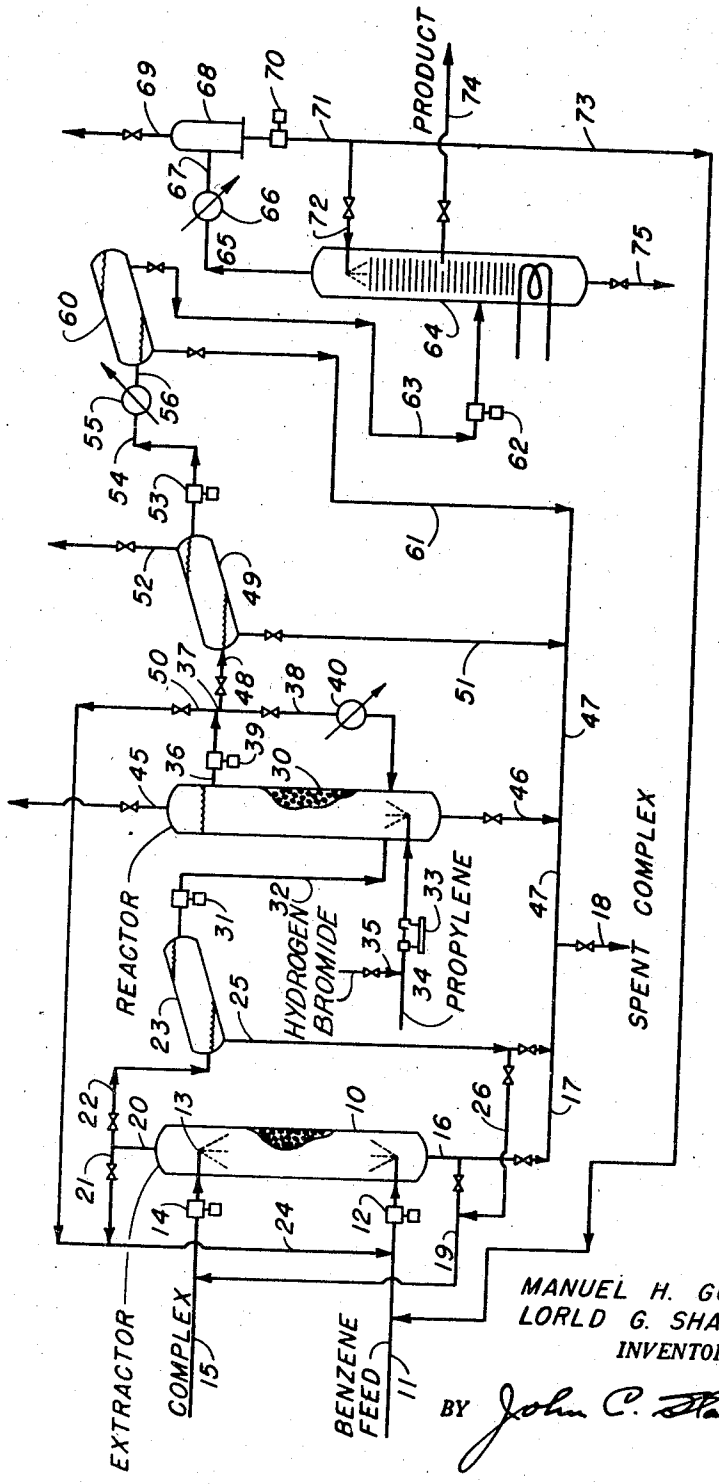
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PROCESS USING ALUMINUM BROMIDE-HYDROCARBON COMPLEX TO PROMOTE ALKYLATION OF AROMATIC HYDROCARBONS BY OLEFINS OF MORE THAN TWO CARBON ATOMS PER MOLECULE

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PROCESS USING ALUMINUM BROMIDE-HYDROCARBON COMPLEX TO PROMOTE ALKYLATION OF AROMATIC HYDROCARBONS BY OLEFINS OF MORE THAN TWO CARBON ATOMS PER MOLECULE

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This invention relates to an improvement in the method of utilizing aluminum bromide catalyst in catalytic hydrocarbon conversion. More particularly, this invention relates to the reuse of catalytically active aluminum bromide material which heretofore has been discarded along with catalytically inactive aluminum bromide tar. This material is associated with the insoluble aluminum bromide hydrocarbon complex which is precipitated when aliphatic hydrocarbons are catalytically converted to more valuable hydrocarbons in the presence of dissolved aluminum bromide. Typical examples of such hydrocarbon conversion processes are the alkylation of isoparaffins with olefins and the polymerization of mono-olefins in the presence of aluminum bromide catalyst. This invention is particularly concerned with the use of regulated amounts of the aromatic hydrocarbon soluble component of spent aluminum bromide catalyst as a catalyst for the alkylation of aromatic hydrocarbons with olefins.

