CONTINUOUS PROCESS FOR PREPARING ETHYLBENZENE USING LIQUID PHASE ALKYLATION AND VAPOR PHASE TRANSALKYLATION

The present invention relates to a process for preparing ethylbenzene using liquid phase alkylation and vapor phase transalkylation.

Ethylbenzene is a valuable commodity chemical which is currently used on a large scale industrially for the production of styrene monomer. Ethylbenzene may be produced by a number of different chemical processes but one process which has achieved a significant degree of commercial success is the vapor phase alkylation of benzene with ethylene in the presence of a solid, acidic ZSM-5 zeolite catalyst. In the production of ethylbenzene by this process, ethylene is used as the alkylating agent and is reacted with benzene in the presence of the catalyst at temperatures which vary between the critical temperature of benzene up to 900°F (480°C) at the reactor inlet. The reactor bed temperature may be as much as 150°F (65°C) above the reactor inlet temperature and typical temperatures for the benzene/ ethylene reaction vary from 600° to 900°F (315° to 480°C), but are usually maintained above 700°F (370°C) in order to keep the content of the more highly alkylated benzenes such as diethylbenzene at an acceptably low level. Pressures typically vary from atmospheric to 3000 psig (20785 kPa abs) with a molar ratio of benzene to ethylene from 1:1 to 25:1, usually 5:1 (benzene:ethylene). Space velocity in the reaction is high, usually in the range of 1 to 6, typically 2 to 5, WHSV based on the ethylene flow, with the benzene space velocity varying accordingly, in proportion to the ratio of the reactants. The products of the reaction include ethylbenzene which is obtained in increasing proportions as temperature increases together with various polyethylbenzenes, principally diethylbenzene (DIEB) which also are produced in increasing amounts as reaction temperature increases. Under favorable operating conditions on the industrial scale, an ethylene conversion

in excess of 99.8 weight percent may be obtained at the start of the cycle.

In the commercial operation of this process, the polyalkylated benzenes, including both polymethylated and polyethylated benzenes are recycled to the alkylation reactor in which the reaction between the benzene and the ethylene takes place. By recycling the by-products to the alkylation reaction, increased conversion is obtained as the polyethylated benzenes (PEB) are converted to ethylbenzene (EB). In addition, the presence of the PEB during the alkylation reaction reduces formation of these species through equilibration of the components because at a given feed composition and under specific operating conditions, the PEB recycle will reach equilibrium at a certain level. This commercial process is known as the Mobil/Badger process and is described in more detail in an article by Francis G. Dwyer, entitled "Mobil/Badger Ethylbenzene Process-Chemistry and Catalytic Implications", appearing on pages 39-50 of a book entitled Catalysis of Organic Reactions, edited by William R. Moser, Marcel Dekker, Inc., 1981.

Ethylbenzene production processes are described in U.S. Patents Nos. 3,751,504; 4,547,605; and 4,016,218. The process described in U.S. 3,751,504 is of particular note since it includes a separate transalkylation step in the recycle loop which is effective for converting a significant proportion of the more highly alkylated products to the desired ethylbenzene product. Other processes for the production of ethylbenzene are disclosed in U. S. Patents Nos. 4,169,111 and 4,459,426, in both of which a preference for large-pore size zeolites such as zeolite Y is expressed, in distinction to the intermediate-pore size zeolites used in the processes described in U.S. Patent Nos 3,751,504; 4,547,605; and 4,016,218. U.S. Patent No. 3,755,483 describes a process for the production of ethylbenzene using zeolite ZSM-12 as the alkylation catalyst.

Ethylbenzene (EB) can be synthesized from benzene and ethylene (C_2=) over a variety of zeolitic catalysts in either the liquid phase or in the vapor phase. An advantage of a liquid phase process is its low operating temperature and the resulting low content of by-products.

U.S. Patent No. 4,891,458 describes the liquid phase synthesis of ethylbenzene with zeolite Beta.

U.S. Patent No. 5,149,894 describes the liquid phase synthesis of ethylbenzene with a crystalline aluminosilicate material designated SSZ-25.

U.S. Patent No. 5,334,795 describes the liquid phase synthesis of ethylbenzene with a crystalline aluminosilicate material designated MCM-22.

Current commercial processes for preparing ethylbenzene (EB) conduct both alkylation and transalkylation steps in the same phase, i.e., either both steps in the vapor phase or both steps in the liquid phase. In the vapor phase commercial process, higher temperatures are required to maintain vapor phase conditions. At the temperatures employed in these vapor phase conditions, considerable quantities of xylene impurities are formed. Since the boiling point for xylenes is very close to the boiling point for ethylbenzene, the ethylbenzene product from such an all vapor phase process exceeds 700 ppm of xylene impurities. Eariler versions of the previously mentioned Mobil/Badger process may produce an ethylbenzene product having 1200-1600 ppm of xylene impurities. These xylene impurities, which coboil with ethylbenzene, may contaminate downstream products derived from ethylbenzene, such as styrene and polystyrene.

The lower operating temperature required for the all liquid phase process produces less than 100 ppm xylene byproducts, but it has now been discovered that certain feed impurities in the form of benzene coboilers, when present in the benzene feed, will tend to accumulate in the all liquid phase system over time. It has further been discovered that certain alkylation byproducts, particularly

C_3-benzenes and C_4-benzenes, tend to accumulate over time in the all liquid phase system.

Less expensive sources of benzene, which are practicable for use as fresh feedstocks to the present process, have considerable levels of impurities. These impurities are difficult to separate from benzene by distillation, because they have boiling points close to the boiling point of benzene. These difficultly separable impurities are referred to herein as benzene coboilers. These benzene coboilers include hydrocarbons having from 5 to 7 carbon atoms. These hydrocarbon impurities include cycloaliphatic, paraffinic, olefinic and aromatic compounds. Particularly problematic benzene coboilers include cyclohexane and methylcyclopentane. Toluene is another particular example of a benzene coboiler which may be present. Altogether, these benzene coboilers may be present in 500-700 ppm levels in benzene sources suitable for use as fresh feeds to the present process.

These benzene coboilers are largely inert under the lower temperature liquid phase conditions. Expensive separation procedures are required to satisfactorily remove these coboilers from benzene. However, if these coboilers are not removed, they will build up in the system, because as benzene is reacted in the system it must be replaced by fresh feed and each introduction of fresh feed introduces more inert benzene coboilers to the all liquid phase system.

In addition to the problem of benzene coboiler build-up caused by continuous introduction of these impurities along with fresh benzene feed, a net production of such coboilers can be realized in the all liquid phase process as a result of ethylene oligomerization reactions in the liquid phase alkylation reactor. More particularly, ethylene may trimerize to form hexene, which, in turn may undergo cyclization reactions to form cyclohexane and/or methylcyclopentane. Ethylene oligomerization reactions in the alkylation reactor can also be the root cause of the generation of other problematic impurities in the all

liquid phase system. These impurities comprise C_9 and C_{10} aromatics, especially propylbenzene and butylbenzene. Butylbenzene may be formed in the alkylation reactor when ethylene first dimerizes to form butene, which, in turn, alkylates benzene. Each ethylene trimer (i.e., hexene) can also exist in an equilibrium state with 2 molecules of propylene, which, in turn, can also alkylate benzene to form propylbenzene.

