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FLUID-BED AROMATICS ALKYLATION

This invention relates to an improved process for alkylating aromatics using a fluidized bed reactor.

5 The process according to the invention can be used for any suitable aromatic alkylation reaction, but is particularly well suited for producing xylene (preferably para-xylene) from toluene and methanol. When the invention is used in this procedure, a significant improvement in toluene conversion, methanol selectivity, and selectivity to para-xylene can be realized. The invention also can be used, for example, in the production of other alkylaromatics including, 10 for example, ethylbenzene, cumene, diethylbenzene, diisopropylbenzene, para-ethyltoluene, para-cymene, and pseudocumene, and for the reduction of benzene in motor fuels.

Aromatic alkylation is an important procedure for producing many useful chemical products. For example, para-xylene, which can be produced by alkylating toluene with methanol, constitutes an important starting material for manufacturing terephthalic acid, which 15 is an important intermediate in production of synthetic polyester fibers, films, or resins. These polyester materials have many practical, well known uses, such as in fabrics, carpets, and apparel. Ethylbenzene, which can be produced by alkylating benzene with ethylene, is used mainly as a precursor for styrene production. Styrenes and polystyrenes are well known for many uses and products, including: packaging and disposable serviceware associated with the 20 food industry; audio and visual cassettes; medical and dental molding products; and synthetic plastics, rubbers, and foams.

Because of the importance of alkylated aromatic products as starting materials and intermediates for producing many common consumer and industrial products, efficient production and use of alkylated aromatics is of great importance. Additionally, most aromatic 25 starting materials, such as toluene and benzene, are obtained during oil and gas production. Therefore, efficient alkylation of these aromatic materials is vital to eliminate wastes and conserve precious natural resources.

A conventional approach for toluene alkylation includes mixing toluene and methanol upstream of a reactor and then feeding the mixture together into the base of the reactor. The 30 reactor includes an alkylation catalyst in one or more fixed beds, and this catalyst promotes the alkylation reaction between the toluene and methanol to produce xylene. While this approach

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has been used successfully, its yield and reactant utilization characteristics leave room for improvement.

In an effort to improve yields in various reaction procedures, stagewise injection of reagents has been used in various fixed bed processes. For example, U.S. Patent Nos. 4,377,718 and 4,761,513 describe toluene alkylation processes wherein the alkylating reagent is fed at different stages between fixed beds. Likewise, U.S. Patent No. 3,751,504 discloses a similar procedure, using multiple injection ports, for preparing ethylbenzene using a fixed bed catalyst reactor. U.S. Patent No. 5,120,890 discloses multiple reactant injection locations into separate fixed beds in a process for reducing benzene and toluene content in light gasoline streams.

In these fixed bed processes, one can easily separate the catalyst load into several different and discrete zones. During use, product from one zone is mixed with additional alkylating reagent, and this mixture is fed to the subsequent zone. One way of providing these separate and discrete zones includes placing each zone in a separate reactor vessel, wherein additional reagent(s) is (are) injected between adjacent zones. This procedure suffers from the drawback that considerable expense is involved in providing separate reactor vessels and the associated hardware for running this type of system.

Additionally, fixed bed reactors are disadvantageous for exothermic reactions because of the potential negative impact of exotherms on product selectivity. Reactor stability concerns with fixed beds also require that the temperature rise per catalyst bed be limited. This could necessitate a large number of beds to accommodate the heat of reaction. Similarly, endothermic reactions would result in reduced reaction rates and excessive catalyst requirements.

It is an object of this invention to provide a process for alkylating aromatic reactants with high conversion and selectivity, e.g., for producing para-xylene from an alkylating reaction between toluene and methanol.

Accordingly the invention relates to a process for alkylating an aromatic reactant to produce an alkylated aromatic product (e.g., methylating toluene to produce xylene), comprising:

introducing the aromatic reactant (e.g., toluene) into a fluidized bed reaction zone at a first location in the fluidized bed reaction zone;

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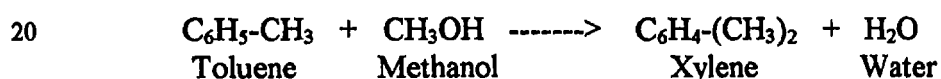
introducing an alkylating reagent (e.g., methanol) into the fluidized bed reaction zone at a second location downstream from the first location; and

recovering the alkylated aromatic product, produced by reaction of the aromatic reactant and the alkylating reagent, from the fluidized bed reaction zone.

