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MAXIMIZING PARAXYLENE PRODUCTION WITH *PARAMAX*

Introduction

With an expected annual demand growth rate of 6% to 8% for the next decade, Paraxylene can be described as a healthy market. In spite of the recent overcapacity situation, industry consultants tell us that demand for paraxylene is expected to catch up with production capacity by the end of 2003. This will require increased production capacity, the lion's share coming from new, world-scale grassroots units. Today, the ParamaX suite of technologies offered by Axens addresses tomorrows challenges: high capacity, flexibility and performance.

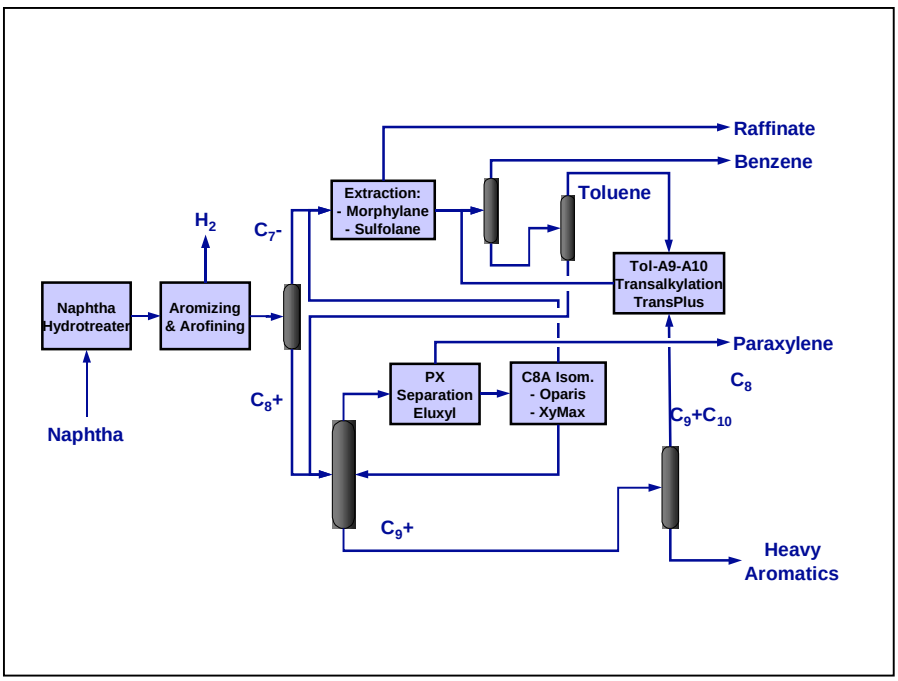
ParamaX™ **- The BTX Aromatics Technology Suite** The processes incorporated into Axens aromatics portfolio provides customers with a complete suite of advanced technologies, unmatched in performance and cost effectiveness for all BTX production goals. Together, they make an attractive first choice when selecting the full complement of BTX technologies and services from a single source. The technologies exclusively licensed by Axens in grassroots *ParamaX* packages are:

- ***Aromizing*** – high severity CCR reforming for aromatics production,
- ***Arofining*** - reformate saturation for drastically reduced clay consumption,
- ***Sulfolane*** (Lyondell) – high purity benzene, toluene and xylenes extraction,
- ***Morphylane*** (Krupp Uhde) – toluene and high purity benzene extraction,
- ***Eluxyl*** - simulated countercurrent adsorption paraxylene separation,
- ***Crystallization*** – enables the production of ultra-high purity paraxylene when combined with *Eluxyl* in the hybrid version,
- ***Oparis™*** – New generation C_8 aromatics (xylenes and ethylbenzene) isomerization,
- ***XyMax***^{sm} (ExxonMobil) – xylenes isomerization with ethylbenzene dealkylation, using the newly commercialized EM-4500 catalyst with improved activity and selectivity,
- ***PxMax***^{sm} (ExxonMobil) - state-of-the-art Selective Toluene DisProportionation (STDP) technology for the production of a highly paraxylene-enriched xylene stream and benzene,
- ***TransPlus***^{sm} (ExxonMobil) – toluene/C_9+C_{10} aromatics transalkylation, with the proven ability to process high amounts of C9 and C10 aromatics, and
- ***MTDP-3*** (ExxonMobil) – toluene disproportionation to benzene and xylenes.

