Patented Mar. 27, 1945 2,372,505

UNITED STATES PATENT OFFICE

2,372,505

ALKYLATION OF AROMATIC HYDROCARBONS

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No Drawing. Application February 11, 1942, Serial No. 430,508

11 Claims. (Cl. 260—671)

This is a continuation-in-part of my co-pending application, Serial No. 342,974, filed June 28, 1940.

This invention is concerned with a combination process for producing alkylated aromatic hydrocarbons from aromatic hydrocarbons and olefinic hydrocarbons. It is more specifically concerned with a simple and easily regulated process involving the use of a liquid catalyst which is altered only slightly in the course of the reaction but which catalyzes the desired reactions with a maximum of efficiency.

Processes for the formation of more-highly alkylated aromatic hydrocarbons from less-highly alkylated aromatic hydrocarbons are of importance not only from the the standpoint of producing high antiknock motor fuel fractions but for preparing alkylated aromatic hydrocarbons as ethyl benzene which are useful as intermediates in the production of synthetic organic chemicals such as styrene.

In one specific embodiment the present invention comprises a process for the manufacture of alkylated aromatic hydrocarbons which comprises producing alkyl fluorides by reacting an excess of hydrogen fluoride with olefins present in a hydrocarbon fraction containing both olefins and normal paraffins, removing the resultant alkyl fluorides and excess hydrogen fluoride as a solution from unconverted normal paraffins which separate as an upper layer from the heavier mixture of alkyl fluorides and hydrogen fluoride, commingling said solution comprising alkyl fluorides and hydrogen fluoride with an aromatic hydrocarbon under alkylating conditions to form a reaction mixture containing substantial proportions of alkylated aromatic hydrocarbons, separating unconverted aromatic hydrocarbons, alkylated aromatic hydrocarbons, and used hydrogen fluoride from said reaction mixture, recycling unconverted aromatic hydrocarbons to further reaction with alkyl fluorides, and returning at least a portion of said used hydrogen fluoride to further contact with the charged fraction containing both olefins and normal paraffins.

According to the process of the present invention, hydrogen fluoride is utilizable for reacting with olefins to produce alkyl fluorides which are readily separable from unconverted normal paraffins and also as catalyst in the alkylation of aromatic hydrocarbons as benzene, toluene, alkylated benzenes, and poly-cyclic aromatic hydrocarbons. Hydrogen fluoride, when substantially anhydrous, is a liquid boiling at about 20° C. and accordingly it can be used in apparatus which is cooled to maintain temperatures below this point or it can be used at a higher temperature if sufficient pressure is maintained upon the system. The olefin-containing fraction used in the first step of the process may consist of cracked gases containing little or no isoparaffins since isoparaffins present would undergo alkylation in the first reaction zone in which it is desired to produce alkyl fluorides. The olefin-containing charging stock may comprise substantially pure olefins as ethylene, propylene, butylene, amylenes, etc., or these may be diluted with normally gaseous straight chain paraffins. In this stage of the process the olefin-containing fraction is contacted with an excess of liquid hydrogen fluoride at a temperature between about −50° and about +50° C. but preferably at a temperature between about −50° and −20° C. although a temperature as high as room temperature is frequently employed. The contacting operation may be carried out by any of the usual methods employed for such purposes. In order to convert substantially all of the olefins into alkyl fluorides, more than an equivalent molecular proportion of hydrogen fluoride is employed. This excess of hydrogen fluoride may, with advantage, be as high as 200 molecular proportions per 1 molecular proportion of olefins charged. I have also found that the excess of hydrogen fluoride over olefins assists in separating the resultant alkyl fluorides from the unconverted paraffinic hydrocarbons because of the relatively high solubility of alkyl fluorides in liquid hydrogen fluoride of 90 to 100% concentration. At temperatures higher than those preferred for the addition of hydrogen to olefins, polymerization occurs which interferes with the direct conversion of the original olefins into alkyl fluorides.

After the hydrofluorination step, the product together with unconverted paraffins is sent to a settling chamber (assuming always a pressure on the system in excess of the combined vapor pressures of the components) in which the top layer consists essentially of normal paraffins such as propane, butane, etc., which can be disposed of as desired, while the bottom layer comprises a solution of alkyl fluorides as ethyl fluoride, isopropyl fluoride, butyl fluorides, etc., in hydrogen fluoride.