5 In addition to introducing alkylating reagent the fluidized bed reaction zone at said second location, alkylating reagent also may be introduced into the fluidized bed reaction zone at the first location. This additional alkylating reagent can be introduced in a common feed stream with the aromatic reactant, or it can be separately fed into the fluidized bed reaction zone.

10 One preferred embodiment of the process according to the invention includes introducing alkylating reagent directly into the fluidized bed reaction zone at one or more further locations downstream of the first location and the second location. These further locations are preferably provided at a gradually increasing distances from the first location. Also, the alkylating reagent can be introduced at a plurality of different locations in a plane
15 perpendicular or substantially perpendicular to the axial direction of the reactor vessel (i.e., at plural locations at each stage of its introduction).

During aromatic alkylation reactions, such as methylation of toluene, an aromatic reactant reacts with an alkylating reagent to form the desired alkylated aromatic product. In toluene methylation, the following desired reaction takes place:



Many competing side reactions, however, also can occur. For example, methanol can react with itself, e.g., to form olefins. Because the cost of methanol is a significant part of the cost
25 involved in xylene production, it is important to minimize or eliminate these undesired side reactions. Other undesirable side reactions that can occur during methylation of toluene involve over-alkylation of toluene to form C₉+ aromatics.

Such undesired side reactions during toluene methylation can be reduced by using a large excess of toluene during the reaction process. Using excess toluene increases the
30 chances that one methanol molecule will react with one toluene molecule to produce xylene, and it reduces the chances that two or more methanol molecules will react with the same toluene molecule or with themselves. Therefore, using excess toluene results in efficient use

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of methanol during the reaction by increasing the "methanol utilization" during performance of the reaction. "Methanol utilization," which provides a measure of methanol selectivity to producing xylene, is defined as:

$$\frac{\text{the number of moles of xylene produced} \times 100}{\text{the number of moles of methanol consumed}} = \% \text{ methanol utilization}$$

A xylene production procedure that provides high toluene conversion and high methanol utilization produces xylene in an efficient, desirable manner. Preferably, the product xylenes are rich in the para-isomer and exhibit high para-xylene selectivity, defined as:

$$\frac{\text{Mass para-xylene} \times 100}{\text{Mass ortho-xylene} + \text{Mass para-xylene} + \text{Mass meta-xylene}} = \% \text{ Para-xylene Selectivity}$$

This invention relates to novel process for improving the conversion, alkylation reagent utilization, and selectivity during alkylation of aromatics in a fluidized bed reactor, e.g., during toluene alkylation to produce xylene. The process provides these improved results by introducing the alkylating reagent (e.g., methanol) into a fluidized bed reactor system at one or more locations downstream in the reactor system from the location where the aromatic reactant (e.g., toluene) is introduced, i.e., in a "stagewise manner." Any number of downstream "stages" can be used for introducing the alkylating reagent, e.g., two to four downstream stages.

More specifically, the alkylating reagent is injected directly into the fluidized catalyst bed at a location downstream from the location where the aromatic reactant is introduced. This alkylating reagent preferably is introduced directly into the catalyst bed without pre-mixing it with the upstream vapors including the aromatic reactant. Given the potential for methanol self-reactions during toluene methylation, as described above, it is surprising that this direct introduction of methanol functions properly in the process of the invention without adversely affecting methanol utilization and xylene yield. This is particularly surprising in the process according to the invention, because the fluidized beds used are relatively dense, such as turbulent sub-transport fluid beds with an operating bed density of 100 to 600 kg/m³, preferably 300 to 500 kg/m³, and the use of these dense beds increases the catalyst concentration and the methanol concentration at the area of methanol injection. As will be

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demonstrated below, however, this direct methanol introduction procedure effectively produces xylene with improved toluene conversion and methanol utilization.

