

**PROCESSES AND SYSTEMS FOR OBTAINING AROMATICS FROM
CATALYTIC CRACKING HYDROCARBONS**

CROSS-REFERENCES TO RELATED APPLICATIONS

- [0001] This Application claims the benefit under 35 U.S.C. § 119(e) of U.S.
5 Provisional Patent Application Ser. No. 61/711,934 filed October 10, 2012, which is
incorporated herein by reference in its entirety as if fully set forth herein.

BACKGROUND OF THE INVENTION

- [0002] Xylene isomers, orthoxylene (OX), metaxylene (MX), and paraxylene (PX),
and ethylbenzene (EB) are C₈ aromatics from reforming process or other petrochemical
10 processes. The purified individual xylene products are used on a large scale as industrial
solvents and intermediates for many products. The most important isomer, PX, is used for the
production of terephthalic acid (TPA) and dimethyl terephthalate (DMT), which are used for
the production of fibers, films and polyethylene terephthalate (PET) bottles. In these
applications high purity (>99.7%) PX is required. Demand for high purity PX has increased
15 greatly over the past years to meet rapidly growing markets.

- [0003] Traditional feedstock for aromatics and paraxylene production is catalytic
reforming (reformate) or pyrolysis (pygas). Catalytic cracking, or fluid catalytic cracking
(FCC), including various variations such as DCC, High-Severity FCC (HS-FCC), Residue
FCC (RFCC), is another well-known process that produces fuels, light olefins, and a similar
20 C₆ to C₁₀₊ aromatics rich stream, known as catalytic naphtha, cat naphtha, or FCC gasoline.

- [0004] Until recently, refiners did not consider recovering aromatics from FCC
gasoline, because the extraction technology would not function with olefinic or sulfur
impurities in the feed. There is a known technology which is designed specifically to make
this operation by extraction, which permits the direct recovery of aromatics, while rejecting
25 the olefin-rich fraction as raffinate. The sulfur species are also extracted into the aromatic
fraction, which are removed in the downstream impurity removing step in the absence of
olefins.

- [0005] There is a known technology, namely Aromatization, to take olefinic
hydrocarbon streams, as well as paraffinic or other type hydrocarbon streams, and produces

BTX (benzene, toluene, and xylenes). This process technology will take any olefinic components in the C₄-C₈ range as feed to produce the aromatics. Byproducts are light paraffins and LPG off gases.

[0006] It is known to produce xylenes by methylation of toluene and/or benzene, for instance methylation of toluene over catalyst using methanol. The feedstock can be toluene, benzene, or a mixture of toluene and benzene, or a pygas feedstock, or a reformat feedstock, and the methylation product has higher paraxylene content than the paraxylene content of the feedstock.

[0007] There are other xylene formation technologies known to the industry which use benzene, toluene, C₉-C₁₀ aromatics, or a combination of them as feedstock. Examples of these are benzene/C₉-C₁₀ transalkylation, toluene/C₉-C₁₀ transalkylation, benzene/toluene/C₉-C₁₀ transalkylation, toluene disproportionation (TDP), selective toluene disproportionation (STDP).

[0008] To date, the art does not disclose a practical process for production of paraxylene from light catalytic cracking hydrocarbons and catalytic naphtha. In addition, the above processes have not been integrated into a single system that creates significant advantages, including higher xylene yields and lower energy consumption over operation of these processes separately.

[0009] In present invention, an improved process is disclosed which uses light and heavy hydrocarbons as feedstock particularly the light and heavy hydrocarbons from catalytic cracking unit, including, in embodiments, the combination of various streams and processes which provides significant advantages over prior systems.

SUMMARY OF THE INVENTION

[00010] In various embodiments, systems and processes for producing paraxylene from catalytic cracking hydrocarbons are disclosed. The methods comprise: 1) a separation section to separate C₅ and C₁₀₊ from the C₅₊ catalytic naphtha, which also includes one extraction zone to separate C₆-C₉ non-aromatics from C₆-C₉ aromatics; 2) an aromatization section to form aromatics from C₄-C₉ non-aromatics (or a subset) that contains significant amount of olefins; 3) providing an optional impurity removal section to clean the aromatics before they are sent to the downstream processes; 4) a second separation section to

separate C₆-C₇, C₈, C₉₊ streams, and to separate non-aromatics in the C₆-C₇ or C₆-C₈ stream to yield high purity aromatics, as final product or as feedstock for downstream paraxylene production section or xylene formation processes; 5) a xylene production section which includes paraxylene separation zone and xylene isomerization zone. The paraxylene separation zone can use crystallization method or adsorption method or a combination of these to produce high-purity paraxylene. The xylene isomerization zone can use EB-dealkylation type of catalyst or EB-isomerization type of catalyst to convert EB either to benzene or xylene; 6) optionally inclusion of a xylene formation section, which include one or more of the following processes: benzene methylation, toluene methylation, benzene/toluene methylation, benzene/C₉-C₁₀ transalkylation, toluene/C₉-C₁₀ transalkylation, benzene/toluene/C₉-C₁₀ transalkylation, toluene disproportionation (TDP), selective toluene disproportionation (STDP).