Aluminum bromide, in contrast with aluminum chloride, is quite soluble in aliphatic hydrocarbons such as paraffinic hydrocarbons, mono-olefins, or mixtures of paraffinic hydrocarbons and mono-olefins. Hence, this catalyst in solution may be used advantageously to catalyze in homogeneous liquid phase such reactions as the alkylation of isobutane with mono-olefins and to polymerize mono-olefins. During the course of these reactions, the solution becomes depleted with respect to aluminum bromide catalyst through the formation of complexes with the aliphatic hydrocarbons by side reactions. The complex material settling out of solution is a relatively fluid tar and has a fairly uniform composition, within the range of from 60 to 75 per cent bromine, 6.7 to 8.4 per cent aluminum and 33.3 to 16.6 per cent hydrocarbons.

The chemical structure of a tarry precipitate is not known but it is undoubtedly a mixture of complex organic compounds derived from the aliphatic hydrocarbons in the reaction with the aluminum bromide. We have found that the tarry material may contain as high as 10 to 25 weight per cent of recoverable catalytically active aluminum bromide material which can be extracted with aromatic hydrocarbons such as benzene. This catalytically active material cannot be extracted from the insoluble tar by use of aliphatic hydrocarbons, at least in appreciable amounts. Without wishing to limit our invention to any theoretical considerations, it appears that in the early stages of aliphatic hydrocarbon conversion in the presence of aluminum bromide,

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relatively simple hydrocarbon complexes with the aluminum bromide are formed. These organo-aluminum bromide complexes which have limited solubility in the aliphatic hydrocarbons are quite soluble in aromatic hydrocarbons. As the aliphatic hydrocarbon conversion reaction progresses, the organo-aluminum bromide compounds become more complex and precipitate from the solution. The more complex and catalytically inactive insoluble material is an excellent solvent for the less complex organo-aluminum bromide compounds presumably carrying out of solution a considerable amount of the catalytically active material. For lack of precise information as to the chemical structure of the aluminum bromide-containing tar we will refer to it as an aluminum bromide-aliphatic hydrocarbon complex. By this term the aliphatic hydrocarbon-insoluble, fluid tar formed by the reaction between aluminum bromide and paraffinic hydrocarbons and/or aliphatic mono-olefinic hydrocarbons or their mixtures is referred to.

We have found that the benzene-soluble fraction of the above tarry material may be used to catalyze the alkylation of normally liquid aromatic hydrocarbons such as benzene, with aliphatic mono-olefins having more than two carbon atoms per molecule, such as propylene to form cumene, or with butylenes and amylenes to produce alkylated benzene with alkyl substituent groups of a greater number of carbon atoms. The process is very simple to carry out since no special equipment is required and the various steps of the process are preferably carried out at atmospheric temperatures or at temperatures not far removed from normal atmospheric temperature. The chief precaution is to avoid heating the tar above about 70° C. while in contact with the benzene. At temperatures above 70° C., the aromatic hydrocarbon apparently reacts quite readily with the aluminum bromide-aliphatic hydrocarbon complex to form a new complex. This new complex which apparently includes ring-type hydrocarbons is insoluble in the aromatic hydrocarbon and is catalytically inactive for the alkylation of aromatics with olefins. Preferably prolonged contact between the tar and the aromatic hydrocarbon should be avoided even at the lower temperatures since this undesirable reaction occurs, though slowly, at ordinary temperatures.