The C_9 and C_{10} aromatic impurities tend to build-up primarily in the polyethylbenzene recycle loop to the transalkylation reactor of the all liquid phase system. However, when these impurities are generated in sufficient levels they can permeate the entire system. In the all liquid phase system, the primary route for removal of the C_9 and C_{10} aromatic impurities is by further alkylation or transalkylation with ethyl groups, followed by rejection from the system as heavies. These side reactions result in a net consumption of ethylene and can reduce overall liquid yields by up to 2%.

As a result of the build-up of impurities in the all liquid phase system, these impurities tend to be carried over into the recovered ethylbenzene product. More particularly, in a typical all liquid phase system, the ethylbenzene product obtained from the all liquid phase system may contain 600 ppm of benzene coboilers and 800 ppm of C_9 and C_{10} aromatics.

All vapor phase processes, such as the Mobil/Badger process, produce an ethylbenzene product which contains little or no (e.g., less than 50 ppm) benzene coboilers and C_9 and C_{10} aromatics. Under the high temperature operating conditions of the all vapor phase process, benzene coboilers and C_9 and C_{10} aromatics are cracked and rejected as lights. However, as mentioned previously, the ethylbenzene product from the all vapor phase system will contain at least 700 ppm of xylene impurities. In summary, a typical ethylbenzene product from an all vapor phase system will contain at least 700 ppm xylene, no benzene coboilers and no C_9 and C_{10} aromatics, whereas a typical

ethylbenzene product from an all liquid phase system will contain at less than 100 ppm xylene, 600 ppm benzene coboilers and 800 ppm C_9 and C_{10} aromatics.

The present invention involves a liquid phase alkylation step coupled with a vapor phase transalkylation step. The present liquid phase alkylation/vapor phase transalkylation system achieves low levels of all of the above-mentioned impurities (i.e., xylene, benzene coboilers and C_9 and C_{10} aromatics) in the ethylbenzene product without the need for prohibitively expensive separation schemes. The separators employed in the present system may be comparable in scale to those employed in the Mobil/Badger all vapor phase system.

The present invention resides in a process for preparing ethylbenzene, said process comprising the steps of:

(a) contacting benzene and ethylene with a solid oxide catalyst in a liquid phase alkylation reaction zone under sufficient liquid phase conditions to generate ethylbenzene product and byproducts comprising diethylbenzene; and

(b) contacting said diethylbenzene byproduct from step (a) and benzene with a solid oxide catalyst in a vapor phase transalkylation reaction zone under sufficient vapor phase conditions to generate an effluent comprising another ethylbenzene product,

wherein benzene feed which is introduced into said vapor phase transalkylation zone of step (b) comprises nonbenzene hydrocarbons having from 5 to 7 carbon atoms, and wherein said nonbenzene hydrocarbons having from 5 to 7 carbon atoms are converted to hydrocarbons having a different boiling point in said transalkylation zone, and wherein unreacted benzene is recycled in said alkylation zone and in said transalkylation zone.

In particular, this process may be a continuous process for preparing ethylbenzene, said process comprising the steps of:

(a) introducing benzene, benzene coboilers, and ethylene into a liquid phase alkylation reaction zone,

wherein said benzene and said ethylene are reacted in the presence of an alkylation catalyst under sufficient liquid phase conditions to generate an effluent comprising ethylbenzene product, unreacted benzene, unreacted benzene coboilers, and byproducts comprising diethylbenzene and butylbenzene, said alkylation catalyst comprising an acidic solid oxide selected from the group consisting of MCM-22, MCM-49 and MCM-56;

(b) passing the effluent from said liquid phase alkylation reaction zone of step (a) to a separation zone, wherein said effluent is separated into separate streams comprising (i) a light stream comprising benzene and benzene coboilers, (ii) an intermediate product stream, and (iii) a heavy stream comprising diethylbenzene and butylbenzene;

(c) passing said heavy stream (iii) from step (b) along with benzene and benzene coboilers to a vapor phase transalkylation reaction zone, wherein said benzene and diethylbenzene are reacted in the presence of a transalkylation catalyst under sufficient vapor phase conditions to generate an effluent comprising another ethylbenzene product and unreacted benzene, said transalkylation catalyst comprising a medium-pore size zeolite;

(d) passing the effluent from said vapor phase transalkylation reaction zone to the separation zone of step (b), wherein said effluent is separated into separate streams comprising (i) a light stream comprising unreacted benzene, (ii) an intermediate product stream, and (iii) a heavy stream comprising unreacted diethylbenzene;

(e) recycling unreacted benzene along with benzene coboilers recovered in separation steps (b) and (d) in a closed recycle loop to said alkylation reactor of step (a) and to said transalkylation reactor of step (c);

(f) introducing fresh benzene feed into said benzene recycle loop at a rate sufficient to make up for benzene converted in said alkylation zone and in said transalkylation zone, wherein said fresh benzene comprises

impurities comprising benzene coboiling nonbenzene hydrocarbons having from 5 to 7 carbon atoms, said benzene coboiling hydrocarbons being at least partially converted to hydrocarbons having a different boiling point in said transalkylation zone of step (c), and butylbenzene being at least partially converted to one or more different hydrocarbons in said transalkylation zone of step (c); and

(g) recovering an ethylbenzene product from the intermediate product stream of steps (b) and (d), the recovered ethylbenzene product comprising less than 200 ppm xylene, less than 100 ppm of hydrocarbons having 7 or less carbon atoms and less than 100 ppm of hydrocarbons having 9 or more carbon atoms.

In the present liquid-vapor phase process, alkylation takes place at low temperatures in the liquid phase, thereby generating little or no xylene. In the vapor phase transalkylation reaction, propylbenzene, butylbenzene and benzene coboilers are converted to hydrocarbons having different boiling points by a variety of reactions, including cracking, dealkylation, alkylation (e.g., with cracked fragments), and transalkylation. Benzene generated by these reactions is recycled, whereas other conversion products are rejected from the system as lights or heavies. Only a small amount of xylene is produced in the transalkylation reaction.

The recovered ethylbenzene product from the present system may have less than 200 ppm xylene, less than 100 ppm of hydrocarbons having 7 or less carbon atoms and less than 100 ppm of hydrocarbons having 9 or more carbon atoms.

The fresh benzene feed for the present system may contain considerable amounts of impurities in the form of benzene coboilers. More particularly, elemental analysis of the benzene feed may reveal the presence of at least 500 ppm of nonbenzene hydrocarbons having from 5 to 7 carbon atoms.

