bed or a gas-entrained mass of selective adsorbent may be employed during the gas phase adsorptive separation operation. After sufficient time, the solid adsorbent is separated from the resulting treated hydrocarbon fraction and the resulting solid adsorbent is then subsequently treated in accordance with the practice of this invention to desorb the hydrocarbon content therefrom.

The desorption operation carried out in the gaseous phase (straight chain olefinic hydrocarbons) from the solid adsorbent material may be carried out at any suitable temperature and pressure. For example, the desorption operation may be carried out at a pressure in the range 0 to 10,000 p.s.i.g. and a temperature in the range 400 to 900°F. In accordance with the practice of this invention, however, the desorption operation is carried out in the gaseous phase, that is, the gaseous desorbing fluid and the resulting desorbed hydrocarbons are both present in the resulting desorption effluent in the gaseous or vapor phase. Accordingly, the desorption temperature and the desorption pressure are adjusted to maintain the desorbed and the desorbed straight chain unsaturated hydrocarbons in the gaseous phase. Generally a desorption pressure in the range 10 to 20,000 p.s.i.g. is suitable. It is sometimes desirable to carry out the desorption operation at a pressure substantially lower than the adsorption pressure. Isobaric adsorption-desorption operations are advantageous during the pressure elevation and desorption operations, the adsorption pressure being 0.1 atm. during the adsorptive separation operation is not deterministic of the desorption pressure.

Generally any suitable desorption temperature sufficiently high to effect desorption of the adsorbed hydrocarbons may be employed in the practice of this invention. Usually there is recovered during the desorption operation. It is generally preferred, however, to carry out the desorption opera-
tion at an elevated temperature in the range 425°-800° F. The desorption temperature employed, however, should not be excessively high, for example not greater than about 1100° F., particularly in the instance wherein a material such as Linde Type 5A Molecular Sieve, that is, a calcium alumino-silicate, is employed as the selective adsorbent since these rather high temperatures are excessive and lead to the destruction of the adsorbent, presumably by collapse of the crystal structure, with resultant loss of the selective adsorption properties of this particular adsorbent.

Various aromatic hydrocarbons may be employed in the practice of this invention to effect the desorption of the adsorbed straight chain olefinic hydrocarbon. The aromatic hydrocarbon employed as desorbent is also at the same time alkylatable by the resulting desorbed straight chain olefinic hydrocarbon. Suitable aromatic hydrocarbons include benzene, and the monocyclic alkylated hydrocarbons such as toluene, the xylenes, ethylbenzene, mesitylene, hemimellitene and the like. It is preferred, however, in the practice of this invention to employ benzene as the aromatic hydrocarbon for the desorption of the adsorbed straight chain olefinic hydrocarbons.

Various alkylation catalysts, liquid and solid, may be employed in the practice of this invention. Also, the alkylation reaction may be carried out in the liquid phase, although gaseous phase alkylation is preferred. Suitable alkylation catalysts include chromia on HF-treated silica-alumina and phosphoric acid treated kieselguhr. Other suitable alkylation catalysts for effecting the alkylation of aromatic hydrocarbons, such as benzene or toluene and the like, by reaction with a straight chain unsaturated or olefinic hydrocarbon, such as ethylene and propylene, are known.

The following example is illustrative of the practice of this invention. A gaseous stream such as is recoverable in a petroleum refinery operation, comprising a major or minor amount of propylene, e.g., in the range 5–70% by volume, is introduced into contact with a sodium calcium alumino-silicate molecular sieve type adsorbent, such as Linde Type 5A Molecular Sieve. The propylene thus introduced into contact with the adsorbent is preferentially adsorbed. After the selective adsorbent is substantially saturated with propylene it is contacted with a gaseous stream of benzene at a temperature in the range 300–700° F., to effect desorption of the adsorbed propylene. During the desorption operation it is desirable to employ a substantial molar excess of benzene such that in the resulting desorption effluent the benzene comprises a major portion thereof, e.g., benzene to propylene mol ratio in the range 4–20:1.

A mixture comparable to the aforesaid desorption mixture, such as a mixture comprising 20,000 cc. of benzene and 1600 grams of propylene, was passed over a solid type alkylation catalyst, chromia on HF-treated silica-alumina at a temperature of 250° F. and a pressure of about 500 p.s.i.g. and at a space velocity of 2.0 v/hr./v. (basis solution). The resulting alkylation reaction effluent was recovered and stripped to 194° F. leaving 5675 cc. of a high boiling residue. This high boiling residue was further distilled to yield a distillate product which had a distinct cumene odor. Tests indicated that the bulk of the propylene was used up in alkylation the benzene adsorbed therewith. Similar results were achieved with a zinc oxide-zinc chromite on HF₃ silica-alumina catalyst.

As will be apparent to those skilled in the art in the light of the foregoing disclosure many modifications, alterations and changes are possible in the practice of this invention without departing from the spirit or scope thereof.

I claim:

1. A method of manufacturing an alkylated aromatic hydrocarbon which comprises contacting a gaseous stream containing a straight chain olefinic hydrocarbon and other hydrocarbons with an alumino-silicate molecular sieve type adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb said straight chain olefinic hydrocarbons from said gaseous stream, contacting the resulting adsorbent, now containing substantially only straight chain olefinic hydrocarbon adsorbed therein, with a monocyclic aromatic hydrocarbon under conditions to effect desorption of the adsorbed straight chain olefinic hydrocarbon, contacting the resulting desorption effluent comprising said aromatic hydrocarbon and the resulting desorbed straight chain olefinic hydrocarbon with an alkylation catalyst under suitable conditions to effect alkylation of said aromatic hydrocarbons by said straight chain olefinic hydrocarbon.

2. A method in accordance with claim 1 wherein the straight chain olefinic hydrocarbon adsorbed by said adsorbent is ethylene.

3. A method in accordance with claim 1 wherein the straight chain olefinic hydrocarbon adsorbed by said adsorbent is propylene.

4. A method in accordance with claim 1 wherein said desorption operation and said alkylation reaction are effected substantially simultaneously.

5. A method in accordance with claim 1 wherein said desorption operation and said alkylation reaction are effected substantially simultaneously by admixing said adsorbent with a solid type alkylation catalyst.

6. A method in accordance with claim 1 wherein said desorption operation and said alkylation reaction are effected substantially simultaneously by admixing said adsorbent with chromia on HF-treated silica-alumina as a solid type alkylation catalyst.

7. A method in accordance with claim 1 wherein said desorption operation and said alkylation reaction are effected substantially simultaneously by admixing said adsorbent with phosphoric acid-treated kieselguhr as a solid type alkylation catalyst.

8. A method in accordance with claim 1 wherein said aromatic hydrocarbon is benzene and said olefinic hydrocarbon is propylene and wherein said desorption operation and said alkylation reaction are effected substantially simultaneously.

9. A method in accordance with claim 1 wherein said molecular sieve type adsorbent has a pore size opening of about 4 Angstrom units, a pore size opening sufficiently large to admit low molecular weight unsaturated hydrocarbons such as ethylene and propylene to the substantial exclusion of higher molecular weight straight chain hydrocarbons.

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