The tar may be added directly to the aromatic hydrocarbon in an agitator-type reactor to which the olefin stream is then added. Alternatively, the tar can be extracted with the aromatic hydrocarbon to dissolve the catalytically active com-

ponent of the tar. The benzene enriched with this solute may then be contracted with the olefin in a tower as described in the drawing hereinbelow. The latter procedure is preferred since it provides a continuous process for the recovery of the catalytic material and for the alkylation of the aromatic hydrocarbon.

The effluent from the alkylation reaction zone is passed to a cold settler for the separation of suspended catalytically inactive aluminum bromide complex. The clarified mixture of unreacted aromatic hydrocarbon and alkylated aromatic hydrocarbon is then heated to a temperature above about 70° C. and is passed to a hot settler. We have found that the product leaving the alkylation reaction zone should contain in solution at least 0.10 per cent by weight of dissolved aluminum bromide in the form of organo-aluminum bromide complex in order to obtain satisfactory conversion of the aromatic-olefin mixtures to alkylated aromatic hydrocarbons. We operate our process to obtain substantially complete reaction of the olefin component of the gaseous feed through the reactor in a single pass therethrough. In order to accomplish this result the aromatic effluent should contain dissolved organo-aluminum bromide equivalent to 0.10 weight per cent aluminum bromide.

The complex-free product from the hot settler is passed to a fractionator for recovery of alkylated aromatic hydrocarbons and unreacted aromatic hydrocarbon. The unreacted aromatic hydrocarbon is recycled to the aluminum bromide-aliphatic hydrocarbon complex extraction step.

The aluminum bromide-aliphatic hydrocarbon complex, that is, the total tar precipitated in the alkylation of paraffins with olefins, will efficiently alkylate from about two to seven and one-half parts by weight of olefin per part by weight of tar. Thus, this proportion of total tar should be added directly to the agitator-type reactor, or in case the tar is extracted in a preliminary extraction step, this proportion of tar will be required as tar feed to the extraction tower.

The concentration of aromatic hydrocarbon-soluble aluminum bromide-aliphatic hydrocarbon complex required in the aromatic solvent in the reaction zone for most efficient operation will depend on the type of operation used. Thus, for continuous operation wherein the withdrawal of reactants from the reaction zone is continuous the concentration of dissolved active catalytic material in the reaction zone will approximate the concentration in the effluent which must be at least 0.10 weight per cent of the aromatic content of the effluent calculated as free aluminum bromide. The aromatic feed to the reactor should therefore contain somewhat more than this minimum amount of dissolved organo-aluminum bromide catalyst to furnish that consumed in the reaction. We prefer to operate with aromatic feed to the reactor containing from about 0.2 weight per cent to about 0.70 or 0.75 weight per cent aluminum bromide equivalent of the organo-aluminum bromide in a continuous process such as that described hereinbelow. The aromatic hydrocarbon feed may contain up to 1.0 per cent aluminum bromide equivalent.

When operating the process batchwise we prefer to add sufficient aluminum bromide-aliphatic hydrocarbon complex to the aromatic hydrocarbon to give a concentration of dissolved organo-aluminum bromide equivalent to from about 0.3 weight per cent to about 1.0, preferably up to about 0.5, weight per cent of aluminum bromide dissolved in the aromatic reactant. The maximum amount of dissolved catalytic material should not greatly exceed the amount necessary to convert the olefin to alkylate. Thus, the concentration of dissolved catalytically active aluminum bromide-aliphatic hydrocarbon complex, that is, the organo-aluminum bromide in the aromatic feed to the reactor will be within the range of somewhat above 0.1 to about 1.0 weight per cent calculated as free aluminum bromide.

The mole ratio of aromatic hydrocarbon to olefin in the alkylation zone should be maintained within the range of from about two moles of benzene to one mole of olefin to about seven moles of benzene to one mole of olefin. High ratios favor the production of monoalkyl substituted benzene where benzene is the aromatic hydrocarbon undergoing alkylation.

The temperature maintained in the extraction step should be within the range of from about 10° C. to about 50° C. Temperatures within the range of from about 20° C. to 40° C. are preferred. As indicated hereinabove, aromatic hydrocarbon complex is formed quite readily at temperatures above about 70° C. and is formed slowly at lower temperatures. Temperatures lower than about 10° C. prevent the efficient extraction of the soluble catalytically active component from the tar. The extraction step may be carried out at pressures within the range of from about atmospheric pressure to about ten atmospheres (gage) or higher pressure.