Typical Paraxylene Production Complex (**Figure 1)** A naphtha heart cut is first hydrotreated to remove sulfur and nitrogen prior to feeding an *Aromizing* unit yielding a full slate of aromatics compounds and hydrogen. Considerably more hydrogen is produced than consumed in the complex, making it a net exporter.

The *Arofining* reactor, located upstream of the *Aromizing* effluent stabilization, hydrogenates undesirable olefin and diolefin compounds present in the high severity reformate. This unit significantly prolongs clay (not shown) lifetime, resulting in lower costs associated with: clay purchase and disposal, reactor loading and unloading operations and reduced bed size. The effluent is then split into C_7- and C_8+ fractions.

Figure 1 Typical Aromatics complex



Non-aromatic compounds are removed from the C_7- fraction either in a *Morphylane* extractive distillation unit or in a *Sulfolane* liquid-liquid extraction process. The latter is preferred when very high purity toluene production is envisaged or when an external feed, such as hydrotreated pygas, is destined to go through BTX extraction. *Morphylane* is ideally used when toluene is internally transalkylated.

The deheptanizer bottoms are sent to the xylenes rerun column, together with the effluent from the *TransPlus*^{sm} unit and the recycle from the isomerization unit. The C_8 fraction, taken overhead, feeds the *Eluxyl* unit, which produces high purity paraxylene from the mixed C_8 stream at high recovery rates. The paraxylene-depleted stream then feeds the isomerization section for which EB-reforming type (*Oparis*) or EB dealkylating type (*XyMax*^{sm}) technologies may be selected. The effluent from the isomerization process, a close to equilibrium mixture of xylenes, is then recycled to the xylenes rerun and *Eluxyl*. The selection of isomerization technology is a function of the desired BTX production pattern and economical concerns.

The xylenes rerun bottoms are sent to a heavy aromatics column where C_9 and C_{10} aromatics are taken overhead for the *TransPlus* feed. *TransPlus* affords a significant increase in paraxylene production capacity by disproportionation / transalkylation of toluene and C_9+ aromatics, yielding additional mixed xylenes and benzene.

Future directions for PX production plant configurations

Ultimate single train capacities:

Tomorrow's Paraxylene producers will have to meet the requirements of the down-stream industry. Recent technical improvements in PTA manufacturing technology now allow the building of grassroots capacity consuming 500 kTA PX or more, and the economy of scale realized owing to these developments needs to be matched with future Aromatics complexes. Axens technology offerings are designed to meet this challenging scenario:

- Aromizing technology, owing to its sound side-by-side reactors arrangement allows high capacities without hitting any technical constraint from mechanical or operational point of views,
- Eluxyl technology was designed to displace the limits of single train capacities owing to advanced concepts that allow flexibility and ideal hydraulics management,
- Axens is also offering breakthrough performance for the surrounding catalytic systems that are used to rearrange the aromatic backbone (Transalkylation, Isomerization),

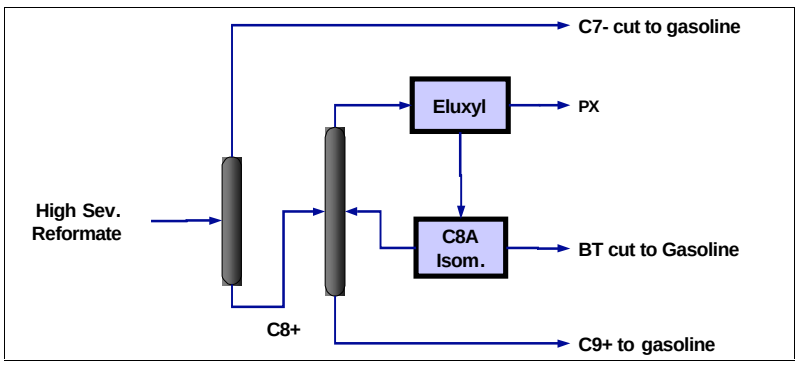
The ParamaX suite provides the best overall answer in both respect of economy of scale and overall performance.

