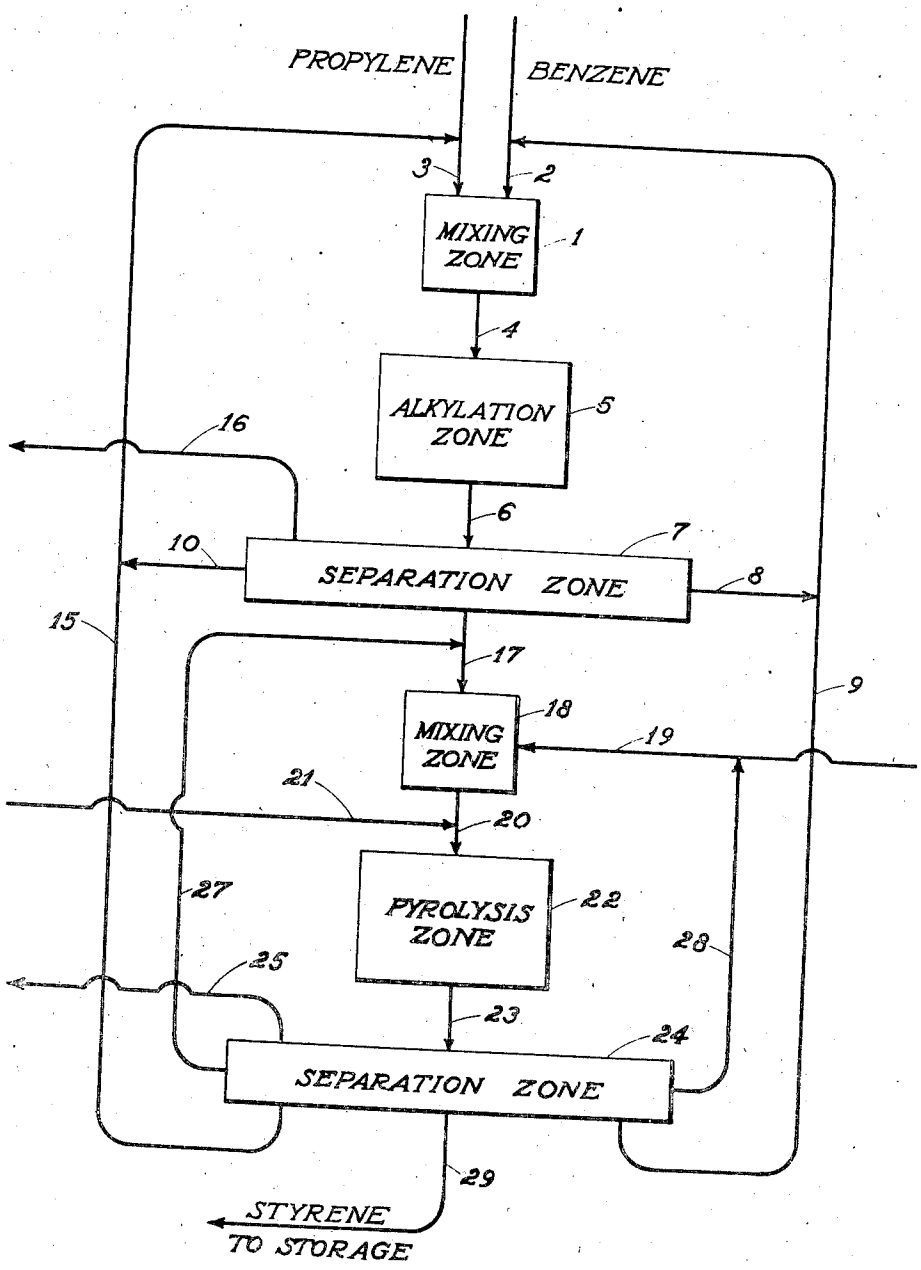
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PRODUCTION OF STYRENE

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PRODUCTION OF STYRENE

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This invention relates to the production of styrene. More particularly, the invention is concerned with an improved process of producing styrene from benzene and propylene, which process is adaptable for commercial scale operation.