Temperatures maintained within the alkylation reaction zone should be within the range of from about 10° C. to about 65° C., preferably within the range of from about 30° C. to about 55° C. Temperatures within the upper part of these ranges favor the rate of alkylation. However, the higher temperatures also accelerate the formation of the inactive aluminum bromide-aromatic hydrocarbon complex and hence the temperature of operation is adjusted to obtain the best economic balance between improved alkylation reaction rate and the undesirable deactivation of the catalytic material.

The pressure in the alkylation reactor is maintained within the range of from about atmospheric to about ten atmospheres' gage. Higher pressures favor polymerization of the olefins. A small amount of hydrogen bromide catalyst activator may be added to the aromatic hydrocarbon feed to the alkylation reactor. However, such addition will not be necessary unless substantially anhydrous aromatic hydrocarbon is used. We prefer to use relatively water-free feed to the process in order to avoid hydrolysis of the catalytic material. From about 2 per cent to 10 per cent by weight of hydrogen bromide based on the aluminum bromide equivalent of catalytically active organo-aluminum bromide material dissolved in the aromatic hydrocarbon is sufficient to promote the reaction. A more detailed description of our process is given in the drawing which represents diagrammatically one method of practicing the invention.

Referring now to the drawing, tower 10 is the zone wherein the catalytically active organo-aluminum bromide component of the aluminum bromide-aliphatic hydrocarbon complex is extracted by the aromatic hydrocarbon solvent, and tower 30 is the alkylation reactor. These towers may be packed with inert packing material to obtain efficient contact of the aromatic hydrocarbon with the aliphatic hydrocarbon complex

in tower 10 and to obtain more even distribution of the olefin throughout the body of aromatic hydrocarbon in tower 30. Substantially dry benzene containing no more than a trace of water is introduced to tower 10 from line 11 by means of pump 12. As the liquid benzene rises in tower 10 it is contacted countercurrently with a spray of aluminum bromide-aliphatic hydrocarbon complex introduced through spray nozzle 13 by means of pump 14 in line 15. The aliphatic hydrocarbon complex from which the major part of the catalytically active component is removed by the benzene collects as a separate insoluble phase in the bottom of tower 10 whence it is withdrawn through line 16 which connects with spent complex manifold line 17. Spent complex passes from line 17 through line 18 to the spent catalyst processing step for the recovery of the bromine content of spent catalyst. If desired, a part of the complex in line 16 may be recycled to line 15 through line 19 in order to more completely remove therefrom the benzene soluble catalytically active component.

The stream of benzene containing dissolved catalytically active organo-aluminum bromide passes overhead from tower 10 through line 20. Line 20 connects with recycle line 21 and with transfer line 22 which leads to cold settler 23. At least a part of the benzene is recycled through lines 21 and 24 to line 12 in order to increase the concentration of the catalytically active organo-aluminum bromide. The catalyst-enriched benzene which also contains suspended insoluble aluminum bromide-aliphatic hydrocarbon complex passes through line 22 to settler 23 wherein the suspended material settles to form a separate body of tar-like liquid. This material which contains only a small amount of catalytically active organo-aluminum bromide is passed through lines 25, 17, and 18 to the bromine recovery zone. If desired, a part of the tarry material may be recycled through lines 26 and 19 in order to remove more completely the benzene soluble active catalyst. Settler 23 is operated at a temperature within the range of from about 25° C. to about 35° C.

The clarified benzene solution of catalytic material in settler 23 is passed to a low point in tower reactor 30 by means of pump 31 in line 32. A C_3 fraction of a cracking still gas containing propylene is introduced to reactor 30 by means of compressor 33 in line 34. A small amount of hydrogen bromide may be introduced to line 34 from line 35. As the mixture of C_3 fraction passes upward through reactor 30 the propylene content of the gas reacts with the benzene in the presence of the dissolved organo-aluminum bromide catalyst. The mixture is circulated through lines 36, 37, and 38 by means of pump 39. The reaction in tower 30 is exothermic and hence the temperature of the cooling liquid in cooler 40 located in line 38 is regulated to maintain the temperature in tower 30 within the range of from about 30° C. to about 55° C. Preferably, tower reactor 30 is operated at a pressure of from about three atmospheres to about six atmospheres pressure gage. Propane from the C_3 fraction passes overhead from tower 30 through line 45. Inactive aluminum bromide-aromatic hydrocarbon complex which forms as the soluble organo-aluminum bromide catalyst becomes spent in tower 30, is withdrawn therefrom through bottom drawoff line 46, and passes thence through lines 47 and 18 to aluminum bromide recovery.