Refinery petrochemicals integration at large

New constraints on Gasoline formulation limiting the total amount of aromatics shall be effective in Western Europe by 2005. These specifications will expand eastwards to the Middle-East, Indian Subcontinent and Asia in the near future. These new regulations, when combined with declining overall gasoline pool (such as in Western Europe), or emerging countries that will aim at high standard mogas specifications, will put refiners under pressure to properly manage their aromatics volumes. At the other end of the scale, Naphtha cracking plants that have been exporting hydro-treated Pyrolysis gasoline to the gasoline pool are also likely to face hard times to sell out their aromatics rich co-product. The expected growth in Ethylene demand will make this Pygas issue even more important in the future. Combining the existing aromatics volumes in the refinery and crackers to set up a gasoline and aromatics production facility is a solution that major operators are already looking into.

The flow schemes below give an illustration of alternate ParamaX configurations corresponding to these new directions.

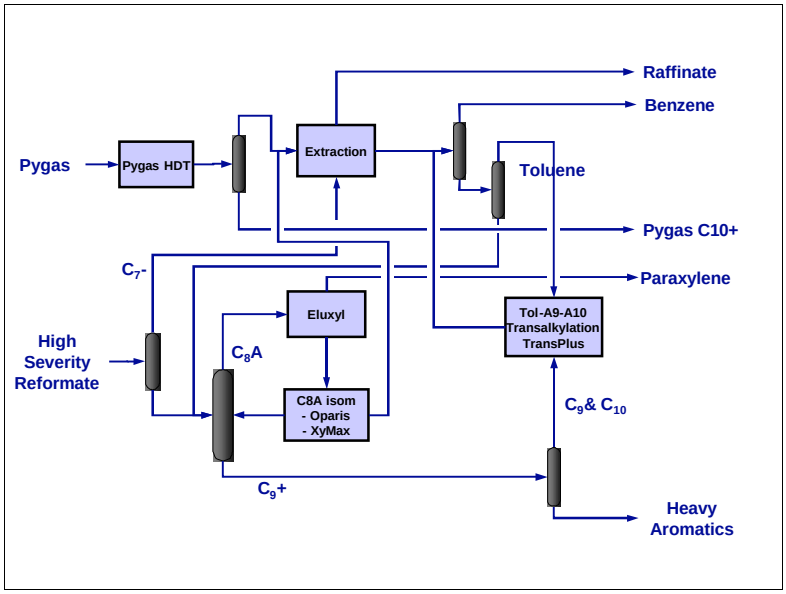
Figure 2 High Severity Reformate(s) to PX route



The high severity reformate to PX route proposes to integrate PX production capacity within a refinery environment, or as a common facility to several plants.

The Pygas and Reformate to PX route shows an overall integration between a Naphtha Cracker plant and a Refinery.

Figure 3 Pygas and Reformate to PX route



To serve the various configurations, Axens proposes the ParamaX suite of Technologies as a single source Licensor and service provider.

Features of Selected *ParamaX* Technologies

The following provides some the key features of selected *ParamaX* technologies.

Aromizing is Axens' state-of-the-art CCR reforming technology for aromatics production. The process employs the AR series of catalysts designed to maximize aromatics yield and operates at low pressure and high severity.

Aromizing, represented in **Figure 4,** is a technically sound technology now backed-up by extensive industrial experience and feedback.