The present alkylation and transalkylation reaction take place in separate zones. Each of these zones may comprise a single reactor or more than one reactor

connected in series. Preferably, these zones are each encompassed within a single alkylation reactor and a single transalkylation reactor.

The catalyst used in the present process comprises at least one acidic solid oxide. Examples of such acidic solid oxides include aluminosilicates and materials, such as SAPO's, which contain oxides of elements other than silicon and aluminum. These acidic solid oxides may be amorphous or crystalline materials. The crystalline materials may have non-layered, 3-dimensional framework structures, or layered structures, such as the layered structures of clays. Preferred acidic solid oxides are zeolites, particularly medium-pore size and large-pore size zeolites.

The catalyst for the present liquid phase alkylation reaction may comprise a medium- or large-pore size zeolite. Particular examples of acidic solid oxides which may be use to catalyze the alkylation reaction include MCM-22, MCM-36, MCM-49, MCM-56, zeolite Beta, zeolite X, zeolite Y, and mordenite. Of these crystalline materials, MCM-22, MCM-49 and MCM-56 are particularly preferred.

The catalyst for the present vapor phase transalkylation reaction may comprise a medium- or large-pore size zeolite. Particular examples of acidic solid oxides which may be use to catalyze the transalkylation reaction include MCM-22, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48 and ZSM-50. Of these crystalline materials, ZSM-5 is particularly preferred.

A convenient measure of the extent to which a zeolite provides control of access to molecules of varying sizes to its internal structure is the Constraint Index of the zeolite. Zeolites which provide a highly restricted access to and egress from its internal structure have a high value for the Constraint Index, and zeolites of this kind usually have pores of small size, e.g., less than 5 Angstroms. On the other hand, zeolites which provide relatively free access to the internal zeolite structure have a low value for the Constraint Index, and usually pores of large size,

e.g., greater than 8 Angstroms. The method by which Constraint Index is determined is described fully in U.S. Patent No. 4,016,218.

A zeolite which may be used in the present reaction may be a medium- or large-pore size zeolite. This zeolite may have a Constraint Index of 12 or less. Zeolites having a Constraint Index of 2-12 are generally regarded to be medium-pore size zeolites. Zeolites having a Constraint Index of less than 1 are generally regarded to be large-pore size zeolites. Zeolites having a Constraint Index of 1-2 may be regarded as either medium- or large-pore size zeolites.

Examples of zeolites having a Constraint Index of from 1 to 12 include ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-38, and ZSM-48.

ZSM-5 is described in U.S. Patent Nos. 3,702,886 and Re. 29,948. ZSM-11 is described in U.S. Patent No. 3,709,979. ZSM-12 is described in U.S. Patent No. 3,832,449. ZSM-22 is described in U.S. Patent No. 4,556,477. ZSM-23 is described in U.S. Patent No. 4,076,842. ZSM-35 is described in U.S. Patent No. 4,016,245. ZSM-38 is described in U.S. Patent No. 4,406,859. ZSM-48 is described in U.S. Patent No. 4,234,231.

The large-pore zeolites, including those zeolites having a Constraint Index less than 2, are well known to the art and have a pore size sufficiently large to admit the vast majority of components normally found in a feed chargestock. The zeolites are generally stated to have a pore size in excess of 7 Angstroms and are represented by zeolites having the structure of, e.g., Zeolite Beta, Zeolite Y, Ultrastable Y (USY), Dealuminized Y (Deal Y), Mordenite, ZSM-3, ZSM-4, ZSM-18, and ZSM-20. A crystalline silicate zeolite well known in the art and useful in the present invention is faujasite. The ZSM-20 zeolite resembles faujasite in certain aspects of structure, but has a notably higher silica/alumina ratio than faujasite, as does Deal Y.

Zeolite ZSM-14 is described in U.S. Patent No. 3,923,636. Zeolite ZSM-20 is described in U.S. Patent No. 3,972,983. Zeolite Beta is described in U.S. Patent Nos. 3,308,069 and Re. No. 28,341. Low sodium Ultrastable Y molecular sieve (USY) is described in U.S. Patent Nos. 3,293,192 and 3,449,070. Dealuminized Y zeolite (Deal Y) may be prepared by the method found in U.S. Patent No. 3,442,795. Zeolite UHP-Y is described in U.S. Patent No. 4,401,556.

A particular acidic solid oxide, which may be use to catalyze either the present liquid phase alkylation reaction or the present vapor phase transalkylation reaction, is MCM-36. MCM-36 is a pillared layered material having zeolitic layers. For the purposes of the present disclosure, MCM-36 shall be considered to be a zeolite. MCM-36 is described in U.S. Patent Nos. 5,250,277 and 5,292,698. U.S. Patent No. 5,258,565 describes the synthesis of alkylaromatics, including ethylbenzene, using a catalyst comprising MCM-36.

As mentioned hereinabove, MCM-22, MCM-49 and MCM-56 are particularly preferred acidic solid oxides for catalyzing the present liquid phase alkylation reaction. These crystalline oxides may also be used to catalyze the present vapor phase transalkylation reaction. MCM-22 and its use to catalyze the synthesis of alkylaromatics, including ethylbenzene, is described in U.S. Patent Nos. 4,992,606; 5,077,445; and 5,334,795. MCM-49 is described in U.S. Patent No. 5,236,575. The use of MCM-49 to catalyze the synthesis of alkylaromatics, including ethylbenzene, is described in U.S. Patent No. 5,371,310. MCM-56 is described in U.S. Patent No. 5,362,697. The use of MCM-56 to catalyze the synthesis of alkylaromatics, including ethylbenzene, is described in U.S. Patent No. 5,453,554. MCM-56 is believed to be a layered material with zeolitic layers. For the purposes of the present disclosure, MCM-56 shall be considered to be a zeolite.

The acidic solid oxide crystals can be shaped into a wide variety of particle sizes. Generally speaking, the

particles can be in the form of a powder, a granule, or a molded product such as an extrudate having a particle size sufficient to pass through a 2 mesh (Tyler) screen and be retained on a 400 mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion, the crystals can be extruded before drying or partially dried and then extruded.

The crystalline material may be composited with another material which is resistant to the temperatures and other conditions employed in the process of this invention. Such materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays and/or oxides such as alumina, silica, silica-alumina, zirconia, titania, magnesia or mixtures of these and other oxides. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels including mixtures of silica and metal oxides. Clays may also be included with the oxide type binders to modify the mechanical properties of the catalyst or to assist in its manufacture. Use of a material in conjunction with the solid crystal, i.e., combined therewith or present during its synthesis, which itself is catalytically active may change the conversion and/or selectivity of the catalyst. Inactive materials suitably serve as diluents to control the amount of conversion so that products can be obtained economically and orderly without employing other means for controlling the rate of reaction. These materials may be incorporated into naturally occurring clays, e.g., bentonite and kaolin, to improve the crush strength of the catalyst under commercial operating conditions and function as binders or matrices for the catalyst. The relative proportions of finely divided crystalline material and inorganic oxide matrix vary widely, with the crystal content ranging from 1 to 90 percent by weight and more usually, particularly when the composite is prepared in the form of beads, in the range of 2 to 80 weight percent of the composite.

