How non-conventional Feedstocks will affect Aromatics Technologies

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Abstract

The abundance of non-conventional feedstocks such as coal and shale gas has begun to affect the availability of traditional base chemicals such as propylene and BTX aromatics. Although this trend is primarily fueled by the fast growing shale gas economy in the US and the abundance of coal in China, it will cause the global supply and demand situation to equilibrate across the regions. Lower demand for gasoline and consequently less aromatics-rich reformate from refineries will further tighten the aromatics markets that are expected to grow at healthy rates, however. Refiners can benefit from this trend by abandoning their traditional fuel-oriented business model and becoming producers of petrochemical intermediates, with special focus on paraxylene (PX). Cheap gas from coal (via gasification) or shale reserves is an advantaged feedstock that offers a great platform to make aromatics in a cost-competitive manner, especially in regions where naphtha is in short supply. Gas condensates (LPG and naphtha) are good feedstocks for paraffin aromatization, and methanol from coal or (shale) gas can be directly converted to BTX aromatics (MTA) or alkylated with benzene or toluene to make paraxylene. Most of today's technologies for the production and upgrading of BTX aromatics and their derivatives make use of the unique properties of zeolites.

Introduction

The petroleum industries are in the midst of a game change. Not only is the traditional and dominating use of liquid hydrocarbons challenged by their short-chain gaseous fellows, triggered by the abundance of shale gas, coal is also about to establish itself as a feedstock for petrochemicals on a regional basis in China, and long-term, we will see biomass become a factor in hydrocarbon supplies. Amongst these non-conventional sources, gas will have the biggest impact by far. As shown in Fig. 1, the total gas supply will grow by 55% from 2010 to 2035 with unconventional gas accounting for nearly two-thirds of the growth and its share in total output rising from current 14 to 32%[1]. At the moment only the US are in an advanced stage of exploiting shale gas but China, Australia and Argentina will follow, though trailing

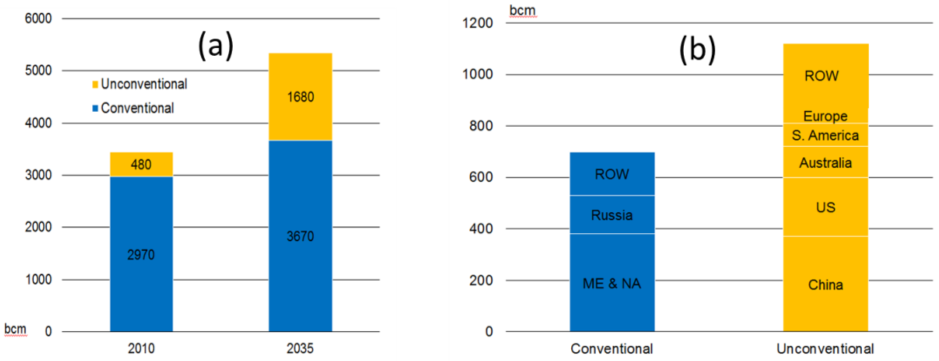


Fig 1: Expected growth of global gas supplies (a) and regional contributions (b) [1]

behind the US by several years. That's why the real impact from shale gas will become visible on a global basis only after 2020. Shale Gas exploration and development in Europe is hindered by regulatory and environmental concerns, despite the economical benefits. However, improvements in the transport sector should allow Europe too to benefit from cheap imported LNG from non-conventional sources.

The abundance of gas is already affecting the petrochemical supply situation in the Middle East and the US. As a direct consequence of cheap gas, naphtha is displaced by ethane as preferred feed for steam crackers, causing shortage of propylene and aromatics that have only a marginal share in the product slate from ethane cracking.

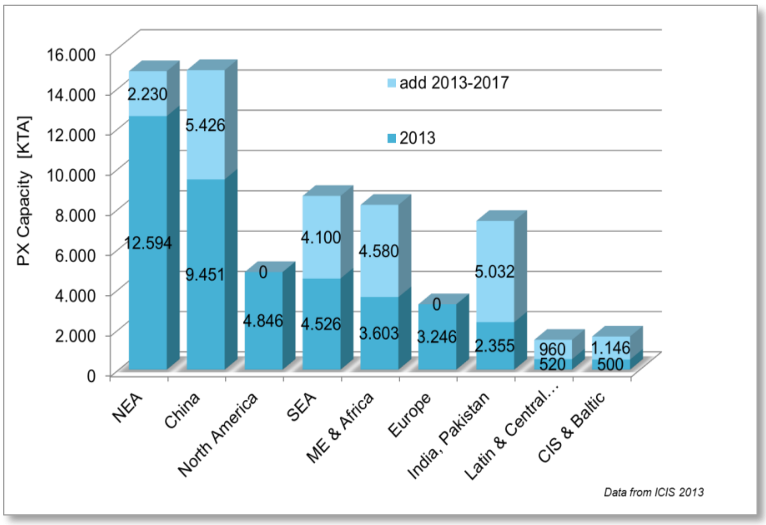
Coal as a raw material for petrochemicals should be confined to China, given the less competitive pricing of coal in other regions, along with environmental challenges associated with the use of coal. From a downstream perspective, coal is not different from gas as its use requires gasification, followed by FT or methanol synthesis.