BRIEF DESCRIPTION OF THE DRAWINGS

[00011] For a more complete understanding of the present disclosure, and the advantages thereof, reference is now made to the following descriptions to be taken in conjunction with the accompanying drawings describing specific embodiments of the disclosure, wherein:

[00012] FIG. 1 shows an illustrative paraxylene production system from catalytic cracking C₄-C₁₀₊ stream with option to include reformat and pygas feedstock in accordance with an embodiment of the invention; and

[00013] FIG. 2 shows an illustrative paraxylene production system from catalytic cracking C₄-C₁₀₊ stream with option to include reformat and pygas feedstock and additional xylene formation systems for additional paraxylene production in accordance with an embodiment of the invention.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[00014] In the following description, certain details are set forth such as specific feedstock, quantities, temperature, etc. so as to provide a thorough understanding of the present embodiments disclosed herein. However, it will be obvious to those skilled in the art that the present disclosure may be practiced without such specific details. In many cases, details concerning such considerations and the like have been omitted inasmuch as such

details are not necessary to obtain a complete understanding of the present disclosure and are within the skills of persons of ordinary skill in the relevant art.

[00015] Fluid catalytic cracking is the most important conversion process used in petroleum refineries. It is widely used to convert the high-boiling, high-molecular weight hydrocarbon fractions of petroleum crude oils to more valuable gasoline, olefinic gases, and other products. There are different variations of the technology for different purposes, and there is a trend to increase the cracking severity to increase propylene yield from the system. High-severity FCC is intended to increase olefin yields, driven by the fast growing global demand for propylene. The propylene yields can be increased from 3-5% in conventional FCC to 15-28% when these units are operated at high severity. In high-severity FCC operation, the aromatic content in the cracked naphtha product is 50-70%, which is suitable for aromatics recovery, but, it contains significant amounts of thiophenic sulfur impurities and is highly olefinic. For example, Sinopec/Shaw's Deep Catalytic Cracking (DCC) uses heavy hydrocarbon feedstocks, such as VGO, VR or VGO blended with DAO to produce light olefins (ethylene, propylene and butylenes), LPG, gasoline, and middle distillates etc.

[00016] Aromatics cannot be directly recovered at high purity by conventional distillation, because of the close-boiling components and azeotropes which form with the aromatics. Therefore, the aromatics are typically recovered by extraction with a selective solvent. This can be accomplished either by liquid-liquid extraction, or by extractive distillation. Extractive distillation offers better plant economics and flexibility, and is generally preferred for BTX purification.

[00017] Until recently, refiners did not consider recovering aromatics from FCC gasoline, because the extraction technology would not function with olefinic or sulfur impurities in the feed. The new technology is designed specifically to make this operation by extraction, which permits the direct recovery of aromatics, while rejecting the olefin-rich fraction as raffinate. The sulfur species are also extracted into the aromatic fraction, which are removed by hydrotreatment in the absence of olefins. Thus, there is very little hydrogen consumption and no octane loss. The hydrogenation unit is much smaller than conventional, and can be a simple HDS design or other means. The raffinate from the extraction unit can be sweetened in a conventional caustic unit, or used directly in the gasoline. However, the raffinate stream contains significant amount of olefins and is an ideal feedstock for aromatization process to produce aromatics.

[00018] The aromatization process takes olefinic hydrocarbon streams and produces BTX, with an aromatic yield approximating the concentration of olefins in the feed. This process technology will take any olefinic components in the C₄-C₉ range as feed to produce the aromatics. Byproducts are light paraffins and LPG off gases. The unit can take
5 the FCC C₄ and C₅ cuts along with the C₆-C₉ raffinate from catalytic cracking naphtha extraction unit mentioned above as feed to add another aromatics increment.