The alkylation reaction is carried out in the liquid phase. Suitable conditions can be selected by reference to the phase diagram for benzene.

In the liquid phase, the reaction is carried out with the benzene feedstock in the liquid phase with the reaction conditions (temperature, pressure) appropriate to this end.

Liquid phase operation may be carried out at temperatures between 300° and 552°F (150° to 289°C), usually in the range of 400° to 500°F (205° to 260°C).

Pressures during the alkylation step may be as high as 3000 psig, (20875 kPa abs) and generally will not exceed 1000 psig (7000 kPa). The reaction may be carried out in the absence of hydrogen and accordingly the prevailing pressures are those of the reactant species. In a high pressure liquid phase operation, the temperature may be from 300° to 552°F (149°C to 289°C) with the pressure in the range of 2800 to 5600 kPa (400 to 800 psig). The space velocity may be from 0.1 to 20 WHSV, based on the ethylene feed, although lower space velocities are preferred for the liquid phase reaction, for example, from 0.5 to 3 WHSV, e.g., from 0.75 to 2.0 WHSV (ethylene). The ratio of the benzene to the ethylene in the alkylation reactor may be from 1:1 to 30:1 molar, normally 5:1 to 20:1 and in most cases from 5:1 to 10:1 molar.

The alkylation process can be carried out as a continuous operation utilizing a fixed, fluidized or moving bed catalyst system.

Particular conditions for carrying out the liquid phase alkylation step may include a temperature of from 150°C to 260°C, a pressure of 7000 kPa or less, a WHSV based on ethylene of from 0.5 to 2.0 hr^{-1}, and a mole ratio of benzene to ethylene of from 1:1 to 30:1.

The vapor phase transalkylation step may be carried out at a temperature of from 260°C to 482°C, a pressure of from 450 to 3500 kPa (50 to 500 psig), a WHSV based on the weight of the total vapor feed to the reaction zone of from 1 to 50 hr^{-1}, and a mole ratio of benzene to diethylbenzene of from 1 to 50.

The benzene feed to the transalkylation reactor may comprise at least 100 ppm, e.g., at least 200 ppm, of benzene coboilers, especially in the form of nonbenzene hydrocarbons having from 5 to 7 carbon atoms per molecule.

In the present vapor phase transalkylation step, ethylbenzene is believed to be produced by an actual transalkylation reaction involving both benzene and polyethylbenzenes (e.g., diethylbenzene) as reactants. However, it is also possible that at least some ethylbenzene is generated by straight dealkylation of polyethylbenzenes during this step.

When conducting alkylation, various types of reactors can be used. Large scale industrial processes may employ a fixed-bed reactor operating in an upflow or downflow mode or a moving-bed reactor operating with concurrent or countercurrent catalyst and hydrocarbon flows. These reactors may contain a single catalyst bed or multiple beds and may be equipped for the interstage addition of ethylene and interstage cooling. Interstage ethylene addition and more nearly isothermal operation enhance product quality and catalyst life. A moving-bed reactor makes possible the continuous removal of spent catalyst for regeneration and replacement by fresh or regenerated catalysts.

In a particular embodiment of the present invention, the alkylation process is carried out with addition of ethylene in at least two stages. Preferably, there will be two or more catalyst beds or reactors in series, wherein at least a portion of the ethylene is added between the catalyst beds or reactors. Interstage cooling can be accomplished by the use of a cooling coil or heat exchanger. Alternatively, interstage cooling can be effected by staged addition of the benzene feedstock in at least two stages. In this instance, at least a portion of the benzene feedstock is added between the catalyst beds or reactors, in similar fashion to the staged addition of ethylene described above. The staged addition of benzene feedstock provides additional cooling to compensate for the heat of reaction.

In a fixed-bed reactor or moving-bed reactor, alkylation is completed in a relatively short reaction zone following the introduction of ethylene. Ten to thirty percent of the reacting benzene molecules may be alkylated more than once. Transalkylation is a slower reaction which occurs in the alkylation zone. If transalkylation proceeds to equilibrium, better than 90 wt.% selectivity to monoalkylated product is generally achieved. Thus, transalkylation increases the yield of monoalkylated product by reacting the polyalkylated products with additional benzene.

The alkylation reactor effluent contains the excess benzene feed, monoalkylated product, polyalkylated products, and various impurities. The benzene feed is recovered by distillation and recycled to the alkylation and transalkylation reactors. A small bleed may be taken from the recycle stream if needed to eliminate unreactive impurities from the loop. However, since benzene coboilers are eliminated via the present vapor phase transalkylation step, this bleeding process is substantially less needed than in an all liquid phase alkylation/transalkylation process. Since little or no benzene needs to be bled out of the present benzene recycle loop, benzene can be essentially recycled to extinction in the present process.

The percentage of ethylene converted in the liquid phase alkylation step may be at least 95%, e.g., at least 97%. The weight ratio of ethylbenzene to diethylbenzene produced in the liquid phase alkylation step may be from 2 to 30.

When MCM-22, MCM-49 or MCM-56 is chosen as the acidic solid oxide to catalyze the present liquid phase alkylation reaction, the reaction is highly selective for the production of ethylbenzene. More particularly, this alkylation product may comprise at least 92 wt% of ethylbenzene, with less than 7 wt% of diethylbenzene and less than 1 wt%, e.g., less than 0.5 wt%, of triethylbenzene. In the present liquid phase alkylation step, MCM-22, MCM-49 and MCM-56 are believed to be

substantially more active than zeolite Y. Therefore, the MCM-22, MCM-49 or MCM-56 catalyzed reaction requires less catalyst and a smaller alkylation reactor for a given level of throughput than a zeolite Y catalyzed reaction. Furthermore, at the end of a reaction cycle, the catalyst containing MCM-22, MCM-49 or MCM-56 can be regenerated in situ in the alkylation reactor, whereas other catalysts may require removal from the reactor for regeneration, due to the large catalyst inventory and possible local overheat during the regeneration process.

The medium-pore size zeolites, especially ZSM-5, used in the present vapor phase transalkylation step, are more shape selective than large-pore size zeolites, such as USY, used as catalysts for liquid phase transalkylations. Consequently, the present vapor phase transalkylation step, catalyzed by medium-pore size zeolites, produces less heavies (e.g., C_{11}+ hydrocarbons) than liquid phase transalkylations catalyzed with large-pore size zeolites.