It is well known that styrene can be produced directly by the pyrolysis of isopropyl benzene. However, a major drawback of the reaction has been the presence of side reactions by virtue of which a substantial proportion of the isopropyl benzene is converted to undesirable end products with a consequent reduction in the yield of styrene. The principal side reactions which take place are (1) the conversion of isopropyl benzene to α-methyl styrene and methane, and (2) the conversion of isopropyl benzene to benzene and propylene. Because of the low yields of styrene obtainable heretofore by pyrolysis of isopropyl benzene, the reaction has been considered unfavorable from an economic standpoint for use on a commercial scale.

The present invention has for its prime object the provision of a method of pyrolyzing isopropyl benzene whereby greatly improved yields of styrene, over those heretofore reported, are obtained.

Another object of the invention is to provide a method of pyrolyzing isopropyl benzene whereby the conditions of the reaction are so selected and adjusted that substantially none of the isopropyl benzene is lost through conversion to α-methyl styrene, i. e., the α-methyl styrene-forming side reaction is practically suppressed.

Another object is to provide a method of producing styrene from benzene and propylene as starting materials.

Another object is to provide a method of manufacturing styrene from benzene and propylene which method utilizes in combination an alkylation step and a pyrolysis step whereby benzene and propylene formed in the pyrolysis step are utilized in the alkylation step to improve the yield of styrene over that obtainable by use of the pyrolysis step alone.

Still another object is to provide a continuous process for manufacturing styrene from benzene and propylene which is adaptable for use on a commercial scale.

Other objects and advantages of our invention will be apparent from the following description thereof and the appended claims.

Broadly stated, our invention comprises a continuous process for the production of styrene from benzene and propylene which involves the following steps: (*a*) reacting benzene and propylene in an alkylation zone, (*b*) fractionating the product obtained to separate isopropyl benzene from unconverted benzene and propylene which are recycled to the alkylation zone, (*c*) passing the isopropyl benzene to a mixing zone wherein it is admixed with α-methyl styrene, (*d*) subjecting the mixture formed to pyrolysis to form styrene, (*e*) fractionating the product mixture to separate benzene, propylene, styrene, α-methyl styrene and unreacted isopropyl benzene (*f*) returning the benzene and propylene to the alkylation zone of the process, (*g*) recycling the α-methyl styrene and the unreacted isopropyl benzene to said mixing zone wherein they are admixed with additional isopropyl benzene derived from the alkylation zone, (*h*) controlling the amount of isopropyl benzene passing from the alkylation zone into admixture with the recycle α-methyl styrene and unreacted isopropyl benzene so that the proportion of α-methyl styrene to isopropyl benzene entering the mixing zone is such that in the subsequent pyrolysis of the mixture formed, the formation of α-methyl styrene is practically completely suppressed, and (*i*) recovering the styrene formed.

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A prominent feature of our invention resides in our discovery that by introducing into the pyrolysis zone a reaction mixture comprising isopropyl benzene and α-methyl styrene in such proportions that the mol ratio of α-methyl styrene to isopropyl benzene is approximately 0.63 to 1, the side reaction which produces α-methyl styrene is practically completely suppressed, while the yield of styrene is accordingly increased. By carrying out the pyrolysis in this way yields of styrene amounting to at least 76 percent of theoretical on the basis of isopropyl benzene decomposed in any one pass through the pyrolysis zone may be attained. Furthermore, the benzene and propylene formed by the dealkylation side reaction in the pyrolysis step are recovered in our process and returned to the alkylation step wherein they are reacted to reform isopropyl benzene which is subsequently sent to the pyrolysis step and ultimately converted to styrene. Since the amounts of propylene and benzene recovered and returned to the process in the manner just described is approximately 7 percent of the isopropyl benzene decomposed, the conversion of isopropyl benzene to styrene is approximately 82 percent of theoretical on the basis of isopropyl benzene decomposed in the pyrolysis. Also, since by the process of our invention provision is made for the return of unreacted isopropyl benzene to the pyrolysis zone (between 30 and 70 per cent of the isopropyl benzene is decomposed in a single pass)