When the concentration of dissolved catalyst in the mixture of aromatic hydrocarbons in the reaction zone has decreased to an extent such that the aluminum bromide equivalent thereof in the effluent in line 36 is about 0.10 weight per cent, the stream is passed from line 37 through line 48 to settler 49 wherein inert aluminum bromide-aromatic hydrocarbon complex settles as a separate layer. If desired, at least a part of the stream of aromatics may be recycled to extraction tower 10 through lines 50, 24, and 11. This recycle procedure following partial conversion of the benzene is particularly desirable where the conversion of benzene to cumene in tower 30 is too low to justify separation of the alkylate, a condition which may arise if the initial concentration of soluble catalyst in the benzene is too low.

Settler 49 is operated at a temperature below about 55° C. and at substantially the same pressure as reactor 30. Aromatic hydrocarbon complex is withdrawn from settler 49 through line 51 and passes through lines 47 and 18 to the bromine recovery zone. Propane is released from the liquid in settler 49 through line 52. The clarified mixture of aromatics is withdrawn from settler 49 by means of pump 53 in line 54 which leads to heater 55. Heater 55 is operated at a temperature above about 70° C., preferably at about 80° C. and at about four or five atmospheres pressure. The higher temperature causes the rapid conversion of the residual soluble organo-aluminum bromide to insoluble aluminum bromide-aromatic hydrocarbon complex. Other methods well known to the art for removing the dissolved catalyst from the product may be used. Thus, the product stream may be treated with an aqueous solution of a base such as caustic soda to hydrolyze the aluminum bromide containing material in which hydrolyzed state the material is no longer soluble in the aromatic hydrocarbon product. The mixture of aromatics and suspended insoluble complex passes through line 56 to settler 60 whence the insoluble complex is passed via lines 61, 47, and 18 to the bromine recovery zone.

The clarified mixture of aromatics in settler 60 is passed by means of pump 62 in line 63 to fractionator 64. Benzene and residual propane from the C_3 fraction are taken overhead through line 65, condenser 66 and line 67 to reflux accumulator 68 whence propane is eliminated through line 69. Liquid benzene is withdrawn from accumulator 68 by means of pump 70 in line 71. A part of the benzene is returned to fractionator 64 through line 72 to serve as reflux. The remainder of the benzene is recycled to line 11 through line 73. Monoisopropyl benzene product is withdrawn through trapout line 74 and a fraction consisting of diisopropyl benzene and triisopropyl benzene is withdrawn as a bottom product through line 75.

Our invention may be better understood by the following examples illustrating the operation thereof. For convenience in comparing the results, the information as to conditions, reactants and products is given in tabular form. The reactions were carried out in a small reactor provided with an agitator, a thermocouple for continuously recording the temperature, and a pressure gage for indicating the pressure in the reactor. In all of the experiments tabulated, an aluminum bromide-aliphatic hydrocarbon tarry complex, obtained from the alkylation of iso-

butane with ethylene in the presence of dissolved aluminum bromide, was used as the source of the catalytic agent. A representative sample of such a tar contains about 70.8 per cent bromine and 7.7 per cent aluminum, or 78.5 per cent of $AlBr_3$ assuming these elements to be present as aluminum bromide in the complex. Such a tar may contain a variable amount of benzene-soluble, aliphatic hydrocarbon-insoluble material comprising organo-aluminum bromide catalyst as indicated by the different amounts of soluble active material extracted from the tar product. The amounts varied from about 10 weight per cent to about 19 weight per cent calculated as free aluminum bromide.