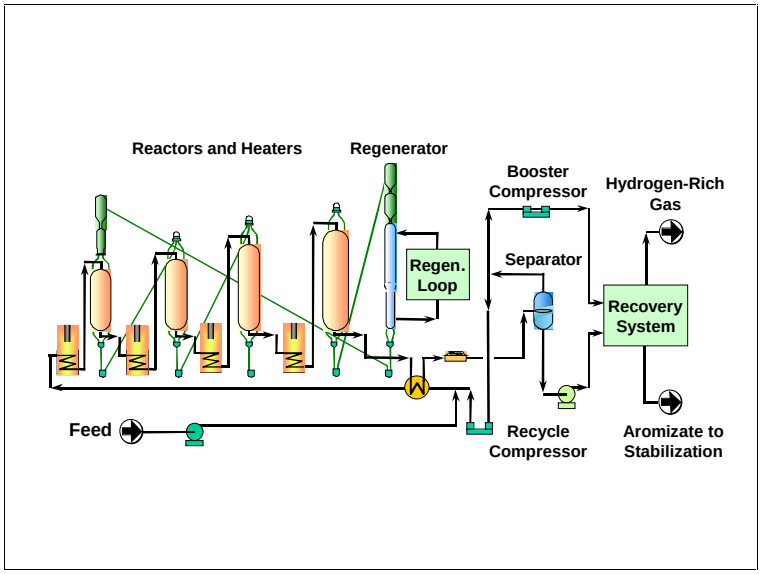
- The continuous catalyst regeneration system is fully automated, controlling all catalyst circulation and regeneration during start-up, shutdown and normal operations. The latest generation CCR system, *RegenC*, provides an independent control of all the key parameters that ensure optimal catalyst regeneration resulting in extended catalyst life and stable performance.

- AR-501 is the latest generation of *Aromizing* catalyst featuring an improved selectivity towards aromatics owing to the uniform and ultra-high dispersion of active metals on the carrier. A harder support material provides excellent mechanical resistance and assures low catalyst consumption rates. The catalyst also features a reduced platinum content, which has a direct impact on investment cost.

- The side-by-side reactor arrangement allows simple reactor design, implementation and maintenance access and easy handling of thermal expansion issues,

resulting in cost-effective engineering and construction particularly when high capacities are considered.

Figure 4 *Aromizing* process flowscheme



Aromizing technology is and will remain one of the key building blocks of future Aromatics plant configurations.

Morphylane technology has imposed itself as the industry standard for the extraction of a narrow boiling range aromatics cuts. It employs the concept of extractive distillation where a solvent is used to modify the relative vapor pressures of various hydrocarbons in such a way that Aromatics can be separated from non-Aromatics by simple distillation.

- **Compact and cost-effective design** is the key characteristic of Morphylane technology that uses a reduced number of pieces of equipment compared to other technologies.
- **Cost effective recovery and high purity aromatics** is achieved owing to a carefully selected solvent: NFM is a non-corrosive material, thermally and chemically stable. No other chemical needs to be injected in the process which contributes to the ease of operation.
- **Divided wall technology** has recently been applied to the Extractive distillation concept, providing for further reduction of investment and operating costs.
- Today, more than forty ***Morphylane*** units have been licensed worldwide.

Eluxyl process achieves the separation of high purity paraxylene from a mixture of C8 aromatics based on the concept of simulated countercurrent adsorption.

Eluxyl incorporates a number of innovations from recent technological advances. The concepts outlined hereafter have all been validated in the world's largest operating single-train paraxylene separation unit, affirming its leading edge position.

- **High performance adsorbent** is the key to reach ultimate Paraxylene purity and high recovery rates. The adsorption capability is combined with adequate mechanical strength, which allows use of the Catapac^{tm} dense loading device: even bed density is perfectly achieved, even on large adsorbers diameters.

- **Efficient distribution/withdrawal trays** are another key feature of Eluxyl technology. Targeting ultra-large single-train capacities requires even distribution of feeds and withdrawal of products in large diameter adsorbers. Blending efficiency, and injection synchronicity issues are properly addressed and industrially proven.
- **The PLC controlled on/off valves system** clearly distinguishes this technology, bringing a high degree of flexibility and a continuously optimized operation.
- **On-stream maintenance** of an individual valve during unit operation is achievable owing to the ability of the microprocessor to automatically detect valve malfunction. Maintenance is performed by plant maintenance personnel with lower incurred costs, while maintaining unit performance.
- **On-line Raman spectroscopic analysis** is applied to visualize concentration profiles along the *Eluxyl* adsorber on a real time basis. This powerful technique allows a fine and continuous supervision of the adsorption section.

