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[54] **PROCESS FOR ALKENYLATION OF ALKYLBENZENES**

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[51] **Int. Cl.** **C07c 3/52**

[58] **Field of Search** .... 260/668 B, 671 A

[56] **References Cited**

UNITED STATES PATENTS

3,766,288	10/1973	Shima et al.	260/668 B

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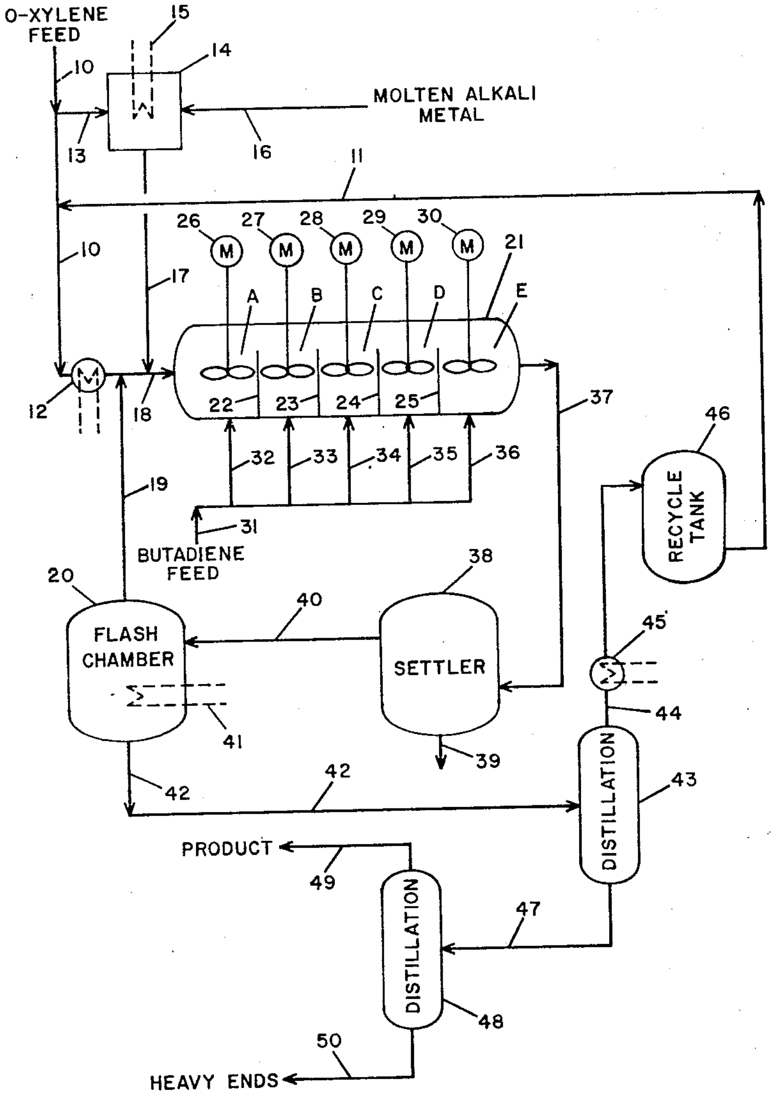
Attorney, Agent, or Firm—George L. Church; Donald R. Johnson; J. Edward Hess

[57] **ABSTRACT**

An improvement is disclosed in the alkenylation of alkylbenzenes with conjugated alkadienes in excess alkylbenzene to increase the yield of the mono-adduct product. The improvement involves an economical manner of substantially increasing the amount of alkylbenzene recycle without increasing the size of the distillation column normally used to separate the alkylbenzene from the mono-adduct in the reaction product. Since mono-adduct yield is directly proportional to the amount of excess alkylbenzene a significant yield increase is obtained without a significant increase in distillation column cost.

