Boost you Xylene Loop Performance with OPARIS™

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Introduction

Axens' ParamaX suite provides the petrochemical industry with a single-source solution for leading edge technologies and services linked to the production and purification of BTX aromatics. Whatever the required needs - from feasibility studies to full-scale grassroots complexes, individual new units or plant debottlenecking, from providing operator training to pre-commissioning, commissioning, start-up and continued services, from process simulators to advanced process control and plant optimization, from unit revamps to drop-in catalyst replacements - Axens, with our web of partnerships and quality design and services, provide solutions to all BTX production needs.

The BTX market, and especially the Paraxylene market, has been affected by economic turmoil and regional over-capacity. Today, there are some positive signs of recovery in the paraxylene market with predicted tight supply to occur in 2002-2003. As a consequence, new major projects will likely resurface to provide for additional capacity in the 2003-2004 timeframe. Experience learned from recent history will clearly favor units with very high single-train production rates, operational flexibility and minimized feed consumption, since these key factors provide for economic resistance during flat market conditions.

The reduction of total aromatics content in gasoline will be effective in 2005 in Western Europe and is likely to expand to other regions of the world. Integrating this new constraint on the gasoline pool will modify the demand and supply balance on the aromatics market, representing an incentive to integrate Paraxylene production facilities downstream of refinery. The Paraxylene market is known for its extreme fluctuations, and those who have survived through the latest down-side of the cycle know that the combination of high performance and versatility are key factors in maintaining plant profitability.
In this respect, the newly developed and commercialized Oparis® catalyst (OPptimized ARomatics ISomerization) for ethyl benzene (EB) and xylenes isomerization represents a breakthrough in terms of performance and activity. Oparis is the right answer for future grassroots applications. It is also ideally suited as a drop-in catalyst in existing units.

ParamaX: the technology and service platform

The ParamaX platform offers aromatics producers a single-source provider with unmatched performance and cost effectiveness for all BTX production goals. Technologies exclusively licensed and serviced by IFP in grassroots ParamaX packages are summarized in Table 1.

Table 1

Key ParamaX Technologies

Technology	Description	Origin
Aromizing	CCR reforming for aromatics production, featuring the *RegenC* catalyst regeneration system.	Axens
Arofining	Reformate purification for drastically reduced clay consumption.	Axens
Eluxyl	Simulated countercurrent adsorption para-xylene purification.	Axens
XyMax	EB dealkylating type Xylenes isomerization.	ExxonMobil
Morphylane	Toluene and high purity benzene extraction, recently integrated in the ParamaX platform.	Krupp Uhde
Oparis	Ultra-high performance C_8 aromatics (xylenes and ethylbenzene) isomerization technology and catalyst	Axens
Sulfolane	High purity benzene and high purity toluene liquid-liquid extraction. Also ideally suited for BTX extraction from pygas.	Lyondell
TransPlus	Toluene/heavy aromatics transalkylation, with the proven ability to process very high content C_{10}+ aromatics components in the fresh feed.	ExxonMobil

New motor gasoline specifications: the impact on the aromatics market

The restriction of total aromatics content in the gasoline pool (from 42% to 35%) will effect the supply of mixed xylenes in the aromatics petrochemical market. To meet this challenging constraint, refiners may consider extraction of excess aromatics, leading to a significant increment in benzene, toluene, and mixed xylenes for petrochemical production. Aromatics extraction is not the only means that will be implemented to meet the new specification, but in view of the relative market volumes of gasoline on one hand, and aromatics intermediates on the other hand (benzene and paraxylene essentially), it is evident that the new gasoline specifications will impact on the aromatics business. Excess aromatics from the gasoline pool will represent a new valuable source for the production of key aromatics intermediates.

Paraxylene market

Paraxylene production is driven by the fiber and PET resin market, which is growing at an estimated 6-7% per year for the next decade. These products are finding a broadening range of applications from textiles to packaging. The highest growth rates are anticipated principally in Asia. Recovering Asian economies will soon catch-up with the current oversupply situation, and allow for new capacity additions. Therefore, and in spite of its wide range cycles, the paraxylene market remains attractive.