[00019] In the process illustrated in FIG. 1, the catalytic cracking naphtha (C₅+ stream) is first sent to a Separation Section 101, where C₅ and C₁₀+ streams are separated from the rest by distillation. The C₆-C₉ stream is then sent to extraction zone to separate non-
10 aromatics from aromatics. The extraction zone can use extractive distillation method or liquid-liquid extraction method. The C₄ stream from catalytic cracking unit and C₆-C₉ non-aromatics from Separation Section 101, along with other olefin rich feedstock (optional) are sent to the Aromatization Section 102 to produce aromatics. The Aromatization Section can contain one reactor or multiple reactors, and they can be fixed bed reactors or continuous
15 regeneration (CCR) type reactor systems.

[00020] The aromatics from the Separation Section 101 and Aromatization Section 102 are sent to an Impurity Removal Section 103, which can be optional depending on the impurities presented in the combined aromatics feed to the section. The Impurity Removal Section 103 can include one or more of the following processes to remove different
20 impurities: hydrogenation, adsorption, absorption, solvent extraction, etc.

[00021] The cleaned-up C₆+ stream from 103 is fed to a second Separation Section 104 to separate benzene, toluene, xylenes, C₉+. Optionally, traditional C₆+ feedstock can also be processed in this section, such as reformat and hydrotreated pygas. Usually C₆-C₇ streams are first separated by distillation and then fed to an aromatics extraction zone to
25 separate non-aromatics from C₆ and C₇ aromatics. The separation of C₆-C₇ non-aromatics from aromatics can be done using an extractive distillation method, liquid-liquid extraction method, or other methods known to the industry. C₆-C₇ aromatics from the extraction zone can be further separated to obtain individual benzene and toluene product. C₈ and C₉+ are also separated from the C₆+ feed stream by distillation. Sometimes the C₆-C₈ stream is separated
30 and fed to the aromatics extraction zone to purify C₆-C₈ aromatics. The C₉+ stream can be used elsewhere and C₈+ stream is sent to Paraxylene Production Section 105.

[00022] Production Section 105 includes two main zones: a paraxylene recovery zone and a xylene isomerization zone. The function of Paraxylene Production Section is to purify the paraxylene, and to convert non-paraxylene C8 aromatics to paraxylene. Two major methods can be used for paraxylene recovery: crystallization and
5 adsorption. A third method is a combination of these two. Xylene isomerization zone can use EB-isomerization type of catalyst, or EB-dealkylation type of catalyst.

[00023] In the method illustrated in FIG. 2, it is similar to the method illustrated in Figure 1 except for the addition of Xylene Formation Section 106. The second Separation Section 104 can be optional and in this section C₉-C₁₀₊ stream is also separated
10 from C₉+ stream in the distillation zone, which can be used as feedstock for the Xylene Formation Section 106. The extraction zone in the second Separation Section 104 can be optional, as the C₆-C₇ stream is consumed in the downstream Xylene Formation Section and does not required high purity. The addition of the Xylene Formation Section allows utilization of the available benzene rings to form xylenes; the resulted xylenes are then
15 recovered in the Paraxylene Production Section. One or more of the following technologies or processes (but not limited to) can be included in the Xylene Formation Section: benzene methylation, toluene methylation, benzene/toluene methylation, benzene/C₉-C₁₀ transalkylation, toluene/C₉-C₁₀ transalkylation, benzene/toluene/C₉-C₁₀ transalkylation, toluene disproportionation (TDP), selective toluene disproportionation (STDP).

[00024] To save the number of pieces of equipment and investment cost, some of the equipment in one section can be shared with other sections. For example, the benzene and toluene columns in the distillation zone of the second Separation Section 104 can be
20 shared with the transalkylation process in the Xylene Formation Section 106.

[00025] From the foregoing description, one skilled in the art can easily
25 ascertain the essential characteristics of this disclosure, and without departing from the spirit and scope thereof, can make various changes and modifications to adapt the disclosure to various usages and conditions. The embodiments described hereinabove are meant to be illustrative only and should not be taken as limiting of the scope of the disclosure, which is defined in the following claims.

