

- (21) Application No. 54261/77 (22) Filed 30 Dec. 1977 (19)
 (31) Convention Application No. 756523 (32) Filed 3 Jan. 1977 in
 (33) United States of America (US)
 (44) Complete Specification published 24 June 1981
 (51) INT. CL.³ C07C 2/70
 (52) Index at acceptance
 C5E 227 241 341 342 383 396 CK
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(54) ALKYLATION OF AROMATIC HYDROCARBONS
 USING SOLID PHOSPHORUS-CONTAINING CATALYSTS

(71) We, UOP INC, a corporation organized under the laws of the State of Delaware, United States of America, of Ten UOP Plaza, Algonquin & Mt. Prospect Roads, Des Plaines, Illinois, 60016, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the alkylation of aromatic hydrocarbons with olefins or olefin-acting compounds in the presence of solid phosphorus-containing catalysts in reaction zones maintained at alkylation-promoting conditions. More particularly it seeks to reduce the corrosion in the fractionation columns utilized to recover the alkylaromatic hydrocarbons.

We have found that good results may be achieved by de-pressurizing the bottoms stream of a first fractionation zone and passing the thus cooled bottoms stream into a settling vessel operated at quiescent conditions which effect the separation of liquid phase phosphoric acid from the bottoms stream. This phosphoric acid is thereby removed from the process and the amount of corrosion in the carbon steel fractionation column downstream of the settling vessel is reduced.

According to the invention, therefore there is provided a process for the production of an alkylaromatic hydrocarbon by contacting an aromatic hydrocarbon and an alkylating agent which is an olefin or olefin-acting compound with a solid, phosphorus-containing catalyst in a reaction zone maintained at alkylation-promoting conditions, passing a reaction zone effluent stream comprising the aromatic hydrocarbon and an alkylaromatic hydrocarbon in a first fractionation zone, removing a bottoms stream comprising the aromatic hydrocarbon and the alkylaromatic

from the first fractionation zone at a first temperature and then passing it into a second fractionation zone at a lower pressure and at a lower second temperature, in which process the bottoms stream is flashed at an intermediate point between the first fractionation zone and the second fractionation zone and then passed into a settling vessel, where phosphoric acid settles out, and released phosphoric acid is removed from the settling vessel, thereby reducing the amount of phosphoric acid which enters the second fractionation zone.

The aromatic hydrocarbons which may be alkylated with a solid, phosphorus-containing catalyst include according to the invention include benzene, toluene, xylenes, ethylbenzene, normal propylbenzene and isopropylbenzene. Higher molecular weight and polycyclic aromatic hydrocarbons may also be alkylated in this way using a solid phosphorus-containing catalyst.

The alkylating agent may be an olefin-acting compound such as an alcohol, ether or ester, the latter including alkyl halides, alkyl sulfates and alkyl phosphates. Preferably, however, the alkylating agent is an olefin, especially a mono- or di-olefin having from 2 to 8 carbon atoms per molecule. The preferred mono-olefins include ethylene, propylene, 1-butene, 2-butene and isobutylene. These olefins may be used as relatively pure streams containing a single hydrocarbons species. Alternatively, mixture of two or more olefins or of olefins and paraffins may be used as the non-aromatic feed stream to the process. Typical products include cumene, ethylbenzene and cymene (isopropyl toluene).

The invention is practiced with a reaction zone containing a solid, phosphorus-containing catalyst. Preferably, the catalyst is one commonly referred to as an SPA catalyst. Suitable SPA catalysts are available commercially. As used herein the term "SPA

5 catalyst" is intended to refer generically to a solid catalyst which contains as one of its principal raw ingredients an acid of phosphorus such as ortho-, pyro- or tetra-phosphoric acid. These catalysts are normally formed by mixing the acid with a siliceous solid carrier to form a wet paste. This paste may be calcined and then crushed to yield catalyst particles, or the paste may be extruded or pelleted prior to calcining to produce more catalyst particles. The carrier is preferably a naturally occurring porous silica-containing material such as kieselguhr, kaolin, infusorial earth and diatomaceous earth. A minor amount of various additives such as mineral talc, fullers earth and iron compounds including iron oxide have been added to the carrier to increase its strength and hardness. The combination of the carrier and the additives normally comprises 15—30 wt.% of the catalyst, with the remainder being the phosphoric acid. However, the amount of phosphoric acid used in the manufacture of the catalyst may vary from 25 8—80 wt% of the catalyst as described in United States Patent 3,402,130. The amount of the additive may be equal to 3—20 wt.% of the total carrier material. Further details as to the composition and production of typical SPA catalysts may be obtained from United States Patents 3,050,472, 3,050,473 and 3,132,109.