Benzene

Benzene enjoys a growth rate that is roughly half of that of paraxylene. The benzene supply is more difficult to predict as this base chemical is a co-product from various sources;

- Extract from reformate C6 cut,
- Hydrodealkylate (HDA) from pygas cuts,
- co-product from disproportionation / transalkylation units included in latest PX plant configurations.

Because of this complex supply pattern, and with the uncertainty related to how refiners are going to handle the excess benzene issue, particularly in Europe and Japan, the benzene co-production option for new aromatics complexes requires careful consideration.

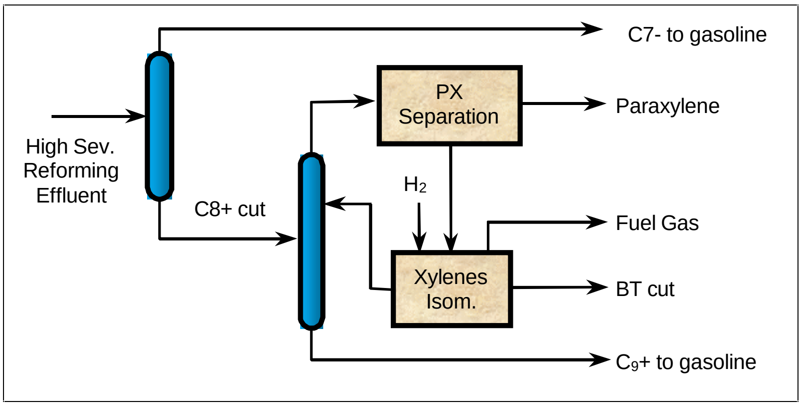
This brief analysis of the aromatics market and the impact of new gasoline specifications indicates future trends in the paraxylene production pattern:

- minimizing benzene side production due to a market surplus,
- privileged integration with refinery environment where excess mixed xylenes are available for processing.

Figure 1

Aromatics complex integration in refining environment

Mixed xylenes to PX route



Typical aromatics complex integration in a refinery environment (figure 1)

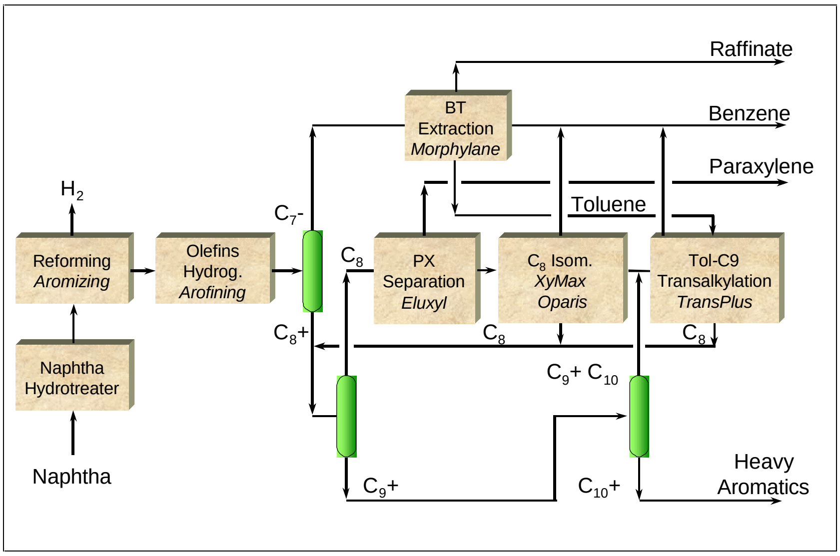
Starting from a fraction of full range high severity reforming, the C_8+ fraction is separated from the C_7- cut and the latter is routed to the gasoline pool. The C_8+ cut feeds what is commonly referred to as the Xylenes loop consisting in;

- a xylenes rerun tower, where C_8 aromatics compounds, originating from the net feed and the isomerization effluent, are separated from C_9+ material, the latter being routed to the gasoline pool,
- The C_8 aromatics taken overhead of the xylenes rerun feed the paraxylene separation section (Eluxyl, crystallization or combination of both). The PX depleted raffinate is then processed in the isomerization section, where the PX depleted C_8 aromatics stream is brought back to near equilibrium concentration. Depending on the type of isomerization unit, EB may be dealkylated to benzene at high conversion rates (XyMax) or isomerized to xylenes at equilibrium limited rate (Oparis).