The benzene was added to the reactor at room temperature and the tar was added with mild agitation. A sample of the benzene layer was then withdrawn and analyzed for bromine and aluminum. The reactor was then sealed and brought to the desired temperature and propylene was admitted under the pressure indicated for the time given in the table. The propylene feed was then shut off and the amount of propylene entering the reactor was determined. The liquid aromatic hydrocarbon layer of the product was analyzed for aluminum bromide after the reaction had been allowed to proceed for the time period given. The difference in dissolved organo-aluminum bromide before and after the reaction is a measure of the amount of organo-aluminum bromide catalytically active material converted to insoluble, inactive aluminum bromide-aromatic hydrocarbon complex during the reaction.

Table

Example	1	2	3	4	5
Temperature, ° C.	32	12	12	45	55
Pressure, lbs./in.² gage	22	2	1	10	8
$AlBr_3$ Concentration in Benzene Layer:					
Init. Wt. Per cent (Benzene Basis)	0.136	0.525	0.35	0.745	0.35
Final Wt. Percent (Hydrocarbon Basis)	0.00	0.313	0.17	0.10	0.14
Time in Minutes:					
Olefin Charge	32	220	139	20	22
Total Time	72	226	139	50	39
Charge:					
Benzene, grams	337	360	334	334	335
Tar, grams	4.5	11.5	6.5	26.0	10
Propylene, grams	35	64	45	70	75
Wt. Ratio, Tar/C_3H_6	1/7.8	1/5.6	1/6.9	1/2.7	1/7.5
Mole Ratio, Benzene/Propylene	5.2	3.1	4.0	2.6	2.4
Wt. Per cent Extract From Tar: Calculated as $AlBr_3$	10.5	17.3	18.9	10.2	12.3
Conversion of C_3H_6	21.0	100	100	100	100
Wt. Per cent Recovery:					
Benzene Plus Tar	94.5	65.0	73.1	47.5	57.5
Isopropyl Benzene	3.5	23.6	16.8	34.3	29.9
Diisopropyl Benzene	1.0	6.7	6.5	15.0	9.7
Triisopropyl Benzene	1.0	4.7	3.6	3.2	2.9

Comparing the results of Example 1 with the other examples, particularly with Example 4, it will be seen that the amount of aluminum bromide-aliphatic hydrocarbon complex tar used was insufficient to alkylate the benzene to the desired extent. Unreacted propylene was observed at the end of the experiment illustrated by Example 1 and an insignificant yield of alkylate was obtained. At the end of the experiment there was no organo-aluminum bromide active catalyst dissolved in the benzene layer. The active catalyst originally present in the benzene layer had reacted to form an insoluble aluminum bromide-aromatic hydrocarbon complex. In Example 4 there remained at the end of the experiment 0.10 weight per cent of the active organo-

aluminum bromide catalyst in the aromatic hydrocarbon, calculated as aluminum bromide. From the results of Examples 1 and 4 it can be seen that about 0.10 weight per cent of the active organo-aluminum bromide catalyst material dissolved in the aromatic hydrocarbon, calculated as aluminum bromide, will effectively catalyze the alkylation reaction although this represents about the minimum requirement. The initial concentration of catalyst to alkylated benzene was high in Example 4 and conversion of benzene was also high. Concentrations of catalyst in the feed, which are substantially higher than illustrated in Example 4, are not preferred, particularly when operating continuously unless temperatures well above 45° C. are used, since greater loss of catalyst in the effluent will result when operating in the low temperature range.

The weight ratio of tar to propylene was high in Example 4 and an excess of the catalytically active material in the tar was provided in this experiment. In Example 5 approximately three times the amount of active catalyst was dissolved in the benzene layer as was dissolved in the benzent layer in Example 1. Example 5 represents conditions for more economical utilization of the tar than does Example 4 since the extent of conversion of benzene to alkylate was only moderately less than in Example 4 although less than half the catalytically active extract was present initially in benzene in Example 5. Somewhat better product distribution was also obtained in Example 5 than in Example 4.

The effect of temperature on the rate of conversion is illustrated by comparing the results of Experiments 2 and 3 with the results of Experiments 4 and 5. Although conversion of benzene to alkylate can be obtained in the lower temperature range as indicated by Examples 2 and 3, we prefer to operate at higher temperatures since the rate of conversion is much higher at higher temperatures. Obviously, additional propylene could have been reacted in Experiments 2 and 3 since the aromatic product contained considerable excess of dissolved catalytically active organo-aluminum bromide at the end of the experiments.

