The Petrochemistry of Paraxylene
Understanding the basics of the paraxylene manufacturing process
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The demand for para-di-methyl benzene, more commonly known as paraxylene (PX), is continuing to grow due to its use as a raw material in the polyester chain. Since 2009, PX demand has risen by 6% per annum, with predictions of increases by 5.1% per year from 2014 to 2018.

Key factors surrounding the production of paraxylene are:

- Economics of scale. There are multiple process units and an extensive infrastructure required to produce paraxylene. The scale of process facilities has increased to gain production economy.
- Raw materials shortage. Because of the high demand for paraxylene, the traditional sources of feedstock are insufficient to produce the large quantity of product needed, especially on a regional basis.
- Transparency. Persons in the industry often confuse technology brand names with process functionality, overlooking the opportunity to optimize the operation with ‘black boxes’.

It is important to understand the basics of paraxylene production, so that engineers can avail themselves of the latest technology and improvements available to use for PX production in the most cost effective manner.

To guide understanding, the elements of production are broken down into the following steps:

- Aromatics generation.
- Aromatics interconversion.
- Paraxylene recovery and purification.

**Aromatics Generation**

The PX molecule is a benzene ring with two methyl groups arranged at opposite ends, and is typically created by catalytic reforming or thermal cracking of naphtha. The most common source of feed is heavy naphtha from refinery streams or condensate from gas fields, which is reformed into a product called catalytic reformate. Pyrolysis gasoline by-product from steam cracker petrochemical plants, and coke oven light oil (COLO) from steel production are used to a lesser extent.
Traditional feed sources

In some regions of the world, there is not enough heavy naphtha to reform into aromatics, creating an incentive to use non-traditional sources of feed. In actuality, some of the non-traditional feeds are more economical to use in any case, making these an important part of a competitive operation.

Among the non-traditional sources of xylenes are those contained within fluid catalytic cracking (FCC or RFCC) gasoline fractions. These aromatics already exist, but happen to be comingled with sulfur and olefins, which are difficult to remove by conventional techniques.

New process technology\(^2\) is now available to purify these aromatics by direct extraction from the raw FCC gasoline. This is in contrast to the practice used by several major producers, which recycles the FCC gasoline back through the naphtha hydrotreater and reforming units as an indirect means of purification and recovery. In such cases, the utility of the NHT/reformer is wasted.

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\(^2\) The diagram is labeled with different process units and products, indicating the flow of the aromatics generation process. The labels include:
- Catalytic Reformer
- Pygas
- COLO
- Hydrotreated Naphtha
- Xylene Column
- Toluene Column
- Benzene Column
- Paraxylene Recovery
- Aromatics Extraction
- Transalkylation
- GT-TolAlk™
- Flows of C5, C7, C9/C10, C11+, C1/C16, C2-C4 Raffinate, and MeOH are shown in the diagram.
The trend in industry is to operate the FCCU at higher severity to yield more propylene. The higher severity operation also increases the aromatics yield, making this source of raw material especially valuable. A beneficial side effect of aromatics extraction from the raw gasoline is that the aromatics content of the gasoline is diminished, as well as eliminating the problem of benzene in gasoline. Sulfur is removed to the specifications for Euro 5 or US Tier 3 grades of gasoline without any loss of octane value, as the unsaturated components never go to the hydrotreater units.

Another non-traditional source of aromatics derives from the olefinic fraction of FCC gasoline. It is convenient to create aromatics by aromatization of the olefins from the C4 - C8 boiling range, as these components are more reactive than paraffins from naphtha or condensate. The C4 - C5 olefins can be obtained by direct fractionation out of the FCC unit, while the C6 - C8 fraction comes from the raffinate of the extraction unit. Both of these can be combined to the aromatization unit, which coincidently reduces gasoline production from the FCC unit.

Figure 2 Aromatics recovery from FCC gasoline.
A third non-conventional source of aromatic raw material comes from methanol via the methanol to aromatics (MTA) process. Methanol can also supplement aromatics production via the toluene methylation process. Naphtha is a product of crude oil, while methanol is produced from natural gas. There are long-term pricing trends which favor gas-based chemicals over oil-based chemicals, so that these methods can become a major contributor to the pool of xylenes.