This plant configuration significantly differs from the typical configuration of complexes erected in the mid-90's (shown in figure 2).

Figure 2

Typical aromatics complex from naphtha to PX



The proposed mixed xylenes to PX route (Figure 1) is a straightforward integration of a petrochemical facility into a refinery environment where excess aromatics are to be eliminated from the gasoline pool in an added value.

- Investment-wise, the mixed xylenes to PX route is much less expensive than the Naphtha to PX route since the aromatics production technologies are already in place,
- The use of EB isomerization type technology enables the elimination of benzene co-production from the xylenes loop.

Aromatics complex performance: introducing Oparis

Whatever the paraxylene production plant configuration, the feed cost represents from about 70% (naphtha to PX) to 80% (mixed xylenes to PX) of the PX production cost. Any improvement in feed consumption rates for an equivalent production of PX is therefore directly beneficial to plant profitability.

The key criteria in the evaluation of the xylenes loop performance is the paraxylene yield, i.e., the ratio of PX produced to the net C_8 aromatics fed to the loop. This ratio directly reflects the feed consumption of the complex. Three parameters affect this performance index:

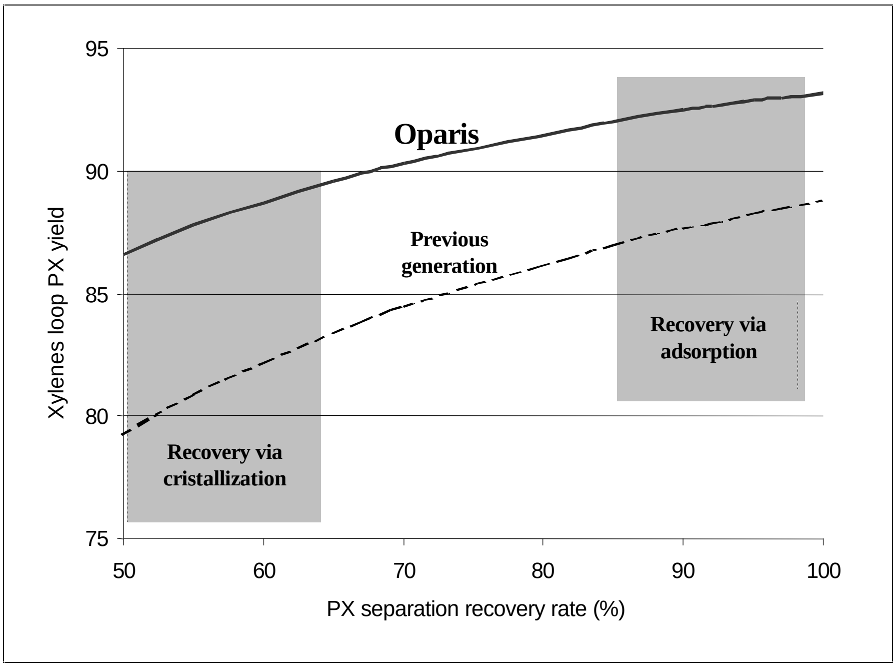
- xylenes isomerization selectivity - xylenes loss per pass is the most sensitive parameter;

- xylenes isomerization activity - EB and xylenes isomerization are equilibrium limited reactions - the closer the approach to equilibrium, the nearer to ideality the operation of the complex;
- PX separation recovery rate - unrecovered PX is recycled through the isomerization section and subject to consecutive per pass losses, that affect PX yield.

From both activity and selectivity point of views, Oparis represents a breakthrough that boosts xylenes loop performance. Figure 3 displays the impact of Oparis compared to former generation of catalysts as a function of PX recovery rate, demonstrating a huge gap in terms of performance.