To further reduce the chances of adverse methanol self-reactions, optionally, the alkylating reagent can be pre-mixed with at least a portion of the upstream reactor vapors and/or fresh aromatic feed, outside the presence of the catalyst. This mixture then is introduced into the fluidized bed at a location in the intermediate portion of the fluidized bed, which contains the alkylation catalyst. The upstream reactor vapors may contain unreacted aromatic and alkylating reagents and some alkylated aromatic product. While this option reduces the chances of adverse methanol/methanol side reactions, it increases expenses and reactor complexity.

Although the process of the invention is primarily intended producing xylene from toluene and methanol, it can be used to effect other aromatics alkylation reactions e.g., ethylation of benzene to produce ethylbenzene, propylation of benzene to produce cumene, ethylation of ethylbenzene to produce diethylbenzene, propylation of cumene to produce diisopropylbenzene, ethylation of toluene to produce para-ethyltoluene, propylation of toluene to produce para-cymene, and methylation of xylene to produce pseudocumene [1,2,4-trimethyl benzene] and reduction of benzene content in motor fuels.

The invention will now be more particularly described with reference to the accompanying drawing which is a schematic view of a fluidized bed reactor system for performing a process according to one embodiment of the invention.

Referring to the drawing, there is shown fluidized bed reactor system 10 including a reactor vessel 12, which contains a fluidized bed reaction zone 14. This reaction zone 14 includes a top portion 16, a bottom portion 18, and an intermediate portion 20 that extends between the top portion 16 and the bottom portion 18.

A fluidized bed reaction zone 14, as is known in the art, contains a volume of small sized particles that are generally kept afloat ("fluidized") by flowing gas as it passes upward through the reactor vessel 12 during reactor operation. Conventional devices, such as cyclone 22, can be used to provide primary separation and recovery of entrained catalyst from the gas, to return the solids to the bed, to recover some or all of the gas necessary to mix and contact the various reactants and catalyst, and to maintain the fluidized bed 14 under suitable operating conditions. Through this gas flow, reactants pass into and/or through the reaction

zone 14, and the small particles provide a large surface area that allows generous contact between the reactants under the alkylation conditions.

Preferably, the fluidized bed 14 will contain a catalyst that promotes the alkylation reaction, and indeed, if desired, the entire volume of the fluidized bed 14 may constitute catalyst particles. Any suitable alkylation catalyst can be used without departing from the invention. For example, the ZSM-5 zeolite alkylation catalyst described in WO 98/14415 is suitable for use in the methylation of toluene by the process of this invention.

For the reaction to proceed, the various reactants must be introduced into the fluidized bed reaction zone 14. Although the specific location is not critical to the process and system according to the invention, in the illustrated embodiment the aromatic reactant (e.g., toluene in this system) is introduced at the bottom portion 18 of the fluidized bed reaction zone 14. This reactant can be introduced using any appropriate introduction device 24, including conventional devices known in the art (e.g., injector nozzles, perforated grids, pipe grids, etc.). The aromatic reactant can be introduced at one or more locations in the fluidized bed reaction zone 14, but preferably these locations are provided at or near its bottom portion 18. The aromatic reactant preferably is introduced in gaseous form and provides at least a portion of the gas flow necessary for maintaining the reaction zone 14 in fluidized form.

The alkylating reagent is introduced directly into the fluidized bed reaction zone 14 at one or more locations along its axial direction, downstream from the location where the aromatic reactant is introduced (via introduction device 24). The illustrated reactor system includes four downstream axial introduction devices 26a, 26b, 26c, and 26d for introducing the alkylating reagent in different "stages." These devices 26a, 26b, 26c, and 26d may be arranged to introduce the alkylating reagent in any appropriate manner. For example, each device 26a, 26b, 26c, and 26d may include one, and preferably more, injector nozzles located around the periphery of the reactor vessel 12 for introducing the alkylating reagent around the vessel periphery. As another alternative, each device 26a, 26b, 26c, and 26d may include a manifold or pipe grid arrangement 28a, 28b, 28c, and 28d, as shown in Fig. 1, for introducing the alkylating reagent at a plurality of locations in the interior of the fluidized bed reaction zone 14. Preferably, each axial stage includes suitable devices for introducing the alkylating reagent at plural locations within the stage. This stagewise introduction of methanol at

various multiple locations increases methanol utilization, the toluene conversion percentage, and the selectivity to the desired xylene product.