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CLAIMS

What is claimed is:

1. A process for producing paraxylene from light and heavy hydrocarbons, particularly C₄ stream and C₅₊ naphtha stream from catalytic cracking unit, said process comprising:
 - a) separating a C₅-C₉ non-aromatics stream and a first C₆-C₁₀₊ aromatics stream from the C₅₊ catalytic naphtha stream;
 - b) forming a second C₆-C₁₀ aromatics stream from the C₄ stream and the C₅-C₉ non-aromatics stream in an aromatization unit, wherein at least one of the C₄ stream and the C₅-C₉ non-aromatics stream contains olefins;
 - c) removing impurities from the first and second C₆-C₁₀ aromatics streams to create a purified C₆-C₁₀ aromatics stream before they are sent to the downstream processes;
 - d) separating from the purified C₆-C₁₀ aromatics stream, a C₆-C₇ stream, a C₈ stream and a C₉₊ stream;
 - e) feeding the C₈ stream into a paraxylene production section to produce a paraxylene product.
2. The process of claim 1, wherein step a) includes a distillation step and an extraction step.
3. The process of claim 2, wherein said extraction step is carried out by using extractive distillation method or liquid-liquid extraction method.
4. The process of claim 1, wherein step b) is carried out in a single reactor or multiple reactors that are fixed bed reactors or continuous regeneration (CCR) type reactor systems.
5. The process of claim 1, wherein said C₄-C₉ non-aromatics or the subset in step b) contains 15-85 wt% olefins.

6. The process of claim 1, wherein the removing of impurities in step c) is carried out using hydrogenation, adsorption, absorption, or solvent extraction, or a combination thereof.
7. The process of claim 1, wherein the removing of impurities in step c) is optional.
8. The process of claim 1, wherein step d) includes a distillation step and an extraction step.
9. The process of claim 8, wherein said extraction step is carried out by using extractive distillation method, or liquid-liquid extraction method.
10. The process of claim 1, wherein the production of paraxylene includes paraxylene recovery and xylene isomerization.
11. The process of claim 10, wherein paraxylene recovery is carried out by using a crystallization method or adsorption method or a combination thereof.
12. The process of claim 10, wherein xylene isomerization uses EB-isomerization type of catalyst or EB-dealkylation type of catalyst.
13. A process for producing paraxylene from light and heavy hydrocarbons, particularly C₄ stream and C₅₊ naphtha stream from catalytic cracking unit, said process comprising:
 - a) separating a C₅-C₉ non-aromatics stream and a first C₆-C₁₀ aromatics stream from the C₅₊ catalytic naphtha stream;
 - b) forming a second C₆-C₁₀ aromatics stream from the C₄ stream and the C₅-C₉ non aromatics stream in an aromatization unit, wherein at least one of the C₄ stream and the C₅-C₉ non-aromatics stream contain olefins;
 - c) removing impurities from the first and second C₆-C₁₀ aromatics streams to create a purified C₆-C₁₀ aromatics stream before they are sent to the downstream processes;
 - d) separating from the purified C₆-C₁₀ aromatics stream, a C₆-C₇ stream, a first C₈ stream, a C₉-C₁₀ stream and a C₁₁₊ stream;

e) feeding the C₆-C₇ stream and the C₉-C₁₀ stream into a xylene formation section to form a second C₈ stream; and

f) feeding the first and second C₈ stream into a paraxylene production section to produce a paraxylene product.

14. The process of claim 13, wherein step a) includes a distillation step and an extraction step.

15. The process of claim 14, wherein said extraction step is carried out by using extractive distillation method or liquid-liquid extraction method.

16. The process of claim 13, wherein step b) is carried out in a single reactor or multiple reactors that are fixed bed reactors or continuous regeneration (CCR) type reactor systems.

17. The process of claim 13, wherein said C₄-C₉ non-aromatics or the subset in step b) contains 15-85 wt% olefins.

18. The process of claim 13, wherein the removing of impurities in step c) is carried out using hydrogenation, adsorption, absorption, or solvent extraction, or a combination thereof.

19. The process of claim 13, wherein the removing of impurities in step c) is optional.

20. The process of claim 13, wherein the separation of the purified C₆-C₁₀ aromatics stream in step d) includes a distillation step and an extraction step.

21. The process of claim 20, wherein said extraction step is carried out by using extractive distillation method, or liquid-liquid method.

22. The process of claim 13, wherein the production of paraxylene includes paraxylene recovery and xylene isomerization.

23. The process of claim 22, wherein paraxylene recovery is carried out using a crystallization method or adsorption method or a combination thereof.

24. The process of claim 22, wherein xylene isomerization uses EB-isomerization type of catalyst or EB-dealkylation type of catalyst.

25. The process of claim 13, wherein the production of xylenes uses benzene methylation, toluene methylation, benzene/toluene methylation, benzene/C₉-C₁₀ transalkylation, toluene/C₉-C₁₀ transalkylation, benzene/toluene/C₉-C₁₀ transalkylation, toluene disproportionation (TDP), selective toluene disproportionation (STDP) or a combination thereof.