Figure 3

Impact of isomerization performance on PX yield



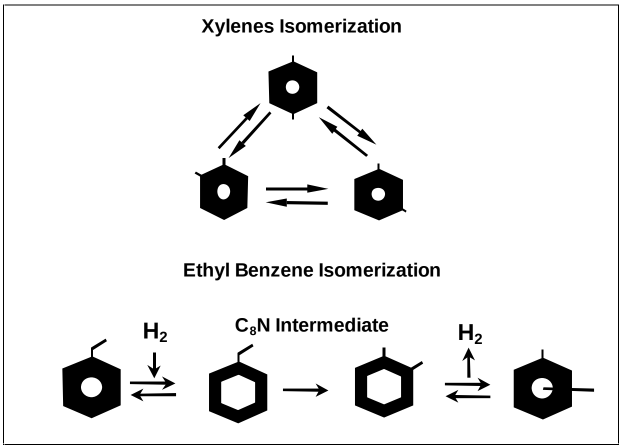
This gain in xylenes loop yield results from the increased selectivity of the Oparis catalyst, which exhibits intrinsically lower xylenes losses compared to mordenite-based catalysts. At the lower PX recovery rates obtained in complexes based on crystallization, there is a huge 8 to 9 % increase in PX yield. For adsorption (Eluxyl and other) based units, the gain in PX yield is on average about 6 %. This yield improvement represents significant savings for the plant, since the same amount of PX may be produced from a lower amount of feed. For a 400,000 MTA PX plant, starting from mixed xylenes (reference price = 280 $/t), a drop-in Oparis catalyst replacement represents 5.0 million US$/year savings on feed consumption alone!

Oparis - optimizing C_8 aromatics isomerization

Essentially all previous generation C_8 aromatics isomerization catalysts have been developed based on partially dealuminated H-mordenite with platinum as the hydrogenation component. This kind of formulation is employed in almost all commercial catalysts available on the market. These catalysts provide good isomerization activity, but the operating conditions required to attain high paraxylene approach to equilibrium result in C_8 aromatics losses that have a severe negative impact on xylenes loop yield. The losses are primarily due to transalkylation side reactions leading to benzene, toluene and C_9+ aromatics formation.

Figure 4

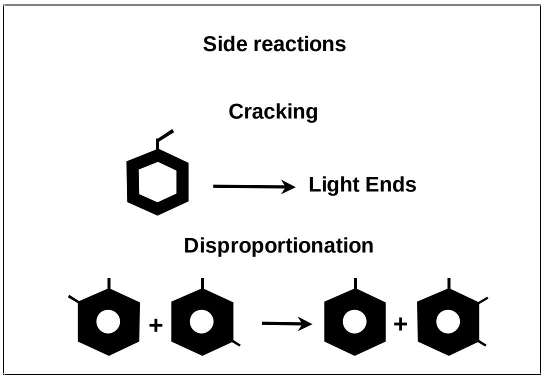
C_8 aromatics isomerization promoted reactions



The xylenes isomerization reaction is favored by temperature, as are the undesired side reactions shown in Figure 5. Since EB isomerization implies the formation of hydrogenated, naphthenic intermediate, the reaction is favored by milder temperatures and the presence of hydrogen partial pressure. The adjustment of a C_8 aromatics isomerization unit requires an optimized balance between; temperature that drives xylenes isomerization reaction, but results in a higher amount of side reactions; and hydrogen partial pressure, which drives the EB isomerization reactions.

Figure 5

C_8 aromatics isomerization side reactions



With the objective of reducing these side reactions, IFP identified the key characteristics required for a new generation catalyst and developed a more active and selective formulation. A new commercial product has been tested and optimized through extensive pilot plant testing, finally resulting in the Oparis catalyst.

Selectivity Leap

Extensive pilot testing with both Oparis and mordenite-based catalysts was carried out to compare C_8 selectivity differences at equivalent activity levels in terms of PX and EB approach to equilibrium (ATE). The pilot results of these tests have been used to provide the comparative differences previously shown in Figure 3. The data clearly demonstrate the outstanding performance gap in favor of Oparis. The C_8 ring losses per-pass are reduced by 40 % to 50%.