**Aromatics Interconversion**

The next important step in the chain of technologies to produce paraxylene is to convert all of the aromatics from the above stated processes, into paraxylene. The materials are first converted into a mixture of xylenes by an aromatics interconversion process, and then paraxylene is extracted.
It is helpful to consider that dimethyl benzene, commonly called xylene, contains eight carbons, consisting of a stable ring with six carbons, and two methyl groups of one carbon each. If the feedstock generation operations create molecules with a six carbon ring and only one or no methyl groups, then one must add methyl groups to adjust the molecule to the eight carbons required. If there are too many methyl groups (or higher alkyl groups) from C9+ aromatics, then these need to be removed to get back to eight carbons. Even for the 8 carbon aromatic molecules with two methyl groups, there is still the need to rearrange the position of the methyl groups on the aromatic rings to produce PX, which is 1, 4-di methyl benzene.

These are the relevant unit operations to transform aromatic species into other types by shifting alkyl groups.

- Hydrodealkylation (HDA) removes all alkyl groups from the benzene ring. This process makes on-purpose benzene instead of xylenes.
- Transalkylation (TA) is the broad category of processes which move methyl groups to a ring with a different number of carbon molecules. The distribution of methyl groups among aromatic rings tends toward an equilibrium based on the ratio of phenyl : methyl groups in the starting feeds.
- Toluene disproportionation (TDP) or selective toluene disproportionation (STDP) are processes which use only toluene as feedstock and produce benzene plus xylenes. The selective version makes xylenes with above equilibrium concentration of paraxylene. This makes it easier to produce the high purity PX, though other drawbacks mitigate this advantage.
• Toluene alkylation (TolAlk or TM) adds methyl groups, typically using methanol as the source of the CH$_3$. A selective version makes a concentration of PX among the isomers of dimethyl benzene along with other unwanted by-products and higher catalyst coking.

![Diagram of Toluene alkylation](image)

**Figure 5** Toluene alkylation, adds methyl groups.

**Isomerization**

Xylene isomerization rearranges the two methyl groups on the aromatic ring to an equilibrium distribution of para, meta, and ortho positions. This ratio is roughly 1:2:1. As paraxylene is depleted in the paraxylene recovery unit, the isomerization unit reestablishes the equilibrium, by converting metaxylene and orthoxylene back into paraxylene. The other isomers are recycled to extinction.

There are two versions of the isomerization catalyst, which convert the ethylbenzene differently. The EB dealkylation (cracking) type converts the ethylbenzene into benzene plus fuel gas. The EB isomerization type converts EB into xylenes, through a complex set of intermediates and additional recycle.

Virtually all paraxylene production facilities have xylene isomerization, in order to gain much more product from a given feedstock.

**Paraxylene Recovery and Purification**

There are three commercial processes available to purify paraxylene from mixture of xylenes.

- Crystallization
- Adsorption, particularly prone to 'black box syndrome'
- Hybrid of crystallization plus adsorption
Crystallization
Paraxylene has a freezing point of +14 °C, which is much higher than the other C8 aromatics. As such, crystallization has been the historical method of choice to separate pure paraxylene. When the mixed xylenes are cooled, paraxylene will progressively precipitate out of solution as pure crystals, which are centrifuged and washed with melted product to remove the residual impurities. The depleted paraxylene mother liquor is recycled to the isomerization unit to establish again the equilibrium.

The advantages of crystallization are that the product is easy to purify, and the units are simple to operate. With an updated flow scheme and reliable equipment choices, crystallization has capital and operating cost advantages.
One of the disadvantages of crystallization for PX recovery is the lower per pass recovery of the product. As the feed mixture is cooled, there is a minimum temperature, where the other C8 aromatics begin to freeze together with the paraxylene. This is called the eutectic point. The eutectic typically limits the per pass recovery to about 65% on equilibrium reformate xylenes, and requires a low temperature refrigeration system. Even so, crystallization is quite competitive with adsorption systems. However, if the feed is enriched in PX by another means (such as selective toluene disproportionation), the per pass recovery is up to 95% and the refrigeration requirements are diminished, making crystallization a much better method for purifying the product compared to adsorption.

**Adsorption**

Selective adsorption separates the xylene isomers on molecular sieve type material. The process flow scheme is set to establish a counter current contacting of the C8 aromatics with the sorbent, by the concept of a simulated moving bed (SMB) arrangement. The hydrocarbon is sequentially adsorbed and desorbed onto the sieve to create a concentration profile such that the high purity product can be withdrawn from the system at one point and the low purity residual xylenes taken out at a different point. The extract and raffinate streams are further distilled from the desorbent before final product or recycle to the isomerization units.

