

PROCESSES AND APPARATUSES FOR TOLUENE AND BENZENE
METHYLATION IN AN AROMATICS COMPLEX

FIELD

[0001] This present disclosure relates to processes and apparatuses for toluene and
5 benzene methylation in an aromatics complex for producing paraxylene. More specifically,
the present disclosure relates to processes and apparatuses for toluene and benzene
methylation within an aromatics complex for producing paraxylene wherein an embodiment
uses a reactor having a refractory comprising a mixed oxide refractory prepared using liquid
phosphate as a chemical binder.

10 BACKGROUND

[0002] The xylene isomers are produced in large volumes from petroleum as
feedstocks for a variety of important industrial chemicals. The most important of the xylene
isomers is para-xylene, the principal feedstock for polyester, which continues to enjoy a high
growth rate from large base demand. Ortho-xylene is used to produce phthalic anhydride,
15 which supplies high-volume but relatively mature markets. Meta-xylene is used in lesser but
growing volumes for such products as plasticizers, azo dyes and wood preservers.
Ethylbenzene generally is present in xylene mixtures and is occasionally recovered for styrene
production, but is usually considered a less-desirable component of C₈ aromatics.

[0003] Among the aromatic hydrocarbons, the overall importance of xylenes rivals that of
20 benzene as a feedstock for industrial chemicals. Xylenes and benzene are produced from
petroleum by reforming naphtha but not in sufficient volume to meet demand, thus
conversion of other hydrocarbons is necessary to increase the yield of xylenes and benzene.
Often toluene is de-alkylated to produce benzene or selectively disproportionated or
transalkylated to yield benzene and C₈ aromatics from which the individual xylene isomers
25 are recovered.

[0004] An aromatics complex flow scheme has been disclosed by Meyers in the
Handbook of Petroleum Refining Processes, 2d. Edition in 1997 by McGraw-Hill, and is
incorporated herein by reference.

[0005] Traditional aromatics complexes send toluene to a transalkylation zone to generate desirable xylene isomers via transalkylation of the toluene with A₉₊ components. A₉₊ components are present in both the reformate bottoms and the transalkylation effluent.

[0006] Paraxylene is most often produced from a feedstock which has a methyl to phenyl ratio of less than 2. As a result, the paraxylene production is limited by the available methyl groups in the feed. In addition, paraxylene production also typically produces benzene as a byproduct. Since paraxylene is more valuable than benzene and the other byproducts produced in an aromatics complex, there is a desire to maximize the paraxylene production from a given amount of feed.

[0007] Toluene methylation or benzene methylation processes use iron or iron-based alloys as reactor materials. Iron can catalyze the hydrocarbon to form filamentous carbon and thus plug the reactors. Additionally, iron can be corroded through a process called metal dusting when hydrocarbon is present. Coke formation and metal dusting reduce reactor life time and add cost to process operation. The impact can be minimized by lowering the process temperature but this could also bring down the catalyst activity. For fluidized bed, a refractory layer was typically applied inside the vessel to protect metal wall from abrasion. The refractories usually contains some level of iron. When exposed to methanol at 600C, the iron can also form metal catalyzed coke and pulverize refractory into small particles. In other cases, if coking is so extreme, the refractory can peel away from the wall and fall into the reactor damaging the internals. This is referred to as 'jacking'. In such case, the refractory cannot be effective any more and may damage other reactor internals.

SUMMARY

[0008] The present subject matter relates to processes and apparatuses for toluene methylation in an aromatics complex for producing paraxylene. More specifically, the present disclosure relates to processes and apparatuses for toluene methylation within an aromatics complex for producing paraxylene wherein a layer of special refractory material has been applied to the internal wall of the reactor. The iron in the material has been passivated; therefore it cannot catalyze coke formation and has no issue with metal dusting. Additionally, the layer of refractory materials can act as thermal barrier to allow the metal wall stay at lower

temperature than the process temperature, thus to further reduce the coke formation on the wall. The refractory may be applied to both fixed bed reactor and fluidized bed reactor.

[0009] Additional objects, advantages and novel features of the examples will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following description and the accompanying drawings or may be learned by production or operation of the examples. The objects and advantages of the concepts may be realized and attained by means of the methodologies, instrumentalities and combinations particularly pointed out in the appended claims.

DEFINITIONS

[0010] As used herein, the term “stream”, “feed”, “product”, “part” or “portion” can include various hydrocarbon molecules, such as straight-chain, branched, or cyclic alkanes, alkenes, alkadienes, and alkynes, and optionally other substances, such as gases, e.g., hydrogen, or impurities, such as heavy metals, and sulfur and nitrogen compounds. Each of the above may also include aromatic and non-aromatic hydrocarbons.