8 Claims, 1 Drawing Figure



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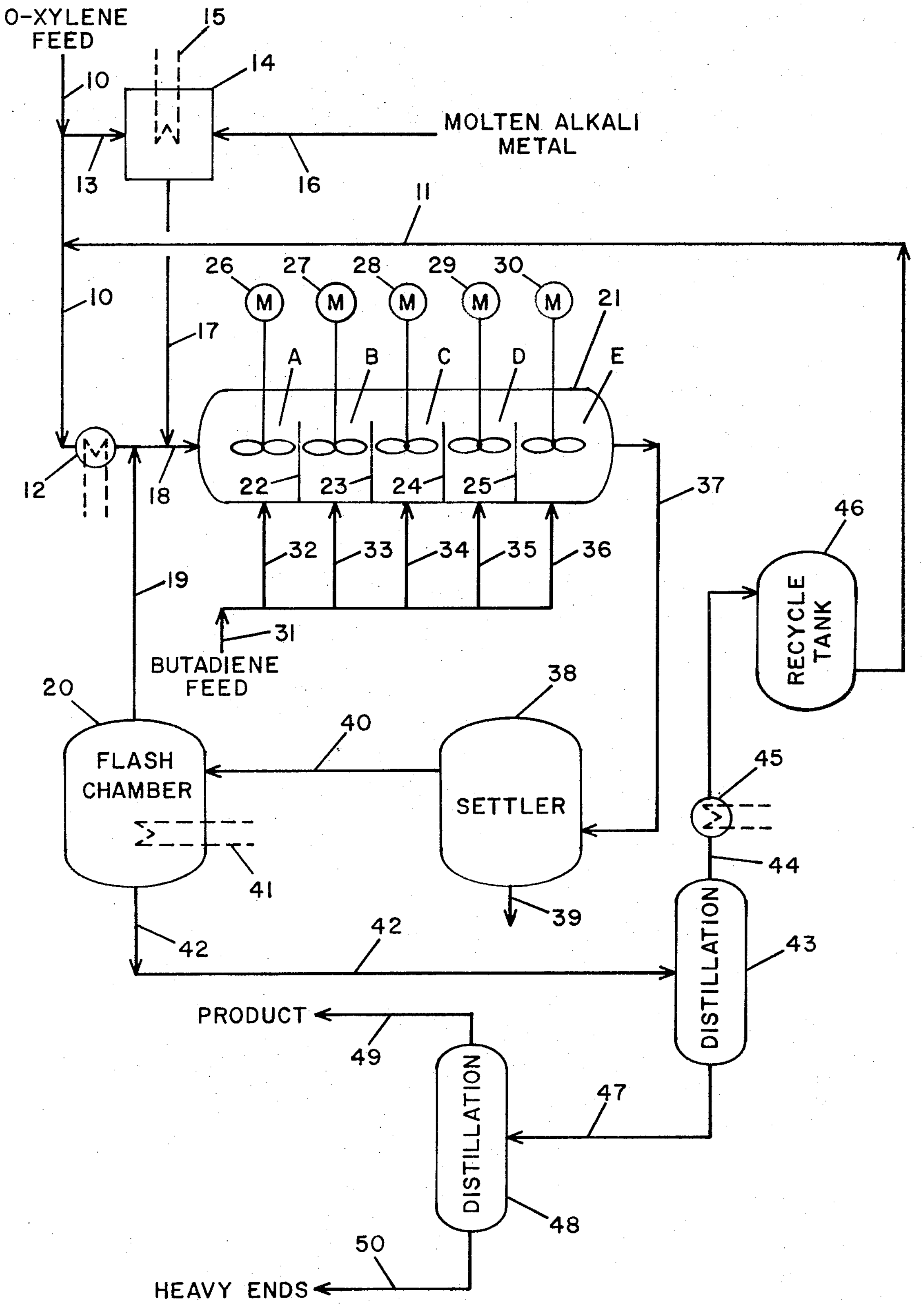