One preferred aspect of the invention includes introducing additional alkylating reagent at or near the location where the initial aromatic reactant is introduced. Fig. 1 shows introduction device 30 at the bottom of the reactor vessel 12 for introducing this additional
5 alkylating reagent. If desired, this additional alkylating reagent and the aromatic reactant can be mixed together prior to introducing the materials into the bottom 18 of the fluidized bed reaction zone 14, such that these materials are introduced in a common feed stream. Alternatively, the materials can be introduced separately into the fluidized bed reaction zone
10 14 and contacted together after their introduction, or the materials can be first mixed together in a nozzle or other device that introduces both concurrently into the fluidized bed reaction zone 14. Any suitable mixing device and method can be used for this introduction without departing from the invention.

If necessary, the devices 24, 26, 28, and 30 for introducing the various reagents and
15 reactants can be maintained under conditions so as to ensure the integrity of these materials through the mechanical device until the reactants or reagents enter the catalyst bed (i.e., to prevent undesired side reactions, conversions, and/or degradation of the reactants or reagents). This can be accomplished in any suitable manner, such as by limiting residence time of the materials in the introduction device or by cooling the introduction device to a
20 temperature that maintains the reagent or reactant under stable conditions.

The reactor vessel 12 and the reactant introduction rates are maintained under suitable conditions to support a chemical reaction between the aromatic reactant and the alkylating reagent to produce the desired alkylated aromatic product. This reaction product preferably is produced in a gaseous form, and it may be collected and recovered from the reactor outlet
25 stream 40 in any suitable manner, such as by condensation and subsequent fractionation of the hydrocarbon liquid using conventional distillation and recovery equipment. Further purification of the product can be accomplished in any suitable manner, for example, by crystallization or solid adsorption.

Unreacted feeds can be recycled to the fluidized bed reaction zone 14. It is generally
30 not necessary to completely purify the recycled methanol and toluene, although this can be done, if desired.

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Suitable reaction conditions, particularly for methylation of toluene with methanol to produce para-xylene, include the following ranges:

- (a) Temperature - 500° to 700°C, and preferably between 500° to 600°C;
- (b) Pressure - 1 atmosphere to 1000 psig (100 to 7000 kPa), and preferably 10
5 psig to 200 psig;
- (c) moles toluene/moles methanol (in the reactor charge) - at least 0.2, and preferably from 0.2 to 20; and
- (d) a weight hourly space velocity ("WHSV") for total hydrocarbon feed to the reactor(s) of 0.2 to 1000, preferably 0.5 to 500 for the aromatic reactant, and 0.01 to 100 for
10 the combined alkylating reagent stage flows, based on total catalyst in the reactor(s).

The process is conducted in the vapor or gaseous phase and preferably in the presence of added hydrogen and/or added water such that the molar ratio of hydrogen and/or water to toluene + methanol in the feed to the reactor is between 0.01 and 10. Those skilled in the art will be capable of adjusting the various reaction parameters and conditions to optimize
15 conversion, yield, and selectivity, using routine experimentation.

EXAMPLE 1

For this example, a fluidized bed pilot plant similar to that illustrated in Fig. 1 was used to produce xylene from toluene and methanol. The reactor vessel 12 was 10.2 cm (4 inches) in diameter and 8.2 m (27 feet) high. Methanol was introduced in a stagewise fashion, split
20 between the various stages shown in the table that follows. At stage 1 (located at the bottom of the reactor), the methanol was pre-mixed with the toluene feed prior to introduction into the fluidized bed. Methanol introduction in each of the subsequent, downstream stages did not including pre-mixing with toluene. Rather, in these later stages, methanol was directly injected into the fluidized bed.

25 The fluidized bed catalyst used contained 4 wt.% phosphorus and 10 wt.% of a 450/1 SiO₂/Al₂O₃ ZSM-5 zeolite in a binder comprising silica-alumina and clay. The catalyst was steamed at 14.7 psi partial pressure and 1000°C for 45 minutes prior to use. It had a particle density of 1.4 g/cc and a particle size range of 20 to 300 microns.