[0011] Hydrocarbon molecules may be abbreviated C₁, C₂, C₃, C_n where “n” represents the number of carbon atoms in the one or more hydrocarbon molecules or the abbreviation may be used as an adjective for, e.g., non-aromatics or compounds. Similarly, aromatic compounds may be abbreviated A₆, A₇, A₈, A_n where “n” represents the number of carbon atoms in the one or more aromatic molecules. Furthermore, a superscript “+” or “-” may be used with an abbreviated one or more hydrocarbons notation, e.g., C₃₊ or C₃₋, which is inclusive of the abbreviated one or more hydrocarbons. As an example, the abbreviation “C₃₊” means one or more hydrocarbon molecules of three or more carbon atoms.

[0012] As used herein, the term “zone” can refer to an area including one or more equipment items and/or one or more sub-zones. Equipment items can include, but are not limited to, one or more reactors or reactor vessels, separation vessels, distillation towers, heaters, exchangers, pipes, pumps, compressors, and controllers. Additionally, an equipment item, such as a reactor, dryer, or vessel, can further include one or more zones or sub-zones.

[0013] As used herein, the term “rich” can mean an amount of at least generally 50%, and preferably 70%, by mole, of a compound or class of compounds in a stream.

DETAILED DESCRIPTION

[0014] The following description is not to be taken in a limiting sense, but is made merely for the purpose of describing the general principles of exemplary aspects. The scope of the present disclosure should be determined with reference to the claims.

5 **[0015]** The claimed invention comprises a first embodiment wherein a toluene methylation process or apparatus for alkylating an aromatic hydrocarbon reactant with an alkylating reagent comprising methanol to produce an alkylated aromatic product, comprising a reactor having a refractory. The refractory lines the inside of the toluene methylation reactor. The iron in the material has been passivated; therefore it cannot catalyze coke
10 formation and has no issue with metal dusting. Additionally, the layer of refractory materials can act as a thermal barrier to allow the metal wall to stay at lower temperature than the process temperature, thus to further reduce the coke formation on the wall. The refractory may be applied to both fixed bed reactor and fluidized bed reactor. The refractory material uses liquid phosphate as the chemical binder system. The iron inside the refractory is
15 passivated by the phosphor and cannot catalyze the coke formation. The mixed oxide can be applied to a holding structure which is attached to the internal reactor wall. The reactor comprises a temperature of 500°C to 700°C. The reactor comprises an operating bed density of 0.05 kg/m³ to 0.29 kg/m³. The weight hourly space velocity of the reactor is 4 hr⁻¹ to 20 hr⁻¹. The weight hourly space velocity of the reactor is 10 hr⁻¹. The reactor may operate at a
20 pressure of 1 barg to 10 barg.

[0016] The second embodiment of the claimed invention comprises a benzene methylation process for alkylating an aromatic hydrocarbon reactant with an alkylating reagent comprising methanol to produce an alkylated aromatic product, comprising a reactor having a refractory. The refractory lines the inside of the benzene methylation reactor. The
25 iron in the material has been minimized; therefore it cannot catalyze coke formation and has no issue with metal dusting. Additionally, the layer of refractory materials can act as thermal barrier to allow the metal wall stay at lower temperature than the process temperature, thus to further reduce the coke formation on the wall. The refractory may be applied to both fixed bed reactor and fluidized bed reactor. The mixed oxide can be applied to a holding structure
30 which is attached to the internal reactor wall. The reactor comprises a temperature of 500°C to 700°C. The reactor comprises an operating bed density of 0.05 kg/m³ to 0.29 kg/m³. The

weight hourly space velocity of the reactor is 4 hr⁻¹ to 20 hr⁻¹. The weight hourly space velocity of the reactor is 10 hr⁻¹. The reactor may operate at a pressure of 1 barg to 10 barg.

EXAMPLES

[0017] The following examples are intended to further illustrate the subject embodiments.

- 5 These illustrations of different embodiments are not meant to limit the claims to the particular details of these examples.

Table 1

Material	Test Conditions	Weight gain (%)
Iron-passivated materials (Thermbond 12-L)	48 hours, 600°C	Negligible
AA-22S	48 hours, 650°C	7.5%
AA-22S	48 hours, 600C	0.7%

Table 2: Feed Composition

Component	Wt %
C ₅ -	1-4
A ₆ -A ₁₁	85-90
Water	6-9
MeOH	0.01-2.5

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[0018] There were four tests that were conducted using different refractory materials under different testing conditions. The first test was run with iron-passivated materials, more specifically Thermbond 12-L. The first test was conducted for 48 hours at 600°C using feed

15 1. The first test resulted in a negligible weight gain of coke, too close to zero to quantify. SEM analysis indicated that there was no presence of metal catalyzed coked, commonly known as ‘filamentous carbon with metal hats’. The refractory surface showed minimal evidence of coke deposition and no indication of metal dusting. The second test was run with a single component refractory material with Fe₂O₃ content of greater than 0.25 wt%, more

specifically AA-22S. The second test was conducted for 48 hours at 650°C using a feed mixture. The third test resulted in a 7.5% weight gain of coke. The refractory was coated in a layer of coke 1mm thick which would have resulted in the refractory pushing away from the wall, or jacking, in commercial operation. The third test was run with a single component refractory material with Fe₂O₃ content of >0.25 wt%, more specifically AA-22S. The third test was conducted for 48 hours at 600°C using a product mixture. The third test resulted in a 0.7% weight gain of coke. This sample had visible metal catalyzed coking on it that was perceivable without the aid of microscopic techniques.