PROCESS FOR ALKENYLATION OF ALKYLBENZENES

BACKGROUND OF THE INVENTION

The alkenylation of alkylbenzenes can be used as a route for preparing various alkylnaphthalenes by following the alkenylation reaction with a ring closure step to form an alkyltetralin and then a dehydrogenation step to produce the corresponding alkylnaphthalene. For example, the reaction of butadiene with toluene gives 1-phenylpentene which upon ring closure forms 1-methyltetralin which can be dehydrogenated to 1-methylnaphthalene. Other examples of analogous conversions are 1,5-dimethylnaphthalene from o-xylene and 1,7-dimethylnaphthalene from p-xylene. These dimethylnaphthalenes can be isomerized, respectively, to the 2,6- and 2,7-isomers, as described by G. Suld et al., J. ORG. CHEM., 29, 2936–2946 (1964); and the 2,6- and 2,7-isomers can be oxidized to the corresponding diacids useful for making polyester resins, as disclosed in U.S. Pat. No. 3,293,223, issued Dec. 20, 1966, Irl N. Duling.

This invention relates to the catalyzed reactions of alkylbenzenes with conjugated alkadienes to produce the mono-adduct product, i.e. the one-to-one addition product of the alkylbenzene and diene.

The use of alkali metals for promoting the addition of alkadienes to alkylbenzenes is known in the prior art. This kind of reaction is shown for such reactants as toluene or xylene with butadiene or isoprene in the following U.S. Pat. Nos: 1,934,123 issued Nov. 7, 1933, F. Hofmann et al.; and 2,603,655, issued July 15, 1962, D. E. Strain. Such alkenylation reactions have also been described by R. E. Robertson et al., CAN. J. RES., 26B, 657–667 (1948). However the conditions disclosed in these references result in the production of large amounts of adducts of higher molecular weight than the mono-adduct product. These references fail to provide conditions under which the mono-adduct product could be obtained in high yield.

Conditions more favorable for securing good yields of the mono-adduct product in such alkenylation reactions have been described by G. G. Eberhardt et al. in J. ORG. CHEM., 30, 82–84 (1965) and in Eberhardt U.S. Pat. No. 3,244,758, issued Apr. 5, 1966. The conditions described in these references include utilizing a granular support on which the alkali metal is distended and slowly adding the conjugated diene to the alkyl aromatic reactant while vigorously agitating the mixture. While these conditions result in good yields of the mono-adduct, nevertheless substantial amounts of higher adducts are formed. For example, in the reaction of o-xylene with butadiene in the disclosed manner, the alkenylated product typically contains 80–85 percent by weight of mono-adduct (i.e. o-tolylpentene) with the remainder being mainly di-adducts.

The principal by-product formed is the di-adduct addition product formed by the combination of two alkadiene molecules with one alkylbenzene molecule, although even higher adducts are formed in small amounts.

One method of reducing by-product formation is to reduce the concentration of mono-adduct in the reaction zone. Since the amount of higher adducts formed is proportional to the concentration of mono-adduct in the reaction zone, procedures for reducing the mono-adduct concentration will reduce by-product formation and improve mono-adduct yield.

My copending application, Ser. No. 398,112, filed Sept. 18, 1973, and incorporated herein by reference, discloses a method for reducing the mono-adduct concentration which involves passing the alkylbenzene through a series of successive reaction zones substantially isolated from each other while adding alkadiene to each zone, the total diene:alkylbenzene mole ratio being less than 0.5:1.

In this system the average concentration of mono-adducts in the slurry for the serially arranged reaction zones is less than the mono-adduct concentration would be for a single stage reaction system. In the latter the final mono-adduct concentration is also the concentration always maintained in the reactor; whereas in a plurality of successive zones the final mono-adduct concentration is only that in the last zone and the average concentration thereof for all zones is considerably less. Since the amount of higher adducts formed is proportional to the concentration of mono-adducts in the reaction zone the use of a plurality of stages in the manner described substantially improves selectivity for the desired product.

My aforesaid copending application also discloses carrying out the alkenylation reaction in the presence of excess alkylbenzene. This also has the effect of reducing the mono-adduct concentration in the reaction zone and thereby, for the reasons mentioned previously, increasing mono-adduct yield.