Optimized Activity

Oparis offers outstandingly high xylenes isomerization activity, attained under a wide range of operating conditions and space velocities, while maintaining very low losses. Compared to former generation catalysts, Oparis affords a 25-30% activity increase. This feature has a direct translation in the isomerization unit operation: EB isomerization activity is essentially the only parameter to be monitored, as xylenes isomerization is close to ideal under most operating conditions. This results in a much easier control of the unit operation.

EB isomerization activity in former generation catalysts was limited by the level of losses that were economically acceptable. Owing to its intrinsically lower loss pattern, Oparis can reach higher EB approach to equilibrium.

- higher EB conversion results in reduced hydraulic load through the xylenes loop,
- adsorption-based PX separation unit operation is easier, as EB is the most difficult C_8 aromatic isomer to separate from PX.

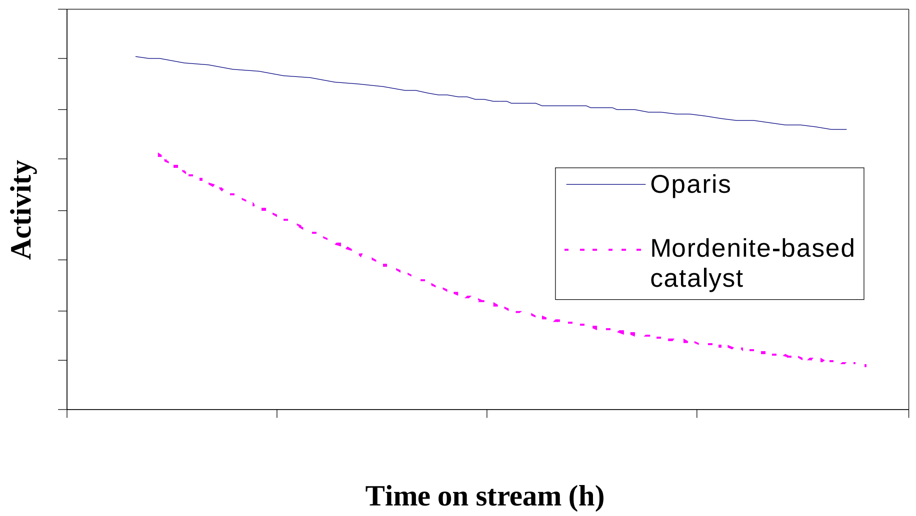
For grassroot application, the reduction of hydraulic load and molecular sieve requirement result in lower investment cost. When used as drop-in replacement in existing units, Oparis will not only offer feed consumption reduction, but also provide an opportunity to increase the PX production capacity owing to a better feed quality to the adsorption section.

<u>Increased Stability</u>

Catalyst aging tests have demonstrated that the Oparis catalyst has a significantly better stability and maintains a higher activity compared to mordenite-based catalysts, see Figure 4. This greatly improved stability will translate into more stable operating conditions, i.e., longer cycle lengths and better throughput for the same catalyst volume.

Figure 4

Comparison of Oparis and mordenite-based catalyst



Oparis boosts xylenes loop performance

Oparis features superior yield, selectivity, activity and cycle lengths over the same range of operating conditions as those employed by previous generation catalysts. The addition of the Oparis catalyst to a grassroots BTX project will ensure unmatched levels of performance. Owing to its exceptional stability and higher activity, Oparis may be dropped into any existing isomerization reactor to provide a PX yield gain with reduced feed consumption. The replacement of previous generation catalysts with Oparis may also be employed to provide an instant debottlenecking when the xylenes loop is not limited by hydraulic constraints.

Paraxylene complexes based on crystallization technology stand to benefit very significant gains from the use of Oparis. A simple drop-in catalyst replacement in an older complex is readily converted into multiple million dollar annual savings.

The ability of Oparis to attain high EB conversion to xylenes is the right answer to the future trend in the aromatics market where low-cost or captive excess C_8 aromatics, will be available for paraxylene production.