35 It is known in the art that the passage of aromatic hydrocarbons through an alkylation zone tends to leach chemically combined water out of an SPA catalyst. This is acknowledged in United States Patents 3,510,534 and 3,520,945, the latter of which is directed to the control of the state of hydration of the catalyst. The water content of the catalyst is important since dehydration causes the SPA catalysts to deteriorate by powdering and caking, while excess water causes the catalysts to soften and eventually form a sludge which would plug the reactor. Water is therefore injected into the feed stream in the prior art in order to maintain the catalyst at the proper state of hydration by replacing the water leached from the catalyst. The rate of this injection is used to control the catalyst hydration level, and the feed streams are therefore maintained as dry as practical prior to the water injection point. This results in the total water content of the feed being essentially the same as the amount injected. Typical water injection rates are from 100 ppm. to 2000 ppm. in aromatic hydrocarbon alkylation operations. A preferred water addition rate during the production of cumene is from 200 to 300 ppm. of the combined feed to the reaction zone.

60 The water which has been leached from the catalyst and the excess water added to the feed stream are contained in the reaction zone effluent stream in the prior art. This

water contains phosphorus from the catalyst and is therefore phosphoric acid of some varying strength. The acid is present at very low concentrations in the reaction zone effluent and is apparently dissolved in the much larger aromatic hydrocarbon stream. However, the reaction zone effluent is normally cooled in the prior art, e.g. by flashing, and at the resultant lower temperature a separate aqueous phase of phosphoric acid is formed. Experience has shown that the hot reaction zone effluent material is not corrosive, but that the cooler, two liquid phase effluent material is fairly corrosive to carbon steel. For this reason at least the lines and vessels immediately downstream of the reaction zone are normally made of stainless steel. The acid therefore collects in the bottom of the first vessel, which in a process flow similar to that shown in the Drawing is the first rectification column. It is for this reason that the previously cited U.S. patents show acid being withdrawn from the first fractionation column into which the reaction zone effluent is charged. This first fractionation column is normally a rectifier and is normally used in conjunction with either a second rectifier, an absorber or a depropanizer. This first fractionation column and any other column associated with it are referred to herein as the first fractionation zone.

70 A bottoms stream containing the alkylaromatic hydrocarbon product of the process is normally removed from the first fractionation zone and passed into a second fractionation zone. Since this bottoms stream often contains benzene it is a common practice to first remove the benzene and other hydrocarbons boiling below cumene in a first column referred to as a benzene recycle column. The cumene or other alkylaromatic hydrocarbon product is then recovered in a second column referred to as a cumene column. Differing column arrangements may be utilized to perform the product recovery. These columns are referred to herein as the second fractionation zone.

100 The benzene recycle column is typically operated at a lower pressure and temperature than the column producing the bottoms stream which is fed to it. In the prior art the bottoms stream of the first fractionation column is flashed into the benzene recycle column, and is therefore cooled to a lower temperature. This lower temperature causes another small amount of the phosphoric acid to drop out of solution in the benzene recycle column. To avoid the high cost of stainless steel, the benzene recycle column is often made of carbon steel. The phosphoric acid therefore corrodes the fractionation trays located in this column. This slowly reduces the efficiency of the corroding trays, and may reduce the efficiency of other trays by causing the accumulation of corrosion prod- 130

ucts or debris on the surface of the trays. The present invention provides a means of reducing the amount of corrosion such as this by lowering the amount of phosphoric acid which is passed into the benzene recycle column.

According to the present invention the alkylaromatic hydrocarbon-containing bottoms stream of the first fractionation zone is flashed to a lower pressure at a point prior to the second fractionation zone. The liquid phase material remaining after the flashing operation is then retained for some time in a quiescent settling zone which is maintained at conditions which allow phosphoric acid to settle out by gravity and to be decanted. This settling operation may be aided by the provision of a coalescing means of either a mechanical or electrostatic type. The preferred type of settling zone is a settling vessel similar to that depicted in the accompanying drawing and described below and which is commonly used as for overhead receivers. Other types of vessels, including those having separate facilities for handling the vapor phase formed by the flashing operation may be used.