When excess alkylbenzene is employed the reactor effluent is sent to a distillation column (after removal of any catalyst particles) and the excess alkylbenzene is separated from the adduct products. The latter are sent to another distillation column where pure mono-adduct is distilled. The separated excess alkylbenzene is recycled to the reaction zone.

Although alkylbenzene:alkadiene weight ratios of greater than, say, 20:1 are desired to maximize mono-adduct yield a distinct disadvantage arises at such a high ratio. This is because all the excess alkylbenzene must be distilled in the above-mentioned distillation column. A point is reached where the increase in column size resulting from an increase in the alkylbenzene:alkadiene ratio is not justified even though this increased ratio begets a significant increase in mono-adduct yield.

SUMMARY OF THE INVENTION

The invention provides a means for increasing the alkylbenzene:alkadiene ratio that can be employed in the alkenylation reaction without excessive costs. Stated in another manner the invention provides a means of increasing the maximum economical alkylbenzene recycle ratio in the alkenylation of alkylbenzenes with an alkadiene. The method involves reacting the alkadiene with excess alkylbenzene, which excess includes recycle alkylbenzene, and, at the end of the reaction, introducing the reaction mass into a flash chamber, flashing off some of the alkylbenzene for use as some of the recycle, introducing the remaining reaction mass into a distillation column to separate adduct product plus more alkylbenzene and utilizing the latter also as recycle.

The flash chamber is considerably cheaper than additional multiplate distillation capacity and functions just as well. As a result the distillation column for the same recycle ratio is smaller or, better yet, additional recycle can be achieved with the same distillation column.

BRIEF DESCRIPTION OF THE DRAWING

One embodiment of the invention is illustrated in the accompanying drawing which is a diagrammatic flowsheet of the process.

DESCRIPTION OF THE INVENTION

The alkylbenzene reactant for the present process can have one to four alkyl groups, and it should contain at least three benzylic non-tertiary hydrogen atoms per molecule. The term "benzylic hydrogen" refers to a hydrogen atom attached to a carbon atom which is directly attached to the benzene ring. Thus toluene or diethylbenzene meets the requirement of containing at least three benzylic nontertiary hydrogen atoms, but ethylbenzene does not. Triisopropylbenzene, while having three benzylic hydrogen atoms, also does not since they are tertiary hydrogen atoms. The size and configuration of the alkyl substituents on the benzene ring are immaterial as long as three or more benzylic hydrogen atoms which are non-tertiary are present. Generally the number of carbon atoms in each alkyl group will be in the range of 1–10 and usually 1–2.

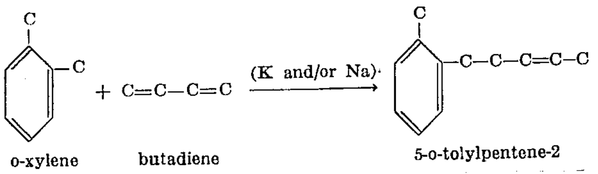
The following are illustrative examples of suitable alkylaromatics which can be alkenylated in an improved manner by means of the present process: toluene; o-, m- or p-xylene; mesitylene; pseudocumene; hemimellitene; durene; isodurene; prehnitene; methylethylbenzenes; cymenes; di-n-propylbenzenes; tri-n-hexylbenzenes; ethyldecylbenzenes; methyl-t-butylbenzenes; and the like.

The diene reaction is a C_4–C_5 conjugated alkadiene, viz. 1,3-butadiene, 1,3-pentadiene and isoprene.

Both reactants should be substantially free of water, sulfur compounds or other impurities, as otherwise excessive loss of deactivation of catalyst may occur. Water can conveniently be removed from the feed materials by treatment with a molecular sieve adsorbent.