Eight *Eluxyl* licenses have been awarded so far, for a total paraxylene production capacity of over 2.9 million metric tons per year and corresponding to 30% PX capacity share since this technology was brought to the market. The production capacities range from 180,000 to 750,000 metric tons per year.

Today , the world's largest single train capacity is based on Eluxyl technology and serves the market with 650,000 tons per year of 99.9% paraxylene purity.

***Oparis*™** is a new generation catalyst for ethyl benzene (EB) and xylenes isomerization. Oparis™ effectively converts EB into additional xylenes.

Breakthrough performance is achieved in both terms of selectivity and activity. When applied in a conventional Xylenes loop, *Oparis*™ yields up to 93% Paraxylene out of C8 aromatics. This unmatched level of performance is achieved with a lesser amount of catalyst compared to previous generation catalysts. *Oparis*™ is the preferred option whenever Benzene co-production needs to be minimized or eliminated. It is also a valuable option whenever Pyrolysis gasoline C8 aromatics, that are known to contain a lot of EB, are used as additional feed to the complex and Benzene co-production is undesireable.

EB isomerization proceeds via a C_8 naphthenic intermediate equilibrium that limits the rate of reaction. Accurate management of the C_8 naphthenes balance through the reactor is therefore essential for optimizing process performance. With the implementation of a dedicated C8 naphthenes recycle column, the Isomerization section performance is finely optimized owing to an internal recirculation.

Oparis™ was successfully commercialized in early 2001 as a replacement for a competitor's catalyst in a recently commissioned plant.

ExxonMobil's *XyMax*^{sm} technology for EB dealkylation type xylene isomerization is exclusively available through the ParamaX Alliance for grassroot applications. The earlier generation MHAI and Advanced MHAI technologies have a well established reputation worldwide. ExxonMobil Chemical Company continues the push toward higher ethylbenzene conversion, while further reducing xylene losses by bringing a new generation catalyst to the market place: The EM-4500 catalyst features a level of performance that will re-enforce the existing strong worldwide market position in xylenes isomerization. At present there are 21 units using ExxonMobil xylenes isomerization technology, and over one-third of the world's xylenes isomerization capacity uses ExxonMobil catalysts. The first batch of EM-4500 catalyst was put on stream in April 2001 in ExxonMobil's Jurong, Singapore plant.

The process is distinguished by a unique dual-bed catalyst system. Ethylbenzene dealkylation to benzene and non-aromatics cracking occur in the first bed, while the near-equilibrium isomerization of xylenes takes place in the second bed.

XyMax using EM-4500 catalyst exhibits some key performance enhancements compared to previous generation catalysts.

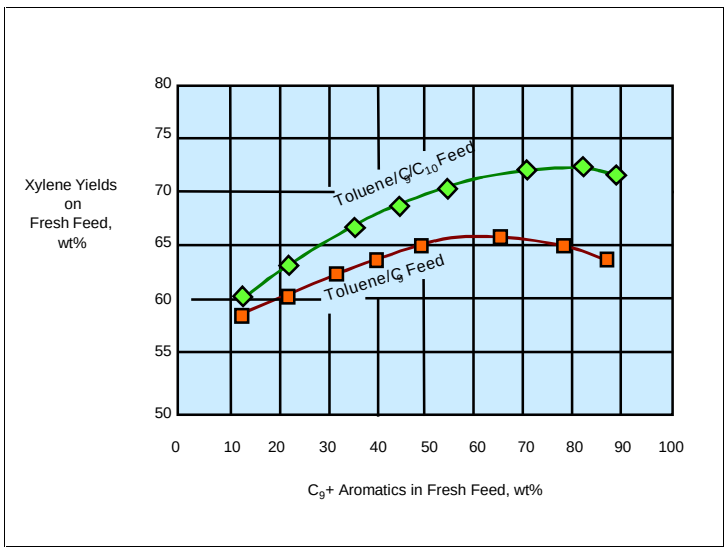
- **Selectivity** is further improved, and compared to Advanced MHAI, EM-4500 features a further 50% reduction in xylenes losses. PX approach to equilibrium remains in the range of 100%, and the selectivity of EB dealkylation to Benzene has been improved.
- **Higher EB conversion** per pass is achieved without detrimental effect on the catalyst cycle length. Based on the aging rate observed so far at the Jurong facility, EM-4500 is expected to exceed a five-year first cycle
- **High space velocity** is one of the trademarks of the ExxonMobil technologies, and EM-4500 maintains the high space velocity standard.
- **Reduced H_2/HC** requirement for EM-4500, resulting in further savings in investment and operating costs.