The present liquid-vapor phase reaction system may comprise one or more separation zones situated downstream from the reaction zones. Preferably, the products from both the liquid phase alkylation zone and the vapor phase transalkylation zone are passed into a single separation zone. This separation zone may comprise a series of three distillation columns. In a first distillation column, the products from the alkylation zone and the transalkylation zone are introduced as a feed and benzene is recovered as an overhead stream. The recovered benzene overhead stream is recycled as a reactant to both the liquid phase alkylation zone and the vapor phase transalkylation zone. The bottoms from the first distillation column are passed as a feed to a second distillation column. Ethylbenzene product is recovered as an overhead stream, and the bottoms from the second distillation column are passed as a feed stream to a third distillation column. Diethylbenzenes and triethylbenzenes are recovered as an overhead stream from the third distillation column, and this stream comprising diethylbenzene may be passed as a reactant stream to the

transalkylation zone. The bottoms from the third distillation column are rejected from the system as heavies.

The separation zone for the present liquid-vapor phase system may be essentially the same as those illustrated in the art for all liquid phase or all vapor phase systems. Such a separation zone for an all liquid phase system is illustrated in U.S. Patent No. 4,169,111, and such a separation zone for an all vapor phase is illustrated in Figure 3 on page 45 of the article by Francis G. Dwyer, entitled "Mobil/Badger Ethylbenzene Process-Chemistry and Catalytic Implications", appearing on pages 39-50 of a book entitled Catalysis of Organic Reactions, edited by William R. Moser, Marcel Dekker, Inc., 1981.

Fresh benzene feed is preferably introduced into the present system directly into the separation zone or at a point immediately upstream from the separation zone. When fresh benzene is introduced into the system in this manner, the benzene, which is introduced into both the liquid phase alkylation zone and the vapor phase transalkylation zone, is essentially a mixture of recycled benzene and fresh fed benzene.

Figure 1 is a graph showing a comparison of the activity of MCM-22, MCM-49, MCM-56 and zeolite Beta for catalyzing the liquid phase synthesis of ethylbenzene.

Figure 2 is a graph showing a comparison of the selectivity of MCM-22, MCM-49, MCM-56 and zeolite Beta for catalyzing the liquid phase synthesis of ethylbenzene.

Example 1

2.0 g of an MCM-22 catalyst (~4 cc 1/16" extrudate, sized to 1/16" length, 35% alumina binder, 620 alpha value, 25 SiO_2/Al_2O_3) was mixed with ~20 cc of 20-40 mesh quartz chips, and then charged to an isothermal, down-flow, fixed-bed reactor. The catalyst was dried at 125°C and 1 atm with 50 cc/min of flowing N_2 for 2 hours. N_2 was turned off. Benzene was fed into the reactor at 16.7 WHSV for 1 hour and then at 8.35 WHSV while the reactor temperature

and pressure were increased to 150°C and 500 psig, respectively. After the desired temperature and pressure were reached, ethylene was introduced from a mass flow controller at 0.55 WHSV (5.5 benzene/ethylene molar ratio). After lining out, liquid products were collected in a cold-trap and analyzed off-line with a Varian 3700 GC. Offgas was analyzed with an on-line Carle refinery gas analyzer. Ethylene conversion was determined by measuring unreacted ethylene in the offgas relative to feed ethylene. Total material balances were 100±2%. During the 18 day experiment, the effects of temperature (200-320°C), ethylene WHSV (1.1 to 2.2 h^{-1}) and benzene/ethylene molar ratio (4.5-6.5) were studied all at 3550 kPa (500 psig). The catalyst activity and selectivity for liquid phase ethylbenzene synthesis are compared with those of MCM-49, MCM-56, and zeolite Beta in Example 7. At the end of the run, no activity loss was observed.

Example 2

4.0 g of the same MCM-22 catalyst (~8 cc, mixed with ~16 cc of 20-40 mesh quartz chips) was used for this run also at 3550 kPa (500 psig). The reaction was brought on stream similarly to what was described in Example 1. The initial conditions were 182°C, 0.55 ethylene WHSV, and 5.5 benzene/ethylene molar ratio. Ethylene conversion decreased from 94 to 82% over 5 days at 182°C. Increasing reactor temperature did not yield stable ethylene conversion until ~210°C. At 220°C, the ethylene conversion stabilized at 97-98% for 18 days without aging. Liquid products obtained at 220°C and 97-98% ethylene conversion were nearly identical to what was observed from Example 1 at similar conditions.

Example 3

Although no aging was observed at 220°C in Example 2, the catalyst was subjected to a regeneration procedure at the end of the stability study to assess its robustness. The catalyst was regenerated in situ at 100 kPa (1 atm) in

a mixture of air and N_2 (total flow of 200 cc/min): 25% of air for 30 minutes at 400°C; 50%, 75% and 100% of air for 30 minutes each at 450°C; then 100% air at 538°C for 2 hours. The temperature was decreased to 220°C. The regenerated catalyst was then tested for 5 days under conditions identical to those before regeneration: 220°C, 3550 kPa (500 psig), 0.55 ethylene WHSV, and 5.5 benzene/ethylene molar ratio. The regenerated catalyst was slightly more active reaching 98-99% ethylene conversion (97-98% before regeneration). The DEB/EB molar ratio also increased slightly after regeneration from 0.05 to 0.07.

Example 4

2.0 g of an MCM-49 catalyst (~4 cc 1/16" extrudate, sized to 1/16" length, 35% alumina binder, 910 alpha value, 18 SiO_2/Al_2O_3, mixed with 20 cc of 20-40 mesh quartz chips) was tested similarly to what was described for MCM-22 in Example 1. Benzene was fed into the reactor at 30 WHSV for 1 hour and then at 16.7 WHSV while the reactor temperature and pressure were increased to 220°C and 3550 kPa (500 psig), respectively. After reaching 220°C and 3550 kPa (500 psig), ethylene was introduced at 1.1 WHSV (5.5 benzene/ethylene molar ratio). During the 25 day experiment, the effects of temperature (200-320°C), ethylene WHSV (1.1 to 2.2 h^{-1}) and benzene/ethylene molar ratio (4.5-6.5) were studied all at 3550 kPa (500 psig). The catalyst activity and selectivity for liquid phase ethylbenzene synthesis are compared with those of MCM-22, MCM-56, and zeolite Beta in Example 7. At the end of the run, the catalyst was tested again at conditions identical to those used at the beginning of the run. No activity loss was observed.

Example 5

1.0 g of an MCM-56 catalyst (2 cc 1/16" extrudate, sized to 1/16", 35% alumina binder, 400 alpha value, 18 SiO_2/Al_2O_3, mixed with ~10 cc of 20-40 mesh quartz chips) was tested similarly to what was described for MCM-22 in

Example 1. Benzene was fed into the reactor at 45 WHSV for 1 hour and then at 16.7 WHSV while the reactor temperature and pressure were increased to 220°C and 3550 kPa (500 psig), respectively. After reaching 220°C and 3550 kPa (500 psig), ethylene was introduced at 1.1 WHSV (5.5 benzene/ethylene molar ratio). During the 13 day experiment, the effects of temperature (200-320°C) and ethylene WHSV (1.1 to 2.8 h^{-1}) were studied at 3550 kPa (500 psig) and ~5.5 benzene/ethylene molar ratio. The catalyst activity and selectivity for liquid phase ethylbenzene synthesis are compared with those of MCM-22, MCM-49, and zeolite Beta in Example 7. At the end of the run, the catalyst was tested again at conditions identical to those used at the beginning of the run. No activity loss was observed.