As far as biomass is used for gasification, it follows the same pattern, i.e. the downstream chemistry is not different from gas or coal. However, biomass conversion offers a great variety of other pathways that lead straight to valuable base chemicals.

Last but not least we should not forget about associated petroleum gas (APG) when it comes to non-conventional feedstocks. Propane and butanes make up about 6% and 4% of APG which comes at virtually zero cost. So it makes a lot of sense to make this "waste" a valuable feed source for petrochemicals production, especially when combined with advanced upgrading technologies that open up new opportunities to make sought-after products.

Aromatics - an Opportunity for non-conventional Feedstocks

The demand for gasoline in key markets such as Europe and the US is steadily declining, owing to improved fuel efficiency, ethanol blending and dieselization. These changes are raising concerns as naphtha reforming which is closely associated with gasoline is still the dominating source for BTX production. With the BTX and PX markets growing at rates clearly above GDP, and outpacing feed supplies, it is likely that downstream markets will find it increasingly difficult to meet the growing demand for aromatics from catalytic reforming 2).



Data from ICIS 2013

Fig 2: Paraxylene capacity by region and its increase by 2017 3)

Shortage of feedstocks for aromatics production creates incentives to use alternative low-cost feeds such as shale gas and coal, especially in the light of available technologies for the conversion of methanol to hydrocarbons (MTH). C3/C4 hydrocarbons from associated petroleum gas (APG) also hold unlocked potential to become the basis for alternative BTX synthesis. Overall, the tight paraxylene (PX) market with prices much stronger than historical levels provides an excellent environment for non-conventional technologies and production schemes.

New Technologies for Aromatics

Before taking a look at alternative ways of producing BTX aromatics, it is worthwhile to recollect the key features of traditional, naphtha-based aromatics processing.

Conventional Aromatics Production

The vast majority of aromatics complexes obtains feed from naphtha reformers that are located in the refinery. The most common conversion and separation processes used to enhance the production of PX as the primary target product are all based on zeolites. Shape selectivity and tailored acidity (catalysts) as well as unique electro-chemical interaction between feed and host (molecular sieve adsorbent) have made zeolites an indispensable core technology for BTX upgrading.

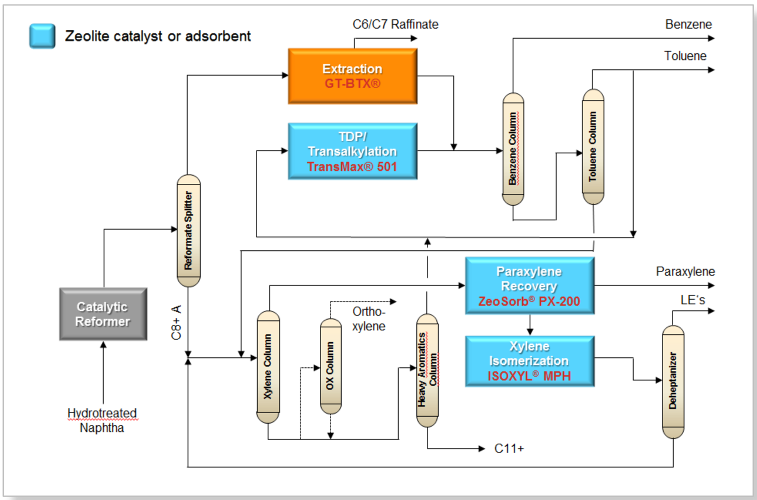


Fig 3: Traditional Process Scheme for BTX production and respective CLARIANT products (marked red)

Core processes are xylene isomerization to establish C8 equilibrium mixtures that are sent to the PX recovery unit where PX is continuously removed from the loop, and OX/MX is recycled to the isomerization unit. The PX separation stage can be based on a molecular sieve or crystallization process. PX production can be further increased by converting toluene and C9/C10 aromatics to PX and benzene in disproportionation and transalkylation units that are fully integrated in the PX enhancement and separation loop. CLARIANT – based on its long-term experience in zeolite R&D and production – offers a complete range of products for BTX/PX production as shown in Fig.3.

Non-conventional Aromatics Production

Zeolite catalysts and specifically MFI (ZSM-5) with its high selectivity to aromatic hydrocarbons play a dominant role in gas-based aromatics production. As methane cannot be converted to more complex hydrocarbons directly, at least not with conversion rates that meet industrial requirements, methanol is used as an easy-to-access intermediate.