The alkyl fluoride-hydrogen fluoride layer so separated from paraffins is then directed to a reactor where it is contacted with a liquid hydrocarbon charge consisting entirely or partially of

aromatic hydrocarbons such as benzene or its homologs. When the process is utilized for the production of alkylated aromatic hydrocarbons of gasoline boiling range, it will be apparent that relatively high boiling aromatics should not be alkylated, otherwise a product will be obtained boiling higher than the boiling range of gasoline. During the alkylation step hydrogen fluoride is liberated by the interaction of an aromatic as benzene with an alkyl fluoride such as ethyl fluoride.

The alkylating step of the process is preferably carried out at a temperature of from about −10° to to about 150° C. but preferably at a temperature of from about 10° to about 30° C. By carrying out the alkylation reaction so that an excess of benzene is present, generally up to approximately 20 times the molecular proportion of the alkyl fluoride, formation of poly-alkylated aromatic hydrocarbons is kept relatively low. The resultant product is fractionally distilled to separate therefrom the excess aromatic hydrocarbon which is recycled to the process while the alkylated aromatic hydrocarbons are fractionated into mono-alkyl and poly-alkyl aromatic hydrocarbons.

The process of the present invention is utilizable for converting benzene and an ethane-ethylene fraction, such as that obtained by pyrolysis of hydrocarbons, into relatively high yields of mono-ethyl benzene together with small amounts of poly-ethyl benzenes. In the first stage of the process liquid hydrogen fluoride of for example 98–100% concentration is contacted with the ethane-ethylene fraction at a temperature between about −50° and about −20° C. and substantially all of the ethylene is converted into ethyl fluoride which is soluble in the excess hydrogen fluoride present. Sufficient pressure is maintained upon the resultant mixture to keep the hydrocarbons and hydrogen fluoride in liquid state. The unconverted ethane is then substantially separated as an upper layer from a lower layer comprising essentially ethyl fluoride and hydrogen fluoride. The lower layer containing both ethyl fluoride and hydrogen fluoride is then contacted with benzene at a temperature between about 0° and 150° C. in the presence of an additional quantity of hydrogen fluoride. If desired, the mixture of hydrogen fluoride and ethyl fluoride may be introduced at intermediate points between the entrance and the exit of the alkylating zone which also contains the aromatic hydrocarbon, benzene. It is also preferable that at least a portion of the alkylation reaction mixture be withdrawn from near the exit of the alkylation reactor and be recycled to commingle with the alkyl fluorides, benzene, and hydrogen fluoride charged thereto. The products from the alkylation reactor are then separated into a hydrogen fluoride layer and a hydrocarbon layer, the latter comprising essentially benzene and ethylated benzenes. The hydrogen fluoride layer so separated from the hydrocarbon products of the alkylation reaction is recycled to further use in either or both stages of the process as described. Fractionation of the hydrocarbon layer of the alkylation product separates unconverted benzene from mono-ethyl benzene and more-highly ethylated benzenes.

The exact temperature and pressure to be employed in converting olefins into alkyl fluorides and in alkylating different aromatic hydrocarbons with various alkyl fluorides will depend upon the activity and physical characteristics of the reactants involved as well as the proportion and activity of the catalyst so that best results will generally be obtained when conditions are first determined on small-scale apparatus. As a rule, excessive temperatures are neither necessary or desirable in the alkyl fluoride-forming stage or in the alkylating stage of the process and only sufficient pressure is necessary to prevent excessive vaporization of the catalyst.