and its ultimate conversion to styrene, a yield of approximately 82 percent of theoretical on the basis of total isopropyl benzene charged to the pyrolysis zone is obtained by our process. Such a yield of styrene cannot be obtained by the use of prior art methods of pyrolyzing isopropyl benzene in so far as we are aware.

The alkylation of benzene with propylene is well known and this step of our invention may be carried out employing any of the methods heretofore proposed. Thus it has been disclosed that the reaction may be effected in the presence of such catalytic agents as sulphuric acid, hydrofluoric acid and metallic salts of the Friedel-Crafts type. Also, certain bleaching earths, kaolins and similar silicates, treated with acids, have been employed as contact catalysts for this reaction. The particular reaction conditions to be employed, such as temperature, pressure, and residence or contact time vary considerably depending upon the particular catalytic agent utilized.

A particularly suitable catalyst for carrying out the alkylation step of our process is our specially prepared "silica-alumina" contact catalyst. The preparation of this catalyst is disclosed in detail and claimed in our co-pending application, Serial Number 460,654, filed October 3, 1942. As disclosed in the co-pending application the silica alumina catalyst may be prepared as follows. A silica gel is prepared from a dilute solution of sodium silicate by precipitation with a slight excess of hydrochloric acid. The gel is washed free of chloride ion and alumina is precipitated on the surface of the gel by contacting the gel with 0.2 N aluminum sulphate solution at 90° C. for two hours. The catalyst is then washed free of sulphate ion and dried at 125° C. for 48 hours.

Employing a "silica-alumina" catalyst prepared in the manner above described we have obtained conversions of propylene to alkylate amounting to 95 percent of theoretical, or better, the alkylate product comprising approximately 90 percent by weight of the desired mono-isopropyl benzene. We have found that best results are obtained when the reaction is conducted in the liquid phase. The particular advantage of this type of operation over vapor phase operation is that of longer catalyst life. The length of catalyst life is, of course, an important consideration from the standpoint of commercial operation.

To conduct the alkylation reaction in the liquid phase in the presence of our silica-alumina catalyst it is generally desirable to dissolve propylene in benzene to form a reaction mixture having a benzene-propylene mol ratio of about 6 to 1, or higher. The mixture may then be pumped into the reaction chamber under pressure and brought into contact with the suitably divided solid catalyst. Liquid space velocities of from about 15 to about 30 cc./cc. of catalyst per hour have been found to give excellent yields of isopropyl benzene. Operating temperatures of from 150° C. to 350° C. have been found satisfactory, the preferred range being from 175° C. to 225° C. Pressures of from 50 to 70 atmospheres should be employed to maintain the reactants in the liquid phase at these temperatures.

From the alkylation step of our process the product mixture is withdrawn, cooled and fractionated. Benzene and propylene, recovered by the fractionation, are recycled to the alkylation zone. The small amount of diisopropyl benzene separated from the product mixture is withdrawn

from the process, while the desired isopropyl benzene product is directed to admixture with α-methyl styrene in the manner which is described herebelow in connection with the appended drawing. The amounts of isopropyl benzene and α-methyl styrene going into admixture are carefully regulated so that a reaction mixture having the desired composition of 0.63 mole of α-methyl styrene per mole of isopropyl benzene is formed. This mixture is passed to a preheating chamber wherein it is vaporized and heated to a temperature approaching that which is sufficient to pyrolyze isopropyl benzene, for example, from 300° C. to 500° C. The vaporized mixture just prior to entering the pyrolysis reactor is admixed with about 3 times its volume of diluent steam or nitrogen. The diluent vapor should be preheated to a temperature of at least that of the reaction mixture, and if desired, to a higher temperature sufficient to supply the necessary heat of pyrolysis. A typical gaseous mixture made up in this way comprises, for example, approximately 18 parts isopropyl benzene, 11 parts α-methyl styrene and 72 parts of steam.