Alkenylation of the alkylbenzene by reaction with the diene is preferably promoted by means of potassium, sodium or a potassium-sodium mixture but other catalysts known in the art may be employed. Preferably the alkali metal promoter is composed of a major proportion of sodium and a minor proportion of potassium on a weight basis, such as 75–98 parts sodium to 2–25 parts potassium. Normally only a small proportion of alkali metal to the alkylbenzene reactant is employed, such as 0.01–5.0 g. moles alkali metal per liter of alkylbenzene and preferably 0.1 to 1.0 g. and a minor proportion of potassium on a weight basis, such as 75–98 parts sodium to 2–25 parts potassium. Normally only a small proportion of alkali metal to the alkylbenzene reactant is employed, such as 0.01–5.0 g. moles alkali metal per liter of alkylbenzene and preferably 0.1 to 1.0 g. mole per liter. The catalyst is not considered to be the alkali metal per se but rather the metallo-organic product resulting from reaction of at least part of the alkali metal with the alkylbenzene. For instance, in the alkenylation of toluene employing potassium as promoter, the effective catalyst is believed to be the reaction product, benzyl potassium, which forms when a dispersion or slurry of molten potassium in heated toluene stands. Thus in order to obtain the catalyst, the alkali metal needs to be in contact with the alkylbenzene at a temperature above the melting point of the metal for enough time to permit substantial reaction. The respective melting points of K and Na are 62.3°C and 97.5°C but alloys of these metals exhibit lower melting points. For example, a 50:50 by weight mixture of the two has a melting point of 10°C. However, since the reaction between the metal and alkylbenzene is slow at low temperatures, it is advantageous to maintain the temperature of the dispersion at least above 50°C to form the metallo-organic catalyst. The latter is slightly soluble in the aromatic hydrocarbon but mainly will be present as a dispersed solid.

The accompanying drawing illustrates the improved method of alkenylating alkylbenzenes in accordance with the invention. For purpose of describing the process, the reactants are considered to be o-xylene and butadiene and the promoter. The desired reaction for producing the monoadduct product is illustrated by the following equation (hydrogen atoms being omitted for simplicity):



As shown, the desired product from these reactants is 5-o-tolypentene-2, which can be converted to 1,5-dimethyltetralin by treatment with an acid catalyst. During this reaction substantial amounts of higher adducts tend to form due to the reaction of more than one mole of butadiene per mole of o-xylene reacted. Reaction of the additional butadiene can occur in several ways to produce higher adducts of various structures. The present method minimizes the formation of these higher adducts by carrying out the alkenylation reaction in the presence of a large excess of o-xylene which is obtained by a much more economical procedure than heretofore employed. This excess results in substantially higher selectivity in conversion of the o-xylene to the desired mono-adduct than otherwise can be secured.

Referring now to the drawing, o-xylene feed in line **10** is mixed with recycled o-xylene from line **11** and then continues through line **10** to heater **12** wherein it is heated to the desired temperature. A minor proportion of the o-xylene is diverted through line **13** to a catalyst preparation tank **14** containing heater **15.** Molten alkali metal obtained from a source not shown is drawn through line **16** into catalyst preparation tank **14.** The latter is provided with a motorized stirrer not shown for effectively dispersing the alkali metal in the hydrocarbon. The temperature in tank **14** is usually held in the range of 50°–170°C, more preferably 90°–140°C, to facilitate reaction of the alkali metal and o-xylene and form the metallo-organic catalyst.

The alkali metal, can be potassium or sodium or any mixture or alloy of these two metals. The effective catalyst tends to form more readily when potassium is used than when sodium alone is employed and the selectivity for mono-adduct production appears to be somewhat better. However mixtures of sodium and potassium containing even as much as 95 percent or more sodium are about as effective as potassium alone. In view of the fact that sodium usually is less expensive than potassium it is distinctly preferred that the alkali metal utilized be composed of a major proportion of sodium and a minor proportion of potassium on a weight basis. Within the zone where the alkenylation reaction occurs, it is desirable to maintain the Na:K proportion within the range of 75:25 to 98:2 and a proportion of about 95:5 is preferred. At this weight proportion the loss of alkali metals from the system due to solubility of their derivatives in the hydrocarbon phase generally involves roughly twice as much sodium as potassium. Accordingly, about a two-to-one Na:K ratio needs to be maintained for the alkali metals added as makeup through line **16** in order to maintain the 95:5 preferred proportion in the system.