[0019] It should be noted that various changes and modifications to the presently preferred embodiments described herein will be apparent to those skilled in the art. Such changes and modifications may be made without departing from the spirit and scope of the present subject matter and without diminishing its attendant advantages.

SPECIFIC EMBODIMENTS

[0020] While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

[0021] A first embodiment of the invention is an apparatus for alkylating an aromatic hydrocarbon reactant with an alkylating reagent comprising methanol to produce an alkylated aromatic product, comprising a line comprising the aromatic hydrocarbon in upstream communication with a reactor having an inner refractory lining; and a line in downstream communication with the reactor comprising the alkylate aromatic product, produced by reaction of the aromatic reactant and the alkylating reagent, from the reactor. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the aromatic hydrocarbon reactant includes toluene, the alkylating reagent includes methanol, and the alkylated aromatic product includes xylene. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the aromatic hydrocarbon reactant includes benzene, the alkylating reagent includes methanol, and the alkylated aromatic product includes xylene. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein

the reactor operates at a temperature of 500°C to 700°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the reactor operates at a pressure of 1 barg to 10 barg. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first
5 embodiment in this paragraph, wherein the entire inside lining of the reactor is coated with the refractory. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the refractory comprises a mixed oxide refractory prepared using liquid phosphate as a chemical binder. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up
10 through the first embodiment in this paragraph, wherein the refractory comprises minimal iron content. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, wherein the refractory comprises passivated iron. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph, further
15 comprising an addition line in upstream communication with the reactor comprising water.

[0022] A second embodiment of the invention is 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 into a reactor having an inner refractory lining; and recovering the alkylate aromatic product, produced by reaction of
20 the aromatic reactant and the alkylating reagent, from the reactor. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the aromatic hydrocarbon reactant includes toluene, the alkylating reagent includes methanol, and the alkylated aromatic product includes xylene. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up
25 through the second embodiment in this paragraph, wherein the aromatic hydrocarbon reactant includes benzene, the alkylating reagent includes methanol, and the alkylated aromatic product includes xylene. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the reactor operates at a temperature of 500°C to 700°C. An embodiment of the invention is
30 one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the reactor operates at a pressure of 1 barg to 10 barg. An

embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the entire inside lining of the reactor is coated with the refractory. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the refractory comprises a mixed oxide refractory prepared using liquid phosphate as a chemical binder. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the refractory comprises minimal iron content. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, wherein the refractory comprises passivated iron. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph, further comprising adding water to the reactor.

[0023] Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present invention to its fullest extent and easily ascertain the essential characteristics of this invention, without departing from the spirit and scope thereof, to make various changes and modifications of the invention and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims. In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

CLAIMS:

1. An apparatus for alkylating an aromatic hydrocarbon reactant with an alkylating reagent comprising methanol to produce an alkylated aromatic product, comprising:
 - a line comprising the aromatic hydrocarbon in upstream communication with a reactor
5 having an inner refractory lining on an inner surface of the reactor, wherein the reactor operates at a temperature in the range of 500 and a pressure in the range of 1 barg to 10 barg; and
 - a line in downstream communication with the reactor comprising the alkylate aromatic product, produced by reaction of the aromatic reactant and the alkylating
10 reagent, from the reactor, wherein an entire inside lining of the reactor is coated with the inner refractory lining and the inner refractory lining comprises Fe_2O_3 passivated with phosphate.
2. The apparatus of claim 1, wherein the aromatic hydrocarbon reactant includes toluene, the alkylating reagent includes methanol, and the alkylated aromatic product includes
15 xylene.
3. The apparatus of claim 1, wherein the aromatic hydrocarbon reactant includes benzene, the alkylating reagent includes methanol, and the alkylated aromatic product includes xylene.
4. The apparatus of claim 1, wherein the refractory comprises a mixed oxide
20 refractory prepared using liquid phosphate as a chemical binder.
5. 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 into a reactor having an inner refractory lining
25 on an inner surface of the reactor, wherein the reactor operates at a temperature in the range of 500 °C to 700 °C and a pressure in the range of 1 barg to 10 barg; and
 - recovering the alkylate aromatic product, produced by reaction of the aromatic reactant and the alkylating reagent, from the reactor, wherein an entire inside lining of the reactor is coated with the inner refractory lining and the inner refractory lining comprises Fe_2O_3 passivated with phosphate.

6. The process of claim 5, wherein the aromatic hydrocarbon reactant includes toluene, the alkylating reagent includes methanol, and the alkylated aromatic product includes xylene.

5 7. The process of claim 5, wherein the aromatic hydrocarbon reactant includes benzene, the alkylating reagent includes methanol, and the alkylated aromatic product includes xylene.