The combination process of the present invention is particularly useful in producing ethyl benzene from benzene and a substantially ethane-ethylene fraction since ethyl fluoride formed in the first step of the process is completely miscible with liquid hydrogen fluoride while ethane is much less soluble in liquid hydrogen fluoride and is therefore readily separable as an upper layer from the hydrogen fluoride solution of ethyl fluoride under the operating pressure which is sufficient to maintain in substantially liquid state the ethane, ethyl fluoride, and hydrogen fluoride. The solution of ethyl fluoride in hydrogen fluoried can then be reacted with benzene to produce ethyl benzene while the ethane is discharged from the process. The alkylation stage is accordingly carried out under substantially liquid phase conditions without interference of ethane which sometimes occurs when an ethane-ethylene fraction is introduced directly to an alkylation reactor in which benzene is contacted with liquid hydrogen fluoride. The present combination process is therefore useful in forming the ethyl fluoride, separating it from the unconverted ethane and effecting the alkylation of benzene under conditions which give a high yield of mono-ethyl benzene and relatively small amounts of more-highly ethylated benzenes.

The following examples are introduced as representative of results obtainable by the process described, although with no intention of unduly limiting the generally broad scope of the invention.

Example I

In a process substantially as described, 3 molecular proportions of a propane-propylene fraction containing about 30% of the latter are contacted with 50 molecular proportions of 98% hydrogen fluoride at −25° C. A mixture comprising essentially the isopropyl fluoride so formed and the excess of hydrogen fluoride is separated as a solution from a substantially propane fraction which is discharged from the process. The solution of isopropyl fluoride in hydrogen fluoride so obtained is then introduced to a second mixing zone together with 3 molecular proportions of benzene and the reaction mixture within said second zone is maintained at 50° C. and stirred to effect intimate contact of the reactants and catalyst. The resultant mixture is separated into a hydrocarbon layer and a hydrogen fluoride layer, the latter being recycled in part to the first stage of the process in which isopropyl fluoride is formed. The hydrocarbon layer is fractionally distilled to separate excess benzene from the alkylated benzenes, the excess benzene being recycled to the alkylation stage while the alkylated benzenes are fractionally distilled and thereby separated into isopropyl benzene, diisopropyl benzene, and more-highly alkylated hydrocarbons. The total alkylated product comprises about 80% by weight of mono-isopropyl benzene and 20% by weight of poly-isopropyl benzenes.

Example II

195 grams of benzene are placed in an autoclave provided with a motor-driven stirrer. The autoclave and contents are then brought to a temperature of 50° C. and 200 grams of a solution, consisting of equal parts by weight of ethyl fluoride and hydrogen fluoride resulting from treatment of an ethane-ethylene fraction with liquid hydrogen fluoride at 50° C., is slowly introduced to the autoclave with stirring during a period of 1 hour and then the stirring is continued for another hour at the operating temperature of 50° C. After the autoclave is cooled to room temperature, the reaction products are removed and separated into 84 grams of unconverted ethyl fluoride and 200 grams of a water-insoluble oil. After distillation to remove unconverted benzene there remains 12 grams of mono-ethyl benzene and 4 grams of more-highly alkylated benzene. In a similar run but at 100° C. reaction temperature, the yield of mono-ethyl benzene is about 100 grams.

The character of the process of the present invention and particularly its commercial value are evident from the preceding specification and examples, although neither section is intended to be unduly limiting in its generally broad scope.

I claim as my invention:

1. A process for the manufacture of alkylated aromatic hydrocarbons which comprises reacting an excess of liquid hydrogen fluoride with olefins present in a hydrocarbon fraction containing both olefins and normal paraffins, separating as a relatively heavy layer a solution of the resultant alkyl fluorides in the excess hydrogen fluoride from a relatively lighter layer comprising essentially unconverted normal paraffins, subjecting said solution to contact with an aromatic hydrocarbon under alkylating conditions to form a reaction mixture containing alkylated aromatic hydrocarbons, separating unconverted aromatic hydrocarbons, alkylated aromatic hydrocarbons, and used hydrogen fluoride from said reaction mixture, recycling said unconverted aromatic hydrocarbons to further reaction with said solution of alkyl fluorides in hydrogen fluoride, and returning at least a portion of said used hydrogen fluoride to contact with the charged fraction containing both olefins and normal paraffins.