The flashing operation performed prior to the settling vessel preferably reduces the pressure of the bottoms stream to the lowest pressure which still provides an adequate pressure differential between the settling vessel and the second fractionation zone to transfer the bottoms stream to the second fractionation zone without the use of a pump. A lower pressure and temperature may be used however if suitable pumping means are supplied. The flashing operation preferably reduces the temperature of the bottoms stream by 80 Fahrenheit degrees or more. No control system need be used to regulate the hydrocarbon flow from the settling vessel, and it may be directly coupled to the second fractionation zone. In the preferred embodiment the pressure in the settling vessel is higher than that in the second fractionation zone only by the pressure drop associated with the flow of the bottoms stream through the connecting lines and any elevation differential.

The conditions of temperature and pressure maintained in the first fractionation zone and also in the second fractionation zone are interrelated and variable. The first fractionation zone is preferably operated at a pressure at least 100 psig. higher than the second fractionation zone and at a temperature more than 100°F above that used in the second fractionation zone. A broad range of conditions for the first fractionation zone include a bottoms temperature of 350°F. to 500°F. and a top pressure of 300 to 600 psig. or higher. A broad range of conditions for use in the second fractionation zone includes a top pressure of 10 to 150 psig. and a

bottoms temperature of 300 to 450°F.

The reaction zone is maintained at alkylation-promoting conditions which typically include a pressure of 300 to 1000 psig. and a temperature of 300 to 600°F. The liquid hourly space velocity of reactants may range from 0.5 to 2.5. It is preferred that an excess of the aromatic hydrocarbon be present in the reaction zone, and the mole ratio of the aromatic hydrocarbon to the alkylating agent (e.g. olefin) is preferably within the broad range of 3:1 to 20:1. A ratio of about 8:1 is preferred for the production of cumene. It is preferred that the reactant stream be mixed-phase through the reactor. The feed stream therefore preferably contains some unreactive light paraffins having the same number of carbon atoms per molecule as the alkylating agent. In the production of cumene it is preferred that the amount of propane in the reaction zone feed stream be at least equal to the amount of propylene in this stream. This may be accomplished by using a dilute propylene feed stream or by recycling propane.

The accompanying drawing is a schematic diagram illustrating a preferred embodiment of the present invention. For clarity and simplicity various subsystems and apparatus associated with the operation of the process have not been shown. These items include flow and pressure control valves, pumps, temperature and pressure monitoring systems, reactor and fractionator internals, etc., which may be of customary design.

Referring now to the drawing, a feed stream comprising a mixture of propane and propylene enters the process in line 1 and is admixed with a stream of recycle benzene from line 2. The resultant admixture is carried by line 3 to the junction with line 4, where it is commingled with additional benzene from line 4. This produces the alkylation zone feed stream carried by line 6. This stream is first heated in heat exchanger 5 and then in heater 7 prior to being inserted into the bottom of reactor 8. Contacting of the alkylation zone feed stream with an SPA catalyst maintained at alkylation-promoting conditions effects the reaction of at least a major portion of the propylene with benzene to form cumene or isopropylbenzene. A reaction zone effluent stream comprising benzene, propane and cumene is therefore removed in line 9.

The reaction zone effluent stream passes through a pressure control valve not shown and then into a first rectifier or rectification column 10 which is operated at a lower pressure and temperature than reactor. Vapors liberated from the reaction zone effluent stream pass upward through fractionation trays countercurrent to liquid generated by the addition of benzene from line 13 at the top of the rectifier. An overhead vapor

stream comprising benzene, propane and a small amount of water is removed in line 11 and heat exchanged against the alkylation zone feed stream. It is then passed into a second rectifier 14. The bottoms stream of this column contains benzene which is passed to the reactor via line 4. A feed benzene stream enters the column through line 15 to be dried. An overhead vapor stream comprising water and propane is removed from the second rectifier in line 16 and passed through an overhead condenser 17. The resultant condensate stream is passed into overhead receiver 18 and separated into an aqueous phase removed in line 20 and a liquid propane stream removed in line 21. A net propane stream removed from the process in line 22 comprises the propane entering through line 1. The remainder of the liquid propane stream is passed into the rectifier via line 23 as reflux.