The main advantage of the SMB system is the higher PX recovery per pass. This reduces the recycle to the isomerization unit.

A major disadvantage of the adsorption method for PX recovery is the difficulty to meet product purity. This can be seen in commercial designs by looking at the volume of adsorbent dedicated to the purification zone. In addition, there are several ways for impurities to contaminate the PX, which requires extreme measures for impurity removal and process control. These are all additive, so a small deviation in any one of these can cause the entire product to become off spec.

- C9 contamination from the xylene column.
- Desorbent contamination from the extract column.
- Raffinate contamination of the desorbent in the raffinate column, which recontacts with the final PX product.
- Leaks in the switching valves, or incomplete flushing of the adsorption chamber lines, allowing impurities to contact the final product.
- Toluene contamination from pre- or post-fractionation towers.
- Ineffective adsorption due to mal-distribution across the adsorption chamber grids, leading to poor performance.
• Ageing adsorbent media over time, or mechanical weakness resulting in poor purification or complete failure.

• Mechanical weakness of the adsorbent in which fine or small pieces of the adsorbent plug the support screens and interfere with the approach to plug flow.

The adsorption systems are also prone to the 'black box syndrome', where users face difficulties in learning about the functional aspects of the process, and are discouraged from taking help from competent technical service providers outside of the original licensor.

Hybrid of crystallization and adsorption
An interesting alternative is a hybrid of crystallization and adsorption. This captures the advantages of both processes, and avoids the disadvantages from each in a stand-alone operation.

In the traditional adsorption system, about half of the separations energy is used to concentrate the feed to 90% purity; the other half is required to attain 99.8%. The hybrid process uses a single stage crystalliser to make the final purification of paraxylene, thus avoiding the high cost and reliability problems with standalone adsorption units.
The process additionally:

- Combines robust purity of crystallization with high recovery of SMB systems.
- Utilizes Zeosorb® PX-200 from Clariant® for high capacity, selectivity and crush strength.
- Enables cost advantages with the optimized combination of SMB, crystallization and absorbent.

The hybrid process is especially robust for large scale units, as the size of the adsorption chamber size can be reduced and the risks associated with an imperfect approach to plug flow are eliminated.

*Stream is sent to Aromatics Complex for Benzene and Paraxylene recovery*
Case Study
One unit in Europe is designed to convert all potential feed molecules into paraxylene and benzene, with no gasoline. The process design shown in Figure 8 uses aromatics extraction from FCC gasoline with aromatization as two primary units to generate the aromatics feedstock. There is supplemental feed from steam cracker pyrolysis gasoline and reformate.

The balance of the operations recycle the toluene with heavy aromatics to a transalkylation unit to produce xylenes, recover paraxylene from among the C8 aromatics, and yield benzene from the surplus of phenyl groups in the mixture of aromatics. The product yield has higher value than gasoline in this region of the world.

Conclusion
It is important to understand the basics of paraxylene production, in order to appreciate the options for product mix, and to take advantage of the latest technology. Economy of scale is not the most important determinant of a profitable operation.

Some unique options distinguish the operation from traditional designs, and address the specific need at an individual producer’s site:

- GT-BTX Plus®: Recovery of aromatics by direct extraction from FCC gasoline. This contrasts with recycle of these aromatics to the naphtha hydrotreater and reforming units.
- GT-AromatizationSM: Creates additional aromatics from the olefins in FCC gasoline. Alternatively, the olefins can be recracked to propylene.
- GT-TolAlkSM: Utilizes a lower cost raw material derived from natural gas in the aromatics complex. Toluene alkylation can eliminate benzene production, and is an essential process to convert all of the aromatic molecules into paraxylene.
- GT-HybridPXSM: Advantaged recovery method for paraxylene, especially suited for the revamp of existing crystallization or adsorption units, and for very large grassroots designs.

Notes
1. Aromatics refer to the sweet-smelling components containing a phenyl group (ie. benzene ring).
2. GT-BTX Plus® removes and purifies BTX from cracked gasoline such as FCC naphtha.
3. GT-AromatizationSM is a fixed bed catalytic process to create aromatics from olefins.
4. Cryst-PXSM: Updated flow scheme with improved heat integration make this the most efficient crystallization process for PX recovery.
5. GT-HybridPXSM: Paraxylene recovery method suited for revamping of existing crystallization or adsorption units as well as for very large grassroots designs.
6. Zeosorb® PX-200: Clariant adsorbent with high capacity, selectivity and crush strength.