2. A process for the manufacture of alkylated aromatic hydrocarbons which comprises reacting an excess of liquid hydrogen fluoride at a temperature of from about −50° to about +50° C. with olefins present in a hydrocarbon fraction containing both olefins and normal paraffins, separating as a relatively heavy layer a solution of the resultant alkyl fluorides in the excess hydrogen fluoride from a relatively lighter layer comprising essentially unconverted normal paraffins, subjecting said solution to contact with an aromatic hydrocarbon under alkylating conditions to form a reaction mixture containing alkylated aromatic hydrocarbons, separating from said reaction mixture unconverted aromatic hydrocarbons, alkylated aromatic hydrocarbons, and used hydrogen fluoride, recycling said unconverted aromatic hydrocarbons to further reaction with said solution of alkyl fluorides in hydrogen fluoride, and returning at least a portion of said used hydrogen fluoride to contact with the charged fraction containing both olefins and normal paraffins.

3. A process for the manufacture of alkylated aromatic hydrocarbons which comprises reacting an excess of liquid hydrogen fluoride at a temperature of from about −50° to about +50° C. under a liquefying pressure with olefins present in a hydrocarbon fraction containing both olefins and normal paraffins, separating as a relatively heavy layer a solution of the resultant alkyl fluorides in the excess hydrogen fluoride from a relatively lighter layer comprising essentially unconverted normal paraffins, subjecting said solution to contact with an aromatic hydrocarbon under alkylating conditions to form a reaction mixture containing alkylated aromatic hydrocarbons, separating from said reaction mixture unconverted aromatic hydrocarbons, alkylated aromatic hydrocarbons, and used hydrogen fluoride, recycling said unconverted aromatic hydrocarbons to further reaction with said solution of alkyl fluorides in hydrogen fluoride, and returning at least a portion of said used hydrogen fluoride to contact with the charged fraction containing both olefins and normal paraffins.

4. A process for the manufacture of alkylated aromatic hydrocarbons which comprises reacting an excess of liquid hydrogen fluoride at a temperature of from about −50° to about +50° C. under a liquefying pressure with olefins present in a hydrocarbon fraction containing both olefins and normal paraffins, separating as a relatively heavy layer a solution of the resultant alkyl fluorides in the excess hydrogen fluoride from a relatively lighter layer comprising essentially unconverted normal paraffins, subjecting said solution to contact with an aromatic hydrocarbon at a temperature between about −10° and about 150° C. to form a reaction mixture containing alkylated aromatic hydrocarbons, separating from said reaction mixture unconverted aromatic hydrocarbons, alkylated aromatic hydrocarbons, and used hydrogen fluoride, recycling said unconverted aromatic hydrocarbons to further reaction with said solution of alkyl fluorides in hydrogen fluoride, and returning at least a portion of said used hydrogen fluoride to contact with the charged fraction containing both olefins and normal paraffins.

5. A process for the manufacture of alkylated aromatic hydrocarbons which comprises reacting an excess of liquid hydrogen fluoride at a temperature of from about −50° to about +50° C. under a liquefying pressure with olefins present in a hydrocarbon fraction containing both olefins and normal paraffins, separating as a relatively heavy layer a solution of the resultant alkyl fluorides in the excess hydrogen fluoride from a relatively lighter layer composed of unconverted normal paraffins, subjecting said solution to contact with an aromatic hydrocarbon at a temperature between about −10° and about 150° C. under a pressure sufficient to maintain in liquid state a substantial proportion of the reactants and hydrogen fluoride to form a reaction mixture containing alkylated aromatic hydrocarbons, separating from said reaction mixture unconverted aromatic hydrocarbons, alkylated aromatic hydrocarbons, and used hydrogen fluoride, recycling said unconverted aromatic hydrocarbons to further reaction with said solution of alkyl fluorides in hydrogen fluoride, and returning at least a portion of said used hydrogen fluoride to contact with the charged fraction containing both olefins and normal paraffins.

6. A process for the manufacture of ethyl benzene which comprises reacting an ethane-ethylene fraction with a substantial molar excess of hydrogen fluoride relative to said ethylene, sepa-

rating as a relatively heavy layer a solution of the resultant ethyl fluoride in the excess hydrogen fluoride from a relatively lighter layer composed essentially of ethane, subjecting said solution to contact with benzene under alkylating conditions to form a reaction mixture containing ethyl benzene, separating from said reaction mixture unconverted benzene, ethyl benzene, and used hydrogen fluoride, recycling said benzene to further reaction with said solution of ethyl fluoride in hydrogen fluoride, and returning at least a portion of said used hydrogen fluoride to contact with the charged ethane-ethylene fraction.