When running the pilot plant under the conditions described below, the following
30 performance test results were obtained:

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TABLE 1

Number of Stages	1	2	3	4
Conditions				
Reactor Top Pressure (psig)	21	21	22	22
Reactor Temperature (°F)	1105	1095	1104	1108
Hydrocarbon WHSV (hr ⁻¹)	1.9	1.6	1.6	1.6
Methanol Overall WHSV (hr ⁻¹)	0.3	0.2	0.2	0.2
% Methanol to Stage 1 (bottom)	100	50	33	35
% Methanol to Stage 2	0	50	33	26
% Methanol to Stage 3	0	0	33	26
% Methanol to Stage 4	0	0	0	13
Stage 2 Elevation (feet)	---	10.8	3.8	3.8
Stage 3 Elevation (feet)	---	---	10.8	10.8
Stage 4 Elevation (feet)	---	---	---	18.0
Overall Molar Ratio of Toluene to Methanol	2.0	2.0	2.0	2.0
Water to Hydrocarbon Ratio	0.5	0.5	0.5	0.5
Reactor Inlet Velocity (ft/s)	2.8	2.2	2.0	2.0
Reactor Outlet Velocity (ft/s)	3.2	3.1	3.0	3.0
Average Reactor Bed Density (lb/ft ³)	23	25	25	25
Performance				
Methanol Conversion (%)	88.7	91.9	91.9	92.9
Toluene Conversion (%)	21.7	26.4	27.4	28.2
Xylene Yield Based on Toluene (wt%)	24.7	30.2	30.9	31.9
Para-Xylene Selectivity (%)	89.9	89.9	89.7	89.3
Methanol Utilization (%)	48.4	57.0	58.2	59.3

The above sample runs demonstrate the improved performance realized by the process according to the invention. Sample Run 1 was outside the scope of the present invention because it did not include introduction of the alkylating reagent (methanol) downstream from the location where the aromatic reactant (toluene) was introduced. Rather, in Sample Run 1, 100% of the methanol was introduced at the bottom of the fluidized bed, with the toluene feed. Sample Runs 2-4 were performed according to the process of this invention and provided improved methanol and toluene conversion, improved xylene yield, and improved methanol utilization over Sample Run No. 1. All of these improved results were achieved with insignificant or no reduction in para-xylene selectivity.

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EXAMPLE 2

This Example demonstrates that generally increasing the number of alkylation reagent introduction stages can improve the performance of the invention for toluene conversion and methanol utilization. The sample runs described below, both run according to the process of this invention, were performed on the pilot plant used in Example 1. The operating conditions and performance results are set forth in Table 2.

TABLE 2

Number of Stages	2	4
Conditions		
Reactor Top Pressure (psig)	20	20
Reactor Temperature (°F)	1104	1102
Hydrocarbon WHSV (hr ⁻¹)	1.5	1.5
Methanol Overall WHSV (hr ⁻¹)	0.2	0.2
% Methanol to Stage 1 (bottom)	49	27
% Methanol to Stage 2	51	24
% Methanol to Stage 3	0	24
% Methanol to Stage 4	0	25
Stage 2 Elevation (feet)	10.8	3.8
Stage 3 Elevation (feet)	---	10.8
Stage 4 Elevation (feet)	---	18.0
Overall Molar Ratio of Toluene to Methanol	1.8	1.8
Water to Hydrocarbon Ratio	0.5	0.5
Reactor Inlet Velocity (ft/s)	2.1	1.9
Reactor Outlet Velocity (ft/s)	3.1	3.2
Average Reactor Bed Density (lb/ft ³)	27	27
Performance		
Methanol Conversion (%)	99.3	97.9
Toluene Conversion (%)	33.2	35.4
Xylene Yield Based on Toluene (wt%)	37.3	38.7
Para-Xylene Selectivity (%)	88.7	89.7
Methanol Utilization (%)	58.8	61.8

As evident from this performance data, both processes according to the invention produced excellent results. When increasing the number of methanol introduction stages from two to four, however, increases in toluene conversion and methanol utilization were realized. This data parallels that shown in Example 1. Additionally, the four stage introduction process showed improvement in xylene yield and para-xylene selectivity.