Example 6

2.0 g of a zeolite-Beta catalyst (~4 cc 1/16" extrudate, sized to 1/16" length, 35% alumina binder, 690 alpha value, 43 SiO_2/Al_2O_3, mixed with 20 cc of 20-40 mesh quartz chips) was tested similarly to what was described for MCM-22 in Example 1. Benzene was fed into the reactor at 30 WHSV for 1 hour and then at 25 WHSV while the reactor temperature and pressure were increased to 160°C and 3550 (500 psig), respectively. After reaching 160°C and 3550 kPa (500 psig), ethylene was introduced at 1.65 WHSV (5.5 benzene/ethylene molar ratio). At 160°C, ethylene conversion declined from 97 to 74% in 4 days and continued to decline thereafter. Increasing temperature to 180°C did not recover catalyst activity. The catalyst was air regenerated using procedures described in Example 3 and was brought on stream again at 220°C, 3550 kPa (500 psig), 1.65 ethylene WHSV, and 5.5 benzene/ethylene molar ratio. The catalyst was then tested under various conditions to study the effects of temperature (180-320°C), ethylene WHSV (1.1 to 3.3 h^{-1}), and benzene/ethylene molar ratio (4.5-6.5) at 3550 kPa (500 psig). Stable and 97+% ethylene conversion was achieved at 180°C, 1.1 ethylene WHSV, and 5.5

benzene/ethylene molar ratio. The catalyst activity and selectivity for liquid phase ethylbenzene synthesis are compared with those of MCM-22, MCM-49, and MCM-56 in Example 7. At the end of the run, the catalyst was tested again at conditions identical to those used at the beginning of the run. No activity loss was observed.

Example 7

Figure 1 compares catalyst activity at 220°C, 3550 kPa (500 psig), and 5.5 benzene/ethylene molar ratio. At constant ethylene conversion (e.g., 95%), the relative catalyst activity is:

MCM-22: MCM-49: MCM-56: zeolite Beta = 1.0: 1.2: 1.6: 2.2

Table 1 indicates that at 96+% C_2= conversion, MCM-22, MCM-49, and MCM-56's overall alkylation selectivities to EB and polyethylbenzene (99.9 mol%) are all higher than that of zeolite Beta. The EB selectivities of MCM-22, MCM-49, and MCM-56 (93-95 mol%) are 5-7 mol% higher than zeolite Beta. MCM-22, MCM-49, and MCM-56 made less polyethylbenzene and less non-EB by-products than zeolite Beta.

Table 1. Ethylbenzene Synthesis - Selectivity Comparison

Catalyst/ 35% Al_2O_3	MCM-22	MCM-49	MCM-56	Zeolite Beta
$C_2^=$ WHSV	1.1	1.1	1.65	2.2
$C_2^=$ Conversion,%	96.6	97.1	96.2	97.0
Product distr. (mol %)				
EB	94.0	95.3	93.7	88.0
DEB	5.7	4.5	6.0	10.6
TEB+	0.2	0.1	0.2	1.1
Σ	99.9	99.9	99.9	99.7
xylenes	0.00	0.00	0.00	0.00
n-C_3-Bz+cumene	0.00	0.00	0.00	0.00
sec-C_4-Bz	0.07	0.06	0.04	0.13
other C_9^+ aromatics	0.02	0.02	0.02	0.14
Σ (by products)	0.09	0.09	0.06	0.27

220°C, 3550 kPa, and 5.5 benzene/$C_2^=$ molar ratio

Catalyst selectivities (further represented as DEB/EB molar ratio) at other temperatures are compared in Figure 2. In the liquid phase (<260°C at 3550 kPa), MCM-22, MCM-49, and MCM-56 catalysts made less DEB than zeolite Beta. At 220°C, MCM-22, MCM-49, and MCM-56 made ~50% less DEB than zeolite Beta.

Example 8

After distillation, the polyethylbenzene (PEB) rich bottoms product is mixed with benzene (recovered by a prior distillation step) and processed in the transalkylation reactor in the vapor phase over a medium pore zeolite such as ZSM-5. Transalkylation conditions are typically 335-350°C (635-662°F), 930 kPa (120 psig), 40 total WHSV (benzene and PEB), and 3:1 benzene/PEB weight ratio. Under

these conditions, DEB conversion per pass is ≥45%. The products are sent to the distillation section for benzene and incremental EB recovery, and PEB is recycled to the transalkylator. The resultant EB quality from the overall process is excellent (<200 ppm xylenes, no benzene coboilers, and no C_9 and C_{10} aromatics).

Claims:

1. A process for preparing ethylbenzene, said process comprising the steps of:

(a) contacting benzene and ethylene with an acidic solid oxide catalyst in a liquid phase alkylation reaction zone under sufficient liquid phase conditions to generate ethylbenzene product and byproducts comprising diethylbenzene; and

(b) contacting said diethylbenzene byproduct from step (a) and benzene with an acidic solid oxide catalyst in a vapor phase transalkylation reaction zone under sufficient vapor phase conditions to generate an effluent comprising another ethylbenzene product,

wherein benzene feed which is introduced into said vapor phase transalkylation zone of step (b) comprises nonbenzene hydrocarbons having from 5 to 7 carbon atoms, and wherein nonbenzene hydrocarbons having from 5 to 7 carbon atoms are converted to hydrocarbons having a different boiling point in said transalkylation zone, and wherein unreacted benzene is recycled in said alkylation zone and in said transalkylation zone.

2. A process according to claim 1, wherein said benzene feed to said vapor phase transalkylation zone comprises at least 100 ppm of said nonbenzene hydrocarbons having from 5 to 7 carbon atoms, and wherein the temperature in said liquid phase alkylation zone of step (a) is lower than the temperature of said vapor phase transalkylation zone of step (b).

3. A process according to claim 1 or 2, wherein the alkylation step (a) comprises contacting said benzene and ethylene with a catalyst comprising a solid crystalline aluminosilicate selected from the group consisting of MCM-22, MCM-36, MCM-49, MCM-56, zeolite Beta, zeolite X, zeolite Y and mordenite.

4. A process according to claim 1 or 2, wherein the alkylation step (a) comprises contacting said benzene and ethylene with a catalyst comprising a solid crystalline aluminosilicate selected from the group consisting of MCM-22, MCM-49, and MCM-56.

5. A process according to any one of claims 1 to 3, wherein the transalkylation step (b) comprises contacting said benzene and diethylbenzene with a catalyst comprising a solid crystalline aluminosilicate selected from the group consisting of MCM-22, ZSM-5, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-48 and ZSM-50.

6. A process according to any one of claims 1 to 3, wherein the transalkylation step (b) comprises contacting said benzene and diethylbenzene with a catalyst comprising ZSM-5.