7. A process for the manufacture of ethyl benzene which comprises reacting an ethane-ethylene fraction with a substantial molar excess of hydrogen fluoride relative to said ethylene at a temperature of from about —50° to about +50° C., separating as a relatively heavy layer a solution of the resultant ethyl fluoride in the excess hydrogen fluoride from a relatively lighter layer composed essentially of ethane, subjecting said solution to contact with benzene under alkylating conditions to form a reaction mixture containing ethyl benzene, separating from said reaction mixture unconverted benzene, ethyl benzene, and used hydrogen fluoride, recycling said benzene to further reaction with said solution of ethyl fluoride in hydrogen fluoride, and returning at least a portion of said used hydrogen fluoride to contact with the charged ethane-ethylene fraction.

8. A process for the manufacture of ethyl benzene which comprises reacting an ethane-ethylene fraction with a substantial molar excess of hydrogen fluoride relative to said ethylene at a temperature of from about —50° to about +50° C. under a liquefying pressure, separating as a relatively heavy layer a solution of the resultant ethyl fluoride in the excess hydrogen fluoride from a relatively lighter layer composed essentially of ethane, subjecting said solution to contact with benzene under alkylating conditions to form a reaction mixture containing ethyl benzene, separating from said reaction mixture unconverted benzene, ethyl benzene, and used hydrogen fluoride, recycling said benzene to further reaction with said solution of ethyl fluoride in hydrogen fluoride, and returning at least a portion of said used hydrogen fluoride to contact with the charged ethane-ethylene fraction.

9. A process for the manufacture of ethyl benzene which comprises reacting an ethane-ethylene fraction with a substantial molar excess of hydrogen fluoride relative to said ethylene at a temperature of from about —50° to about +50° C. under a liquefying pressure, separating as a relatively heavy layer a solution of the resultant ethyl fluoride in the excess hydrogen fluoride from a relatively lighter layer composed essentially of ethane, subjecting said solution to contact with benzene at a temperature between about —10° and about 150° C. under a pressure sufficient to maintain in liquid state a substantial proportion of the reactants and hydrogen fluoride to form a reaction mixture containing ethyl benzene, separating from said reaction mixture unconverted benzene, ethyl benzene, and used hydrogen fluoride, recycling said benzene to further reaction with said solution of ethyl fluoride in hydrogen fluoride, and returning at least a portion of said used hydrogen fluoride to contact with the charged ethane-ethylene fraction.

10. A process for the manufacture of propylated benzene which comprises reacting a propane-propene fraction with a substantial molar excess of hydrogen fluoride relative to said propene at a temperature of from about —50° to about +50° C. under a liquefying pressure, separating as a relatively heavy layer a solution of the resultant isopropyl fluoride in the excess hydrogen fluoride from a relatively lighter layer composed essentially of propene, subjecting said solution to contact with benzene at a temperature of between about —10° and about 150° C. under a pressure sufficient to maintain in liquid state a substantial proportion of the reactants and hydrogen fluoride to form a reaction mixture containing isopropyl benzene, separating from said reaction mixture unconverted benzene, isopropyl benzene, and used hydrogen fluoride, recycling said benzene to further reaction with said solution of isopropyl fluoride in hydrogen fluoride, and returning at least a portion of said used hydrogen fluoride to contact with the charged propane-propene fraction.

11. A process for producing alkylated aromatics which comprises subjecting a mixture of olefins and paraffins to reaction with liquid hydrogen fluoride to react olefins with hydrogen fluoride and thereby form alkyl fluorides, said reaction being effected in the presence of an amount of hydrogen fluoride which is in excess of that required to react with the olefins, thereby forming a solution of the alkyl fluorides in the excess of hydrogen fluoride, separating said solution from unreacted paraffins and commingling an aromatic hydrocarbon therewith, and subjecting the resultant mixture to alkylating conditions to alkylate the aromatic hydrocarbon.

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