TransPlus^{sm} is ExxonMobil's toluene/C_9+ aromatics transalkylation technology which was co-developed with the Chinese Petroleum Corporation (CPC) of Taiwan. The first industrial unit was put on stream in June 1997 in CPC's petrochemical plant in Lin-yuan where an existing transalkylation unit was retrofitted with the *TransPlus* process. This technology builds on ExxonMobil's extensive experience in toluene disproportionation that began in the mid-1970's.

The *TransPlus* process utilizes a proprietary catalyst that has superior yield performance. This is achieved with a careful catalyst design that maximizes desirable reactions such as disproportionation, transalkylation and dealkylation and minimizes undesirable side reactions. In addition, *TransPlus* has the advantage of low capital and operating costs due to more favorable operating conditions relative to competitor processes, which result from the more robust nature of the catalyst.

- **Feedstock flexibility:** *TransPlus* technology has the flexibility to process up to 100 wt% of C_9+ aromatics in the fresh feed while maintaining long cycle lengths. In addition, the robust nature of the *TransPlus* catalyst allows extensive recycle of the C_{10}/C_{11} aromatics in the C_9+ feedstock enhancing the yields towards xylenes production as illustrated in **Figure 5**.

Figure 5 Improved xylene yields via transalkylation of C_9/C_{10} aromatics



- **Long cycle length**: Typical performance of the fully regenerable *TransPlus* catalyst shows that cycles in excess of several years can be expected even when processing feedstocks having up to 100 wt% C_9+ aromatics in the fresh feed.
- **Benzene co-product purity** is higher than 99.85 wt% purity thereby reducing the need to re-process it through the extraction section.
- **Low H_2/HC mole ratio and higher weight hourly space velocity** also characterize *TransPlus* technology and make it possible to build grassroots plants at lower capital costs relative to competitor technology. This also results in reduced operating cost.

Considering the structure of present and future aromatics plants, TransPlus technology is due to take a growing share of the C8 aromatics production to feed the xylenes loop. TransPlus performance and versatility shall definitely be a key to competitive plant operation.

PxMax^{sm} is ExxonMobil's State-of-the-Art technology for Selective Toluene DisProportionation for the production of a highly paraxylene-enriched xylene stream and benzene. The *PxMax* technology was first offered for licensing beginning in the fall of 2000, and is the subject of a separate paper at this conference.

Conclusion

Axens' *ParamaX* Technology Suite contains a complete set of technologies from a single source which can be configured to meet all BTX production needs. The ParamaX Alliance is committed to servicing the industry with continuously upgraded technologies. Since the advent of the ParamaX Alliance, five major technology advances have been integrated into the portfolio, including, Morphylane extractive distillation technology, the latest AR 501 CCR catalyst, the new XyMax process for EB dealkylation based xylene isomewrization, the new Oparis isomerization catalyst for EB isomerization applications, and PxMax for Selective TDP: our objective is to improve your performance.

Scott Ramsey co-authored the portions of this paper associated with the ExxonMobil technologies (XyMax^{sm}, PxMax^{sm}, TransPlus^{sm}, and MTDP-3).