7. A process according to any one of claims 1 to 6, wherein the molar ratio of benzene to ethylene in the liquid phase alkylation step (a) is greater than or equal to 1 and wherein the percentage of ethylene converted in step (a) is at least 95%; wherein the weight ratio of ethylbenzene to diethylbenzene produced in liquid phase alkylation step (a) is from 2 to 30; wherein the liquid phase alkylation step (a) is carried out at a temperature of from 150°C to 260°C, a pressure of 7000 kPa or less, a WHSV based on ethylene of from 0.5 to 2.0 hr^{-1}, and a mole ratio of benzene to ethylene of from 1:1 to 30:1; and wherein the vapor phase transalkylation step (b) is carried out at a temperature of from 260°C to 482°C, a pressure of from 450 to 3550 kPa (50 to 500 psig), a WHSV based on the total vapor feed to the reaction zone of from 1 to 50 hr^{-1}, and a mole ratio of benzene to diethylbenzene of from 1 to 50.

8. A continuous process according to claim 1 for preparing ethylbenzene, said process comprising the steps of:

(1) introducing benzene, benzene coboilers, and ethylene into a liquid phase alkylation reaction zone, wherein said benzene and said ethylene are reacted in the presence of an alkylation catalyst under sufficient liquid phase conditions to generate an effluent comprising ethylbenzene product, unreacted benzene, unreacted benzene coboilers, and byproducts comprising diethylbenzene and butylbenzene, said alkylation catalyst comprising an acidic solid oxide selected from the group consisting of MCM-22, MCM-49 and MCM-56;

(2) passing the effluent from said liquid phase alkylation reaction zone of step (1) to a separation zone, wherein said effluent is separated into separate streams comprising a light stream comprising (i) unreacted benzene and benzene coboilers, (ii) an intermediate product stream, and (iii) a heavy stream comprising diethylbenzene and butylbenzene;

(3) passing said heavy stream (iii) from step (2) along with benzene and benzene coboilers to a vapor phase transalkylation reaction zone, wherein said benzene and diethylbenzene are reacted in the presence of a transalkylation catalyst under sufficient vapor phase conditions to generate an effluent comprising another ethylbenzene product and unreacted benzene, said transalkylation catalyst comprising a medium-pore size zeolite;

(4) passing the effluent from said vapor phase transalkylation reaction zone to the separation zone of step (2), wherein said effluent is separated into separate streams comprising (i) a light stream comprising unreacted benzene, (ii) an intermediate product stream, and (iii) a heavy stream comprising unreacted diethylbenzene;

(5) recycling unreacted benzene along with benzene coboilers recovered in separation steps (2) and (4) in a

closed recycle loop to said alkylation reactor of step (1) and to said transalkylation reactor of step (3);

(6) introducing fresh benzene feed into said benzene recycle loop at a rate sufficient to make up for benzene converted in said alkylation zone and in said transalkylation zone, wherein said fresh benzene comprises impurities comprising benzene coboiling nonbenzene hydrocarbons having from 5 to 7 carbon atoms, said benzene coboiling hydrocarbons being at least partially converted to hydrocarbons having a different boiling point in said transalkylation zone of step (3), and butylbenzene being at least partially converted to one or more different hydrocarbons in said transalkylation zone of step (3); and

(7) recovering an ethylbenzene product from the intermediate product stream of steps (2) and (4), the recovered ethylbenzene product comprising less than 200 ppm xylene, less than 100 ppm of hydrocarbons having 7 or less carbon atoms and less than 100 ppm of hydrocarbons having 9 or more carbon atoms.

9. A process according to claim 8, wherein the feed to the vapor phase transalkylation zone comprises at least 200 ppm of benzene coboilers based on the weight of benzene in the feed.

10. A process according to claim 8 or 9, wherein said medium-pore size zeolite in step (3) is ZSM-5.

11. A process according to any one of claims 8 to 10, wherein at least 95% of said ethylene is converted in step (1); wherein the alkylation product from step (1) comprises at least 92 wt% of ethylbenzene, less than 7 wt% of diethylbenzene and less than 1 wt% of triethylbenzene; wherein the liquid phase alkylation step (1) is carried out at a temperature of from 150°C to 260°C, a pressure of 7000 kPa or less, a WHSV based on ethylene of from 0.5 to 2.0 hr^{-1}, and a mole ratio of benzene to ethylene of from 1:1 to 30:1; and wherein the vapor phase transalkylation

step (3) is carried out at a temperature of from 260°C to 482°C, a pressure of from 450 to 3550 kPa (50 to 500 psig), a WHSV based on the total vapor feed to the reaction zone of from 1 to 50 hr^{-1}, and a mole ratio of benzene to diethylbenzene of from 1 to 50.

12. A process according to any one of claims 8 to 11, wherein fresh benzene feed is introduced immediately upstream from said separation zone of steps (2) and (4); and wherein the alkylation product from step (1) comprises less than 0.5 wt% of triethylbenzene.

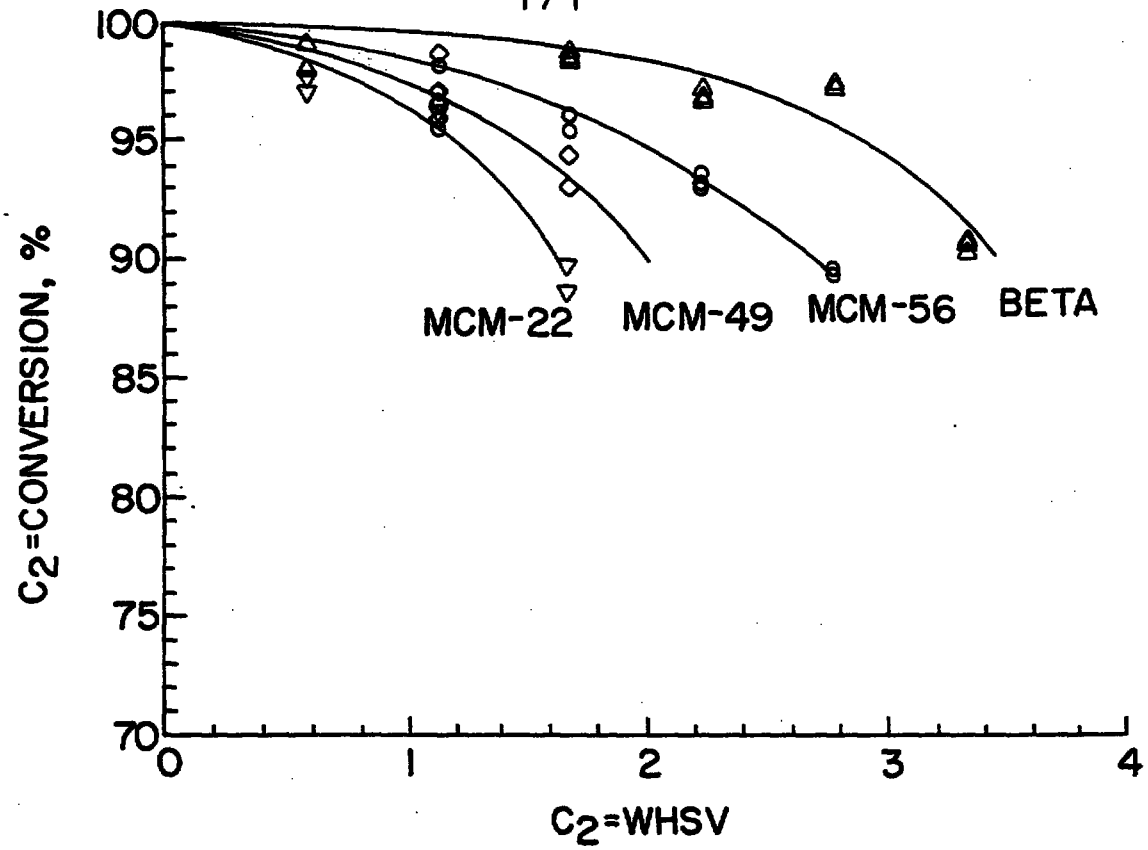
100
95
90
85
80
75
70
C_2=CONVERSION, %
MCM-22
MCM-49
MCM-56
BETA
0
1
2
3
4
C_2=WHSV