The proportion of alkali metal to alkylbenzene in catalyst preparation tank **14** is not critical and can vary widely. Generally from 5 to 20 parts by weight of the alkylbenzene per part of alkali metal are used in preforming the catalyst dispersion. The minimum residence time in tank **14** for forming the catalyst will vary with temperature, decreasing as higher temperatures are employed. Typically, for a temperature level of 110°C, a residence time of 0.5–2.0 hours is employed.

The catalyst dispersion flows from tank **14** through line **17** to line **18** where it meets the stream of o-xylene from heater **12**. Also meeting the stream of o-xylene from heater **12** in line **18** is o-xylene recycle in line **19** from flash chamber **20**. As will be explained hereafter this recycle is normally at about the boiling point of o-xylene (144°C) and will usually be vapor. In any event the heat input in heater **12** should be such that the o-xylene feed in line **10** plus the recycle in line **11**, both of which are usually well below the o-xylene boiling point, plus the line **19** recycle and line **17** catalyst addition, yield a total mixture at about 144°C at the inlet to reactor **21**.

The amount of o-xylene recycled should be such that the total o-xylene (i.e., recycle plus makeup) is at least 15 pounds per pound of total butadiene (i.e., line **31** butadiene). Normally this ratio will be at least 20:1, preferably at least 25:1. The data below show the improved mono-adduct yield (moles momo-adduct per mole of butadiene times 100) at different o-xylene ratios (pounds total o-xylene divided by pounds butadiene) at typical operating conditions. By employing my invention yields of at least 84 percent are obtained, usually at least 86–88 percent.

o-Xylene Ratio	Mono-adduct Yield
13	78%
15	80
18	84
20	86
24	88

If it is desired to express the o-xylene recycle in terms of makeup o-xylene then the weight ratio of total o-xylene recycled (lines **11** and **19**) to makeup or fresh o-xylene added will usually be 5:1, preferably at least 10:1 and more preferably is at least 15:1.

The rate of addition of dispersion from line **17** to the o-xylene stream in line **18** typically is such that the resulting slurry contains 0.01–5.0 gram moles of alkali metal (combined and uncombined) per liter of o-xylene, more preferably 0.05–1.0 gram mole per liter.

Reactor **21** is preferably divided into several independently stirred reaction zones. The number of such zones can vary, for example, from 2–10 but preferably is in the range of 3–6. As illustrated in the drawing, five independent zones, designated by A, B, C, D and E, are utilized. The zones are separated by baffles **22, 23, 24** and **25** each of which is somewhat spaced from the top of tank **21** to permit overflow of the reaction mixture to the next zone. The zones are provided with motorized stirrers **26, 27, 28, 29** and **30** and with individual spargers not shown at the bottom of each zone for independently admitting a continuous stream of butadiene from feed line **31** to each reaction zone via lines **32, 33,** 34, 35 and **36.**

Effective mixing conditions are maintained in each of zones A, B, C, D and E by the respective motorized mixers, and the butadiene is fed relatively slowly through the sparger provided in each zone. The butadiene in each zone is thus immediately dispersed into the slurry at a rate whereby a low concentration of the diene therein is maintained. Preferably each zone has about the same volumetric capacity and the rates of butadiene addition to the zones are approximately the same, although this is not essential. The amount of total diene to all five zones is preferably controlled so as to provide less than 0.5 mole diene per mole of o-xylene feed. Best results are usually obtained by holding this ratio in the range of 0.5–0.30 mole diene per mole of o-xylene fed through line **18** to reactor **21.** The slurry of catalyst in o-xylene passes from the inlet end of reactor **21** successively through the series of reaction zones, flowing over the baffles **22, 23, 24** and **25** from one zone to the next. The final slurry from reaction zone E passes out of reactor **21** via line **37.**

The reaction in reactor **21** is exothermic and, if necessary, reactor **21** can be provided with cooling coils or other heat removal means (not shown) to keep the temperature constant from inlet to outlet. The process can also be conducted, however, by introducing the slurry through line **18** at somewhat below the average desired temperature and allowing the temperature to rise above the average level as the mixture flows to outlet line **37.**