A very small amount of aqueous phosphoric acid is removed from the first rectifier in line 12. The hydrocarbonaceous bottoms stream of this column is removed in line 24 and comprises benzene and cumene. This bottoms stream is subjected to a flashing operation which lowers its pressure and temperature by passage through valve 25 into a settling vessel 26. The lower temperature and quiescent conditions maintained in the settling vessel cause a phosphoric acid phase to form in the settling vessel. This additional acid is removed in line 27 and therefore does not enter the downstream vessels.

Substantially all of the hydrocarbons in the rectifier bottoms stream continue through line 28 to a benzene recycle column 29. This column is operated at conditions which are effective to vaporize substantially all of the benzene in the rectifier bottoms stream and form an overhead vapor stream comprising benzene. This vapor stream is condensed in overhead condenser 31 and passed into overhead receiver 32 via line 30. The resultant benzene-rich liquid is removed in line 33, with a first portion delivered to the recycling column in line 34 as reflux and a second portion entering line 35. A drag stream is removed in line 36 to prevent the buildup within the process of hydrocarbons having boiling points between benzene and propane. The remainder of the benzene is passed through line 37 for recycling to the reactor and for reflux to the first rectifier.

Cumene and other alkylaromatic hydrocarbons are withdrawn from the benzene recycle column as a bottoms stream in line 38 and passed into a cumene column 39. The operation of this column is effective to cause the production of an overhead vapor stream of relatively pure cumene. This vapor stream is passed through condenser 42 into overhead receiver 43 via line 41. The cumene is

withdrawn from the receiver in line 44 and divided between the reflux stream carried by line 45 and a net product stream carried by line 46. A net bottoms stream comprising polyalkylated aromatic hydrocarbons is removed from the cumene column in line 40.

EXAMPLE

The invention is further illustrated by this example of a preferred embodiment based on the production of cumene by the alkylation of benzene with propylene. For clarity, reference will be made to lines and vessels shown in the accompanying drawing. The feed stream to the reaction zone is derived from a bottoms stream of rectifier 14 which comprises about 4,890 mph (moles per hour), of which about 67 mol% is benzene and 26 mol.% is propane, and a recycle stream from line 2 comprising about 2,980 mph of benzene and some propane. About 133 lb/hr. of water is injected into this mixture to maintain the proper state of hydration of the catalyst. The propylene feed stream enters the process at the rate of about 852 mph. The combined feed stream contains about 9,195 mph of which 6275 mph is benzene. It is split into two identical streams, each of which is passed into the bottom of a reactor at a pressure of about 550 psig. and a temperature of about 383°F. The reactors each contain four catalyst beds of sufficient overall volume to provide a WHSV of about 1.25 hr.⁻¹. The catalyst used is a standard SPA catalyst.

The mixed-phase effluents of the two reactors are cooled from about 437°F. to about 395°F. by being lowered in pressure from about 500 psig. to about 271 psig. and are then combined. The resultant alkylation zone effluent enters the first rectifier 10 at a rate of about 8419 mph. Also fed to the first rectifier is a 519 mph benzene-rich stream from line 13 at a temperature of about 120°F. The first rectifier is operated with a bottom temperature of 394°F. at 271 psig. The overhead vapor stream is removed at a temperature of approximately 379°F. and cooled to about 310°F. in the heat exchanger 5 before being passed into the second rectifier. The first rectifier contains eight fractionation trays and the second rectifier contains 28 fractionation trays. A very small acid stream of about 1 gal/day is removed from the bottom of the rectifier.

The benzene feed stream enters the second rectifier at the eighteenth tray from the bottom at about 746 mph and at a temperature of approximately 80°F. The overhead vapor of this column has a temperature of about 123°F. and is cooled to about 100°F. in the overhead condenser. The overhead receiver is maintained at 250 psig. About 7 mph of water and 57.7 mph of liquid hydrocarbons are removed from the receiver.

About 92 mol.% of this stream is propane with the rest being ethane, isobutane and hydrogen. The reflux stream has a flow rate of about 2,482 mph. A stabbed-in reboiler is used in the second rectifier to provide a 251°F. bottoms stream.