1. A process for alkylating an aromatic hydrocarbon reactant with an alkylating reagent comprising methanol to produce an alkylated aromatic product, comprising:
 - introducing the aromatic hydrocarbon reactant into a reactor system at a first location, wherein the reactor system includes a fluidized bed reaction zone comprising a temperature of 500° to 700°C and an operating bed density of about 300 to 600 kg/m³, for producing the alkylated aromatic product;
 - introducing a plurality of streams of said alkylating reagent directly into said fluidized bed reaction zone at positions spaced apart in the direction of flow of the aromatic hydrocarbon reactant, at least one of said streams being introduced at a second location downstream from the first location; and
 - recovering the alkylate aromatic product, produced by reaction of the aromatic reactant and the alkylating reagent, from the reactor system.
2. A process according to claim 1, wherein said fluidized bed reaction zone includes a top portion, a bottom portion, and an intermediate portion extending between the top portion and the bottom portion, wherein the first location where the aromatic hydrocarbon reactant is introduced is provided at or near the bottom portion of the fluidized bed reaction zone, and the second location where said at least one stream of the alkylating reagent is introduced is provided in the intermediate portion of said fluidized bed reaction zone.
3. A process according to claim 2, wherein a plurality of streams of the alkylating reagent are introduced directly into the intermediate portion of the fluidized bed reaction zone at a plurality of different axial positions in the intermediate portion of the fluidized bed reaction zone.
4. A process according to claim 2, wherein the fluidized bed reaction zone is a dense fluid bed, and a plurality of streams of the alkylating reagent are introduced directly into

the intermediate portion of the fluidized bed reaction zone at a plurality of different axial positions in the intermediate portion of the fluidized bed reaction zone.

7. A process according to claim 1, wherein the aromatic hydrocarbon reactant includes toluene, the alkylating reagent includes methanol, and the alkylated aromatic product includes xylene.
8. A process according to claim 1, further including introducing a stream of alkylating reagent at the first location where the aromatic hydrocarbon reactant is introduced into the reactor system.
9. A process according to claim 8, wherein the additional alkylating reagent is introduced in a common feed stream with the aromatic hydrocarbon reactant.
12. The process of claim 1 which comprises an operating bed density of 300 to 500 kg/m³, pressures of 1 atmosphere to 1000 psig, a weight hourly space velocity for total hydrocarbon feed to the reactor(s) of 0.2 to 1000 for the aromatic reactant, and about 0.01 to 100 for the combined alkylating reagent stage flows, based on total catalyst in the reactor(s).
13. The process of claim 12 wherein said aromatic reactant comprises toluene and said alkylating reagent comprises methanol, and which further comprises moles toluene/moles methanol (in the reactor charge) of at least about 0.2.
14. The process of claim 13 which is conducted in the presence of added hydrogen and/or added water such that the molar ratio of hydrogen and/or water to toluene + methanol in the feed to the reactor is between 0.01 and 10.
15. The process of claim 12 which comprises temperatures of 500° to 600°C, pressures of 10 psig to 200 psig, a weight hourly space velocity of 0.5 to 500 for the

aromatic reactant, and 0.01 to 100 for the combined alkylating reagent stage flows, based on total catalyst in the reactor(s).

16. The process of claim 15 which further comprises moles toluene/moles methanol (in the reactor charge) of 0.2 to 20.

17. The process of claim 1 wherein said reactor system contains a ZSM-5 zeolite alkylation catalyst.

18. The process of claim 1 wherein said reactor system contains a selectivated catalyst.

19. The process of claim 1 wherein said reactor system contains 50/1 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ZSM-5 zeolite in a binder comprising silica-alumina and clay.

20. The process of claim 1 wherein said fluidized bed reaction zone is operated at a temperature of 590° to 700°C.

24. A process for alkylating an aromatic hydrocarbon reactant with an alkylating reagent comprising methanol to produce an alkylated aromatic product, comprising;
introducing the aromatic hydrocarbon reactant into a reactor system at a first location, wherein the reactor system includes a fluidized bed reaction zone comprising a temperature of 500° to 700°C and an operating bed density of about 300 to 600 kg/m^3 , for producing the alkylated aromatic product and wherein the fluidized bed reaction zone has a substantially uniform cross-section;

introducing a plurality of streams of said alkylating reactant directly into said fluidized bed reaction zone at positions spaced apart in the direction of flow of the aromatic hydrocarbon reactant, at least one of said streams being introduced at a second location downstream from the first location; and

recovering the alkylate aromatic product, produced by reaction of the aromatic reactant and the alkylating reagent, from the reactor system.