By proper regulation of the quantity of the aluminum bromide-aliphatic hydrocarbon tar complex added to the benzene to furnish sufficient soluble catalytically active organo-aluminum bromide to react the olefin with the benzene, care being taken that the concentration of the catalytically active material is not too low, a large part of the active complex may be used efficiently prior to regeneration of the aluminum bromide-aliphatic hydrocarbon complex to produce catalytically active aluminum bromide-containing material or prior to recovering the bromine content thereof. The exact amount of tar required will depend on the amount of propylene fed to the process, on the composition of the tar, on the concentration of the soluble component of the tar in the aromatic hydrocarbon, and on the temperature used in carrying out the alkylation process.

The presence of water in the benzene or in other aromatics will also exert a considerable effect on the preferred amount of tar. Traces of water tend to hydrolyze the aluminum bromide in the original tar. The HBr liberated by hydrolysis exerts a promotional effect on the catalyst, decreasing the amount of tar required even though the reaction is at the expense of the active organo-aluminum bromide component of the

tar. Preferably, the HBr should be added from an external source. For example, a part of the aluminum bromide-aromatic hydrocarbon complex from line 18 can be hydrolyzed to produce the necessary HBr activator. We prefer to use dry benzene, although absolutely anhydrous benzene is not necessary.

Although we have described our process as including a preliminary extraction step and subsequent alkylation of the aromatic in homogeneous phase operation, we do not wish to be limited to this type operation. As indicated hereinabove, the extraction of the catalytically active component from the tar and the alkylation of the extractant can be carried out simultaneously in the same reaction zone. Somewhat better control of the reaction may be accomplished by the latter method. However, the presence of the insoluble part of the aluminum bromide-aliphatic hydrocarbon complex in the alkylation reaction zone promotes the precipitation of the unreactive aluminum bromide-aromatic hydrocarbon complex which is formed from the active component and tends to carry down the active component from solution and hence from the zone of effective contact with the reactants.

This application is a continuation-in-part of our copending application entitled Alkylation process, Serial No. 487,036, filed May 14, 1943 now abandoned.

We claim:

1. The continuous process for alkylating a normally liquid aromatic hydrocarbon with an aliphatic olefin containing at least three carbon atoms per molecule which comprises the steps of (1) continuously contacting said liquid aromatic hydrocarbon with a liquid aluminum bromide-aliphatic hydrocarbon complex in a contact zone to extract from said complex a sufficient amount of an organic, aluminum bromide-containing component of said complex to obtain an aromatic hydrocarbon solution containing an amount of said component equivalent to at least 0.2 weight per cent of aluminum bromide and not more than 1.0 weight per cent of aluminum bromide, (2) continuously passing the aromatic hydrocarbon solution of step 1 to a reaction zone at a temperature within the range of from 10° C. to about 65° C. and contacting said solution therein with an amount of said aliphatic olefin equal to at least two times the weight and not more than seven and one-half times the weight of the liquid aluminum bromide-aliphatic hydrocarbon complex from which the aluminum bromide-containing component is extracted in step 1 for a sufficient time to convert at least a part of said aromatic hydrocarbon to alkylated aromatic hydrocarbon and to convert a part of said aluminum bromide-containing component to insoluble, aluminum bromide-aromatic hydrocarbon complex and maintaining said contacting for an insufficient time to reduce the concentration of organic, aluminum bromide-containing component dissolved in the aromatic hydrocarbon reaction mixtures below an aluminum bromide equivalent of 0.1 weight per cent based on the weight of the aromatic hydrocarbons in said reaction mixture, (3) continuously separating the insoluble aluminum bromide-aromatic hydrocarbon complex from the aromatic hydrocarbon solution of aluminum bromide-containing component of step 2, (4) continuously separating the residual dissolved organic, aluminum bromide-containing component from the aromatic hydrocarbon solution of step 3, (5) fractionating the aromatic hydrocarbons of step 4 to obtain a stream of unreacted aromatic hydrocarbon and alkylated aromatic hydrocarbons produced in step 2, (6) recycling the unreacted aromatic hydrocarbon of step 5 to step 1, and (7) recovering at least one alkylated aromatic hydrocarbon from step 5 of the process.