The net bottoms stream is flashed from approximately 394°F. and 271 psig. to about 50 psig. and passed into the settling vessel 26 as a two phase stream having a temperature of about 291°F. This temperature reduction causes an additional small amount of phosphoric acid to come out of solution in the hydrocarbon stream. It is removed from the vessel at a rate of less than 1 gal./day. The bottoms stream of the first rectifier is then passed into a 36-tray recycle column. This column is operated with a bottoms temperature of about 418°F. A largely benzene overhead vapor stream is removed at about 40 psig. and condensed at a temperature of 120°F. The overhead liquid is divided between reflux and a recycle stream. A drag stream of about 4 mph is withdrawn to remove unreactive hydrocarbons, and the remainder of the recycle stream forms the previously specified rectifier reflux and reactor feed streams.

A 750 mph bottoms stream of the recycle column is passed into the 45-tray cumene column. The overhead vapor stream of this column has a pressure of approximately 20 psig. at a temperature of about 374°F. It is condensed to form reflux and a 716 mph net cumene product stream. The cumene column is operated with a bottoms temperature of about 478°F., and a net bottoms stream of impurities is removed at the rate of about 33.6 mph.

WHAT WE CLAIM IS:—

1. A process for the production of an alkylaromatic hydrocarbon by contacting an aromatic hydrocarbon and an alkylating agent which is an olefin or olefin-acting compound with a solid, phosphorus-containing catalyst in a reaction zone maintained at alkylation-promoting conditions, passing a reaction zone effluent stream comprising the aromatic hydrocarbon and an alkylaromatic hydrocarbon in a first fractionation zone, removing a bottoms stream comprising the aromatic hydrocarbon and the alkylaromatic from the first fractionation zone at a first temperature and then passing it into a second fractionation zone at a lower pressure and at a lower second temperature, in which process the bottoms stream is flashed at an intermediate point between the first fractionation zone and the second fractionation zone and then passed into a settling vessel, where phosphoric acid settles out, and released phosphoric acid is removed from the settling vessel, thereby reducing the amount of phosphoric acid which enters the second fraction-

ation zone.

2. A process as claimed in claim 1 wherein the alkylating agent is a mono- or di-olefin having from 2 to 8 carbon atoms.

3. A process as claimed in claim 1 wherein the aromatic hydrocarbon is benzene, toluene, a xylene, ethylbenzene, a propylbenzene or a mixture of two or more thereof and the alkylating agent is ethylene, propylene, a butene or a mixture of two or more thereof.

4. A process as claimed in claim 1 wherein the aromatic hydrocarbon is benzene and the alkylating agent is an olefin having two or three carbon atoms per molecule.

5. A process as claimed in any of claims 1 to 4 wherein the catalyst is a solid phosphoric acid catalyst on a siliceous carrier.

6. A process as claimed in any of claims 1 to 5 wherein water is injected into the feed stream in an amount of from 100 to 2000 ppm to maintain the catalyst in an adequate state of hydration.

7. A process as claimed in any of claims 1 to 6 wherein the settling in the settling vessel is aided by mechanical or electrostatic coalescing means.

8. A process as claimed in any of claims 1 to 7 wherein the flashing intermediate the first and second fractionation zones reduces the pressure of the bottoms stream to the lowest pressure which still provides sufficient pressure differential over the second fractionation zone to enable material to be transferred from the settling vessel to the second fractionation zone without the aid of a pump.

9. A process as claimed in any of claims 1 to 8 wherein the flashing reduces the temperature by at least 80°F.

10. A process as claimed in any of claims 1 to 9 wherein the first fractionation zone is operated at a bottoms temperature of 350 to 500°F and a top pressure of 300 to 600 psig, and the second fractionation zone is operated at a top pressure of 10 to 150 psig and a bottoms temperature of 300 to 450°F, the first fractionation zone being operated at a temperature over 100°F higher and a pressure over 100 psig higher than the second fractionation zone.

11. A process as claimed in claim 1 carried out substantially as hereinbefore described with reference to the accompanying drawing.

12. A process as claimed in claim 1 carried out substantially as hereinbefore exemplified.

13. An alkylaromatic hydrocarbon when produced by a process as claimed in any of claims 1 to 12.

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Chartered Patent Agents,
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Printed for Her Majesty's Stationery Office by Burgess & Son
(Abingdon) Ltd. 1981. Published at The Patent Office,
25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.