In the pyrolysis zone a reaction mixture of the above defined composition is passed through a metal tube, or tubes, lined with a ceramic material or graphite, preferably the former. Where ceramic lined tubes are employed the heat of reaction is preferably supplied by superheating the diluent vapor to a temperature sufficiently high to furnish the heat of pyrolysis. Where graphite-lined reaction tubes are employed the heat of pyrolysis may be supplied either by externally heating the reaction tubes, or preheating the diluent vapor. The temperature of the vaporous mixture in the pyrolysis zone should be from 600° C. to 800° C. Generally, pyrolysis is conducted at about atmospheric pressure, though pressures up to 5 atmospheres may be used. The time of contact for the pyrolysis should be such that from 30 to 70 percent of the isopropyl benzene in the feed to the pyrolysis zone is decomposed at the operating temperature employed. For example, at 700° C. the contact time should be no longer than 3 seconds, and preferably about 2 seconds. Longer heating times have been found to induce cracking and undesirable tar formation, which occasionally results in a clogging of the reaction tubes. The reacted mixture is withdrawn from the pyrolysis zone into an efficient cooling apparatus wherein it is rapidly cooled sufficiently to condense the normally liquid components thereof.

The uncondensed portion is separated from the condensed components of the product mixture and fractionated to separate propylene, which is returned to the alkylation step. Light gases, comprising mostly methane and with small amounts of ethylene, are withdrawn from the process. Where a gas such as nitrogen has been employed as the diluent vapor for the pyrolysis reaction, separation and recovery of the unconverted propylene reactant is not considered economically feasible. However, if the diluent vapor is steam, recovery of the propylene can be readily accomplished.

The condensed portion of the produce mixture is fractionated to separate benzene, styrene, unconverted isopropyl benzene and α-methyl styrene. The benzene is returned to the alkylation step, while the unconverted isopropyl benzene and the α-methyl styrene are recycled to admixture with isopropyl benzene, deriving from the alkylation step, and subsequently returned to the py-

rolysis step. Since under the conditions employed, α-methyl styrene is neither formed nor decomposed in the pyrolysis zone, no substantial continuous accumulation or deficit of this compound will occur in the system and it is only necessary to continuously return all of the α-methyl styrene to the mixing zone of the process, further admission of α-methyl styrene to the process system not being required. The composition of the feed mixture going to the pyrolysis step may be conveniently controlled by adjusting the relative amount of isoproyl benzene, deriving from the alkylation step, which is being admitted to the mixing zone. In commercial practice, an advantageous procedure for controlling the composition of the pyrolysis feed mixture, without lowering the production rate of the plant process is the provision of a reserve supply of α-methyl styrene from which sufficient amounts may be withdrawn from time to time for admixture with isopropyl benzene in the mixing zone to take care of fluctuations in the amount of this material in the recycle stream.

For the purpose of more clearly illustrating the combination of steps characteristic of our invention the attached drawing shows diagrammatically a typical process flow for producing styrene from benzene and propylene as starting materials.

Referring to the drawing, benzene and propylene are admitted to the "pre-alkylation" mixing zone 1 of the process by way of lines 2 and 3 respectively, in such proportions that a reaction mixture comprising benzene and propylene in the approximate mol ratio of 7 to 1 is formed therein. The reaction mixture is withdrawn from zone 1 and forced under pressure in line 4 to alkylation zone 5.