FIG. 1

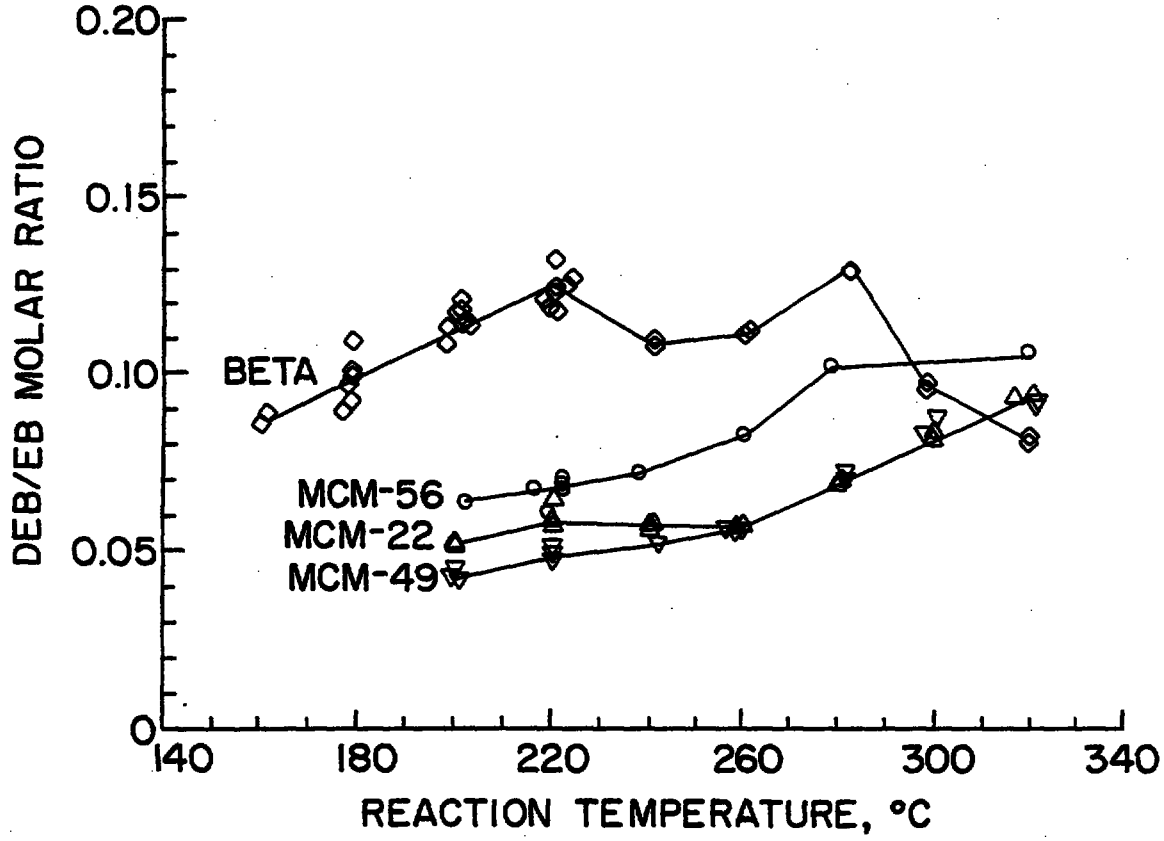
0.20
0.15
0.10
0.05
0
DEB/EB MOLAR RATIO
BETA
MCM-56
MCM-22
MCM-49
140
180
220
260
300
340
REACTION TEMPERATURE, °C

FIG. 2

SG9701216-4

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07C 2/66 | A1

(11) International Publication Number: WO 96/20148

(43) International Publication Date: 4 July 1996 (04.07.96)

(21) International Application Number: PCT/US95/15660

(22) International Filing Date: 4 December 1995 (04.12.95)

(30) Priority Data: 08/364,145 27 December 1994 (27.12.94) US

(71) Applicant: MOBIL OIL CORPORATION [US/US]; 3225 Gallows Road, Fairfax, VA 22037 (US).

(72) Inventors: CHENG, Jane, Chi-Ya; 26 Deer Trail Drive, Clarksburg, NJ 08510 (US). SMITH, Charles, Morris; 19 Locust Street, Princeton, NJ 08540 (US). VENKAT, Chaya, Rao; 35 Littlebrook Road North, Princeton, NJ 08540 (US). WALSH, Dennis, Edward; 36 Redwood Drive, Northampton Township, Richboro, PA 18954 (US).

(74) Agents: KENEHAN, Edward, F. et al.; Mobil Oil Corporation, 3225 Gallows Road, Fairfax, VA 22037 (US).

(81) Designated States: AU, CA, CN, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

RINP's copy

(54) Title: CONTINUOUS PROCESS FOR PREPARING ETHYLBENZENE USING LIQUID PHASE ALKYLATION AND VAPOR PHASE TRANSALKYLATION

(57) Abstract

The present invention relates to a process for preparing ethylbenzene using liquid phase alkylation and vapor phase transalkylation. The liquid phase alkylation reaction may be catalyzed by an acidic solid oxide, such as MCM-22, MCM-49 and MCM-56. The vapor phase transalkylation may be catalyzed by a medium-pore size zeolite such as ZSM-5. The process may be run continuously with the continuous introduction of fresh benzene feed containing at least 500 ppm of nonbenzene hydrocarbon impurities. The combined ethylbenzene product of these alkylation and transalkylation reactions has very low levels of impurities including xylene, hydrocarbons having 7 or less carbon atoms and hydrocarbons having 9 or more carbon atoms.