The above-described staged reactor system is the preferred manner of carrying out the present invention and is described and claimed in my aforesaid copending application. By using several independently stirred reaction zones with separate butadiene feed streams, as compared with a single reaction zone to which both reactants are fed continuously, permits a substantial increase in selectivity for mono-adduct production, i.e., this arrangement materially reduces the percentage of the reacted o-xylene that is converted to di-adducts and other higher adducts. On the other hand the staged reactor system is not essential to the success of the present invention and insofar as the latter is concerned it can be employed with either a one-stage or a multistage reactor. My aforesaid copending application shows the improved mono-adduct selectivity that can be achieved by staging. The data hereinabove show the improvement achieved by higher recycle ratios.

The reaction mixture next passes to settler **38** wherein the alkali metal, including that in the form of undissolved metallo-organic catalyst, is allowed to settle from the bulk of the hydrocarbon phase. The alkali metal solid material is removed from the settler **38** by line **39** and discarded. If desired the catalyst can be recycled by means not shown to catalyst preparation tank **14** for reuse but in most cases very small amounts of catalyst are employed and it will be more economical to discard the catalyst rather than recycle it. In some cases, depending on reactor **21** temperature, a cooler, not shown, will be employed in line **37** between reactor **21** exit and settler **38** but the reaction mixture is preferably not cooled much below the o-xylene boiling point.

From the upper part of settler **38** the hydrocarbon phase is withdrawn via line **40** and is sent to flash chamber **20,** which is equipped with heating means **41.** Flash chamber **20,** is in effect a single stage vaporizer as opposed to a distillation column which has many stages to achieve desired purities. However in one stage o-xylene recycle containing 90+% o-xylene can be obtained by heating the catalyst-free reaction product mixture to its boiling point by heating means **41.** The vapor exits the flash chamber through line **19** to meet o-xylene feed in line **18.**

The material entering the flash chamber will normally be at about the boiling point of o-xylene. Accordingly any heat supplied via means **41** will result in some o-xylene vaporization. On the other hand heat does not need to be the means by which o-xylene is separated in flash chamber **20.** For example the chamber could be maintained under vacuum so that as soon as reaction product entered it would vaporize in part.

It will now be apparent that the heat input in heater **12** will depend, inter alia, upon the temperature of the o-xylene in line **19.** In some cases a condenser may be employed in line **19** to condense the flash chamber vapors, depending on how flash chamber **20** is operated. This will also affect heater **12** input.

Normally the amount of o-xylene separated in flash chamber **20** will be at least 20 percent by weight of the total recycled o-xylene, i.e., line **11** plus line **19** o-xylene. Preferably the amount is at least 30 percent, more preferably at least 40 percent.

From the bottom of flash chamber **20** the unvaporized material is withdrawn through line **42** and sent to fractional distillation tower **43.** The unreacted o-xylene is removed overhead via line **44,** cooled in condenser **45** and passes to recycle tank **46.** The recovered o-xylene is recycled for reuse through line **11.** The relatively pure mono-adduct bottoms from tower **43** pass through line **47** to a second distillation column **48** from which the desired mono-adduct product is recovered via overhead line **49.** The higher adduct material, obtained in minor proportion as bottoms through line **50,** is composed principally of di-adduct with lesser amounts of tri-adduct and higher material.

The following are specific examples of the process of the invention compared with a process which does not utilize my improvement.