When employing our solid "silica-alumina" catalyst in the alkylation step of the process, the alkylation zone 5 may comprise a group of reactors, containing the contact catalyst in a suitably divided state, which may be operated interchangeably for the continuous operation of the process in the manner well known to the art. Suitable means are provided for the reactors so as to maintain the reactants at the desired temperature level of from 150° C. to 350° C. Since the reaction is exothermic in character, the reaction temperature may be conveniently controlled by limited preheating of the reactants, the reaction itself supplying the remainder of the required heat. A pressure of from 40 to 70 atmospheres will be required for liquid phase operation at these temperatures when employing the reactant in the mol ratio specified. This pressure may be attained by utilizing a suitable pump to force the reaction mixture into the reaction zone.

The product mixture is withdrawn from the alkylation zone 5 by way of 6 and conducted to separation zone 7. Separation zone 7 comprises suitable stabilizing and fractionating equipment in which the components of the product mixture from the alkyalation zone may be separated. From the separation zone, unreacted benzene and propylene are recycled to the reactant mixing zone 1 of the process, the benzene being returned by way of lines 8, 9 and 2, and the propylene by way of lines 10, 15 and 3. The small amounts of diisopropyl benzene contained in the alkylate product mixture are withdrawn from the separation zone and removed from the process in line 16. Isopropyl benzene is withdrawn from the separation zone by way of line 17 and sent to "prepyrolysis" mixing zone 18. Here the isopropyl benzene is brought into contact with α-methyl styrene which enters the mixing zone from line 19. The source of the α-methyl styrene in line 19 is described herebelow. The amount of isopropyl benzene admitted to the mixing zone 18 from line 17 is carefully controlled so that the pyrolysis mixture formed therein will have a composition of about .63 mol of α-methyl styrene per mol of isopropyl benzene. The temperature in the zone 18 is maintained sufficiently high to vaporize the reaction mixture and preheat it to a temperature approaching that which will cause pyrolysis of the isopropyl benzene. The hot vaporous mixture is withdrawn from the mixing zone in line 20 wherein it is joined by a steam of superheated diluent steam entering this line from line 21. The amount of steam delivered to line 20 from line 21 is regulated so as to form a mixture containing from 2 to 5 volumes of steam for each volume of reactant gas mixture deriving from mixing zone 18. The vaporous streams thus combined in line 20 are delivered by this line to pyrolysis zone 22. Zone 22 may comprise one or more ceramic-lined metal tubes. The heat contained in the reaction mixture due to the heating in the mixing step and the addition of superheated stem should be such as to supply the necessary pyrolysis temperature of from 600° C. to 800° C. As stated hereinbefore, the contact time should be sufficient to allow a decomposition of from 30 to 70 percent of the isopropyl benzene passing through the pyrolysis zone. The particular contact time to be employed will be governed in accordance with the particular temperature used. Thus, where the temperature of pyrolysis is near the lower limit of the temperature range given, the contact time will be longer than where the higher temperatures are employed.

Upon withdrawal from the pyrolysis zone the reacted gases are directed in line 23 to separation zone 24 where they are quickly and efficiently cooled, and the various components separated by fractional distillation.

Light gases such as methane, ethylene, etc., are withdrawn from the process by way of line 25. Propylene and benzene, formed by the dealkylation side reaction in the pyrolysis zone, are separated from the product mixture in zone 24 and recycled to the initial step of the process for reuse in the alkylation zone. Benzene is returned to the mixing zone 1 by way of lines 9 and 2, while propylene is returned to the mixing zone 1 by way of lines 15 and 3. Unreacted isopropyl benzene is withdrawn from separation zone 24 and returned to the mixing zone 18 by way of lines 27 and 17. The α-methyl styrene content of the product mixture is entirely returned to mixing zone 18 by way of lines 28 and 19, for recirculation through the pyrolysis zone of the process, while the desired styrene product is withdrawn in line 29 and sent to storage.