2. The process as described in claim 1 wherein the liquid aromatic hydrocarbon of step 1 is benzene.

3. The process as described in claim 1 wherein the mono-olefin is propylene.

4. The process as described in claim 1 wherein the aluminum bromide-aliphatic hydrocarbon complex is obtained as an aliphatic hydrocarbon-insoluble liquid in the alkylation of an isoparaffin with an aliphatic mono-olefin.

5. The process as described in claim 1 wherein the residual dissolved organic, aluminum bromide component of step 4 is precipitated from solution in the aromatic hydrocarbon product as aluminum bromide-aromatic hydrocarbon complex by heating the solution to a temperature above about 70° C.

6. The process for the manufacture of cumene from benzene and propylene which comprises the steps of (1) contacting at a temperature within the range of from about 10° C. to about 65° C. a mixture of benzene and propylene containing at least 2 moles and not more than 7 moles of benzene per mole of propylene in a reaction zone in the presence of sufficient aluminum bromide-aliphatic hydrocarbon complex to provide in solution in said benzene a concentration of an organic, aluminum bromide-containing component of said complex equivalent to 0.2 weight per cent and not more than 1.0 weight per cent of aluminum bromide to alkylate a part of said benzene and precipitate from solution therein an aluminum bromide-aromatic hydrocarbon complex, (2) separating from the insoluble aluminum bromide-aromatic hydrocarbon complex and insoluble aluminum bromide-aliphatic hydrocarbon complex a mixed benzene and alkylated benzene solution of said organic, aluminum bromide component containing not less of said component than the equivalent of 0.1 weight per cent of aluminum bromide based on the weight of the aromatic hydrocarbons in said solution, (3) heating the mixed benzene and alkylated benzene solution of step 2 to a temperature above 70° C. to convert the solute therein to aromatic hydrocarbon-insoluble aluminum bromide-aromatic hydrocarbon complex and to form a mixture consisting substantially of benzene and alkylated benzene, (4) separating the mixture of benzene and alkylated benzene of step 3 from the aluminum bromide-aromatic hydrocarbon complex, and (5) fractionating the mixture of benzene and alkylated benzene of step 4 to recover cumene.

7. The continuous process for alkylating benzene with an olefin selected from the class consisting of propylene, butylene, and amylene which comprises the steps of (1) continuously contacting at a temperature within the range of from about 10° C. to about 65° C. in a reaction zone a reaction mixture comprising at least 2 moles and not more than 7 moles of benzene per mole of said olefin with a stream containing an amount of an aluminum bromide-aliphatic hydrocarbon complex sufficient to maintain in solution in said reaction mixture at least 0.1 weight per cent aluminum bromide equivalent and not more than 1.0 weight per cent aluminum bromide equivalent based on the aromatic hydrocarbons in said mixture said aluminum bromide equivalent consist-

ing of an aliphatic hydrocarbon-insoluble, benzene-soluble aluminum bromide-containing component of said aluminum bromide-aliphatic hydrocarbon complex whereby a part of said benzene is alkylated to form a reaction product comprising unreacted benzene and alkylated benzene and whereby said olefin is completely reacted and aromatic hydrocarbon-insoluble aluminum bromide-aromatic hydrocarbon complex is precipitated, (2) continuously separating from the unreacted benzene and alkylated benzene reaction product of step 1 the insoluble aluminum bromide-aromatic hydrocarbon complex in admixture with the aromatic hydrocarbon insoluble portion of the aluminum bromide-aliphatic hydrocarbon complex of step 1, (3) continuously heating to a temperature above about 70° C. the unreacted benzene and alkylated benzene reaction product of step 2 to precipitate therefrom the equivalent of at least 0.1 weight per cent of aluminum bromide based on the combined weight of said benzene and alkylated benzene in the form of aluminum bromide-aromatic hydrocarbon complex, (4) adjusting the flow of aluminum bromide-aliphatic hydrocarbon complex with relation to the olefin feed to the reaction zone of step 1 to an amount within the range of from 1 part by weight per 2 parts by weight of olefin to about 1 part by weight per 7.5 parts by weight of olefin, (5) and recovering alkylated benzene from aluminum bromide-aromatic hydrocarbon complex-free aromatic hydrocarbon reaction product of step 3.

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