In a conventional manner, not employing a flash chamber, 167 parts of o-xylene per unit time are fed to the system (line **10**). Fresh o-xylene at this rate admixes with 1,500 parts of recycled o-xylene from line **11** and most of the mixture passes through heater **12,** where the temperature is raised to 145°C, and then to reactor tank **21.** About 6 parts of the 167 parts of o-xylene are diverted through line **13** and heated to 100°–115°C in tank **14** and are mixed in tank **14** with 0.7 parts sodium and 0.3 parts potassium. After an average residence time of about one hour in tank **14,** the resulting catalyst dispersion flows through line **17** to reactor **21.** 100 parts butadiene (line **31**) is added to the reactor. The latter preferably is provided with cooling means to prevent the temperature from rising above 145°–150°C as the reaction occurs and also preferably is of a size such that the total residence time in the tank is 2–3 hours. The slurry leaving reactor **21** through line **37** (1,770 parts excluding catalyst) passes through settler **38** whereby the alkali metal components are separated from the bulk of the hydrocarbon phase. The hydrocarbon phase (1,767 parts) is sent directly to distillation column **43** (bypassing flash chamber **20**) in which 1,500 parts of o-xylene are recovered for recycling. The bottoms from column **43** are distilled in column **48** to yield an overhead product containing 245 parts mono-adduct.

The above example is repeated except that flash chamber **20** is employed. The fresh o-xylene feed is the same, 167 parts. The line **11** recycle is 1,500 parts and line **19** recycle is 833 parts making a total feed to reactor **21** of 2,500 parts. 100 pounds of butadiene are added and 2600 parts reaction product (excluding catalyst) are removed through line **37** and ultimately enter flash chamber **20** at a temperature of about 144°C. Heat is supplied via heater **41** to vaporize 833 parts o-xylene enters line **18** via line **19.** The balance of 1,767 parts is distilled in distillation columns **43** and **48** as in the first example with **271** parts of mono-adduct being recovered overhead in line **49.**

It is apparent from the above that increased o-xylene recycle has been achieved by means of the flash chamber. The total o-xylene to butadiene ratio being 16.7:1 and 25:1 in the first and second examples respectively. In both examples, however, the amount of material delivered to distillation column **42** is the same. The yield improvement from the higher recycle ratio is evident.

Analogous results can be obtained in the alkenylation of other alkylbenzenes by conjugated diolefins by the procedure of the invention. Other particularly useful alkenylations are the reaction of toluene with butadiene to given phenylpentene and the reaction of other xylenes with butadiene to yield other tolylpentenes, via m-tolylpentene-2 from m-xylene or p-tolylpentene-2 from p-xylene.

The invention claimed is:

1. In a process in which an alkadiene is reacted with excess alkylbenzene including recycle alkylbenzene hereinafter specified to form a reaction mass containing the mono-adduct alkadiene-alkylbenzene addition product, the reaction mass is fractionated in a distillation column to separate a relatively pure mono-adduct and alkylbenzene, the latter being employed as said recycle, the improvement which comprises:

a. introducing the reaction mass to a flash chamber to separate a portion of the alkylbenzene therein;

b. fractionating the remaining reaction mass in said distillation column to separate relatively pure monoadduct and additional alkylbenzene;

c. and employing alkylbenzene separated in both the flash chamber and the distillation column as said recycle.

2. Method according to claim **1** wherein said alkylbenzene is o-xylene and said alkadiene is butadiene.

3. Method according to claim **2** wherein the ratio of total o-xylene to butadiene is at least 25 to 1 by weight.

4. Method according to claim **2** wherein at least 20 weight percent of the recycled o-xylene is separated in the flash chamber.

5. Method according to claim **2** wherein the yield of mono-adduct product is over 84 percent by weight based on butadiene.

6. Method which comprises:

a. reacting butadiene with excess o-xylene, including recycle o-xylene from step (f), in a reaction zone to form reaction product containing 5-o-tolylpentene-2;
b. removing reaction product from the reaction zone and introducing same into a flash chamber;
c. separating in the flash chamber a portion of the o-xylene in the reaction product;
d. introducing remaining material into a distillation zone;
e. separating additional o-xylene in the distillation zone to produce relatively pure 5-o-tolylpentene-2;
f. utilizing o-xylene separated in (c) and (e) as said recycle.

7. Method according to claim **6** wherein the ratio of total o-xylene to butadiene is at least 25 to 1 by weight.

8. Method according to claim **6** wherein at least 20 percent of the recycled o-xylene is separated in the flash chamber.

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