The following example is presented for the sole purpose of illustrating a suitable mode of carrying out the process of our invention and the results which may be obtained by its use, and the invention is not to be construed as limited to the particular catalysts or conditions of operation specified in the example.

Example

Streams of benzene and propylene were admitted to a "pre-alkylation" mixing zone to form a reaction mixture in which the propylene is sub-

stantially completely dissolved in the benzene, the mol ratio of propylene to benzene in the mixture formed being approximately 1 to 7. The mixture was withdrawn from the mixing zone and delivered under pressure into an alkylation reactor wherein it was passed over a "silica-alumina" catalyst at a liquid space velocity of 18 cc./cc. of catalyst per hour. The temperature of the reaction zone was maintained at approximately 210° C. and the pressure at about 50 atmospheres. The charge of reaction mixture to the alkylator consisted of 52,600 grams of benzene, and 4050 grams of propylene.

The product derived from the alkylation reactor was cooled and fractionated. From the fractionation, 9380 grams of mono-isopropyl benzene and 1101.6 grams of diisopropyl benzene were recovered. This combined alkylate product represents a 95% of theoretical conversion of the propylene charged of which 89 percent by weight constituted the desired mono-alkylate product.

The isopropyl benzene recovered from the separation zone was sent to a "prepyrolysis" mixing zone wherein it was commingled with a stream of α-methyl styrene to produce a homogeneous mixture which comprised approximately .63 mol of α-methyl styrene per mol of isopropyl benzene. The mixture was heated in this zone to a temperature of about 400° C. A stream of this vaporous mixture was brought into contact with a stream of superheated steam, which served as a diluent and heat supplying medium, at the entrance of the pyrolysis zone. The flow in each of the streams was regulated so that a mixture having a ratio of approximately 3 volumes of steam to 1 volume of reaction mixture was formed. The combined stream in the pyrolysis reactor attained a temperature of about 700° C. for 2.3 seconds. The effluent stream from the reactor was immediately cooled in a water cooled apparatus. The gaseous portion of the product mixture was fractionated to remove light gases. The condensed portion upon fractionation yielded 2600 grams of styrene, 5420 grams of isopropyl benzene, 179 grams of benzene and 106 grams of propylene. Of the 5500 grams of α-methyl styrene introduced to the "prepyrolysis" mixing step of the process, a total of 5415 grams were recovered from the fractionation of the pyrolysis product. 407 grams of tar were obtained from the distillation of the pyrolysis product.

From the foregoing example it may be seen that from the 9380 grams of isopropyl benzene, obtained by the consumption of 3853 grams of propylene and 6300 grams of benzene in the alkylation step, which were subsequently charged to the pyrolysis step, 5420 grams were available for recycle to the pyrolysis step, 285 grams were available as propylene and benzene for recycle to the alkylation step, and the balance 3675 grams were consumed. Of the isopropyl benzene converted to product not available directly for reuse in the process, 2600 grams or 81.7% of theoretical were converted to the desired styrene product.

It will thus be understood by those skilled in the art that by operating our process in a continuous manner as described in connection with the drawing, whereby the benzene, propylene and isopropyl benzene, recovered in the fractionation of the pyrolysis product, are recycled and utilized by the process to produce additional styrene, the actual yield of styrene which may be obtained by our process is in the order of 80 to 85 percent.

As pointed out at the outset of this specification and indicated by the example, the α-methyl styrene content of the reaction mixture charged to the pyrolysis step is practically completely recoverable in our process and may be conveniently recycled to the pyrolysis zone. This feature of our process affords a distinct advantage from the standpoint of continuous operation, since no provision for the addition or removal of this substance from the process system is required. Thus, small losses of α-methyl styrene from the process system, due to incomplete recovery of this material in the fractionation of the pyrolysis product, may be replenished by temporarily decreasing the proportion of α-methyl styrene in the reaction mixture to allow additional α-methyl styrene to form in the pyrolysis.

While we have indicated that the mixture charged to the pyrolysis zone should contain about 0.63 mole of α-methyl styrene per mole of isopropyl benzene for optimum yield of styrene, it is realized that exact control of the composition of this mixture is difficult to obtain and it should be understood that such control is not necessary to obtain substantially the full benefit of our invention. Thus, so long as a ratio of from about 0.60 to about 0.65 mole of α-methyl styrene to one mole of isopropyl benzene is maintained in the pyrolysis mixture the benefit of our invention will be obtained, and such operation is considered as coming within the scope of our invention.

The foregoing specification has described and disclosed the general and broad character of the invention and the example is sufficiently indicative of its value from a commercial standpoint. However, it should be understood that the invention is not limited in scope to the specific conditions and catalyst described or the experimental data given, but rather only as indicated in the appended claims.

We claim:

1. A process of manufacturing styrene comprising the steps of (1) reacting a mixture of benzene and propylene in an alkylation zone to form isopropyl benzene, (2) fractionating the product obtained to separate isopropyl benzene therefrom, (3) mixing the isopropyl benzene derived from step 2 with α-methyl styrene and additional isopropyl benzene obtained in the manner hereinafter defined to form a mixture having a ratio of 1 mol of isopropyl benzene to between .60 and .65 mol of α-methyl styrene, (4) diluting the mixture formed with from 2 to 5 times its volume of an inert diluent gas, (5) subjecting the diluted mixture obtained in step 3 to reaction in a pyrolysis zone at a temperature of from 600° C. to 800° C. and at a pressure of from 1 to 5 atmospheres to form styrene, (6) subjecting the product obtained in step 5 to fractional distillation to separate benzene, propylene, isopropyl benzene and α-methyl styrene therefrom, (7) returning the benzene and propylene obtained in step 6 to step 1, (8) returning the isopropyl benzene obtained in step 6 to step 3 as the additional isopropyl benzene in step 3, (9) returning the α-methyl styrene from step 6 to step 3 as at least the major portion of the α-methyl styrene in step 3, and (10) recovering the styrene formed in step 5.

2. A process for producing styrene comprising as principal steps, subjecting a mixture of benzene and propylene to reaction in an alkylation zone to form isopropyl benzene, fractionating the product obtained from said alkylating zone to separate benzene, propylene and isopropyl benzene, returning the benzene and propylene to the

alkylation zone, mixing the isopropyl benzene with an inert diluent gas, α-methyl styrene, and additional isopropyl benzene obtained in the manner hereinafter defined, subjecting the mixture thus formed to pyrolysis in a ceramic lined reactor to form styrene, fractionating the product obtained from said pyrolysis zone to separate propylene, benzene, styrene, isopropyl benzene and α-methyl styrene, returning the propylene and benzene thus obtained to the alkylation zone, returning the separated isopropyl benzene to the mixing step as the additional isopropyl benzene in said mixing step, returning the separated α-methyl styrene to the mixing step as the α-methyl styrene in said mixing step, controlling the proportions of isopropyl benzene and α-methyl styrene being admitted to said mixing step so that the mol ratio of α-methyl styrene to isopropyl benzene in said mixture is between .60 and .65, and recovering the styrene formed.

3. In a method of producing styrene by the pyrolysis of a mixture of isopropyl benzene and α-methyl styrene in which α-methyl styrene is produced by an undesirable side reaction and in which α-methyl styrene is recycled to the pyrolysis zone along with unreacted isopropyl benzene for the purpose of suppressing said undesirable side reaction, the step which comprises regulating the proportion of recycle α-methyl styrene to recycle isopropyl benzene plus fresh isopropyl benzene in the mixture subjected to pyrolysis so that the mol ratio of α-methyl styrene to isopropyl benzene in said mixture is from .60 to .65 whereby the side reaction which forms α-methyl styrene in said pyrolysis is substantially completely suppressed.

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