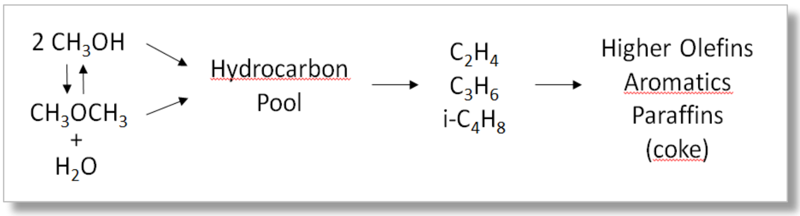


Fig 4: Hydrocarbon Pool mechanism in methanol conversion with MFI Zeolites[4),5)]

Depending on the location, the synthesis gas for methanol can be obtained from methane steam reforming (MSR) or gasification of coal, oil sands, biomass, etc. (Fig.5). The conversion of methanol to hydrocarbons (MTH) is subject to the “hydrocarbon pool” mechanism which has been widely discussed in the literature. A simplistic scheme is shown in Fig.4. It involves the dehydration to dimethyl ether in a first step. The equilibrium mixture formed, consisting of methanol, DME and water, is then converted to light olefins. In the last step of this scheme, the light olefins react to form paraffins, aromatics, naphthenes and higher olefins by hydrogen transfer, alkylation and polycondensation$^{4)}$.

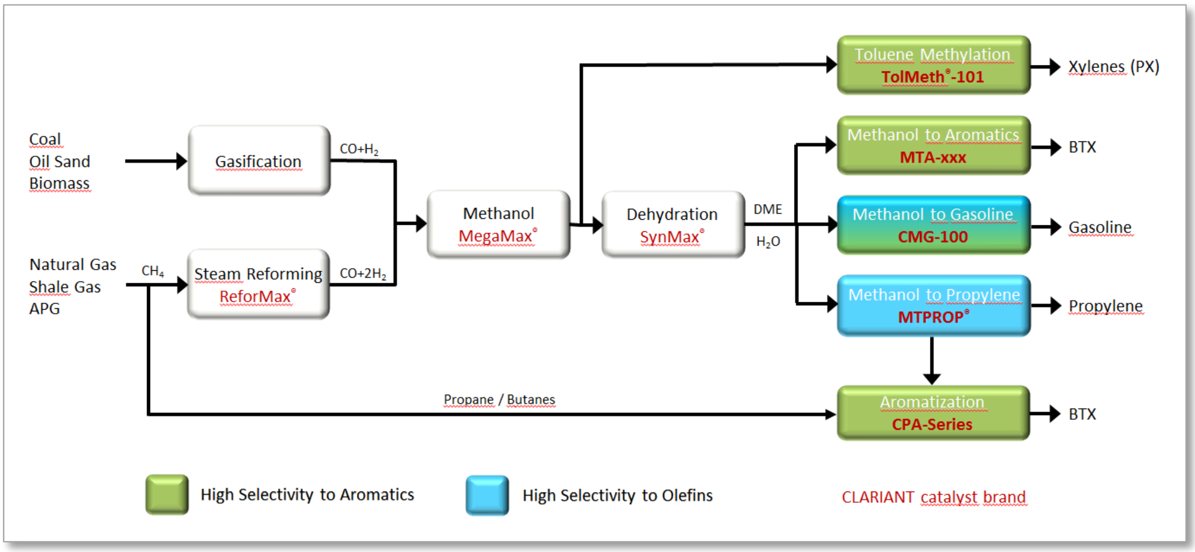


Fig 5: Processing options for non-conventional feeds with MFI (ZSM-5) Zeolites

Facilitation of any of the above reactions will drive the reaction either towards olefins or aromatics as the final product. In the methanol-to-propylen (MTP) process, hydride transfer is suppressed by pressure, temperature and catalyst properties so that the reaction does not proceed to aromatics, and high selectivity to olefins, specifically propylene, prevails. Conversely, the methanol-to-aromatics (MTA) process uses conditions that are unfavorable for olefins as the target product. Methanol-to-Gasoline (MTG) is in between the two extremes. It also produces a decent amount of aromatics (which boosts octane in gasoline) but still has quite some olefin selectivity. Fig.5 shows the three basic options of MTH processing. In the following, MTA and the other BTX process/catalyst options in Fig. 5 are further highlighted.

Methanol to Aromatics (MTA)

In contrast to the MTO/MTP reaction, a combination of higher catalyst acidity and moderate temperature is vital in maximizing aromatics selectivity. Metal loadings on the catalyst and isomorphous substitution of aluminum in the zeolite with other metals have been found to further increase aromatics yield. Fig. 6 illustrates the performance improvements obtainable by modified MFI catalysts in comparison with standard (plain) MFI catalysts.

With the catalyst's tendency towards alkylated aromatics, and polyalkylated aromatics being a coke precursor, the cycle times in fixed bed reactor systems are relatively short which led to the development of fluid bed processes. However, at this stage of immature technologies, it is unclear if the extra cost and complexity is worth the effort. The success of MTA will rather be determined by its efficiency in terms of aromatics yields and BTX selectivity. State-of-the-art technology achieves 95-100% methanol conversion, 60-70% aromatics yield per pass and up to 80% selectivity to BTX. As a result more than 3 tons methanol is needed to make 1 ton BTX. It is obvious that only cheap methanol will allow for attractive process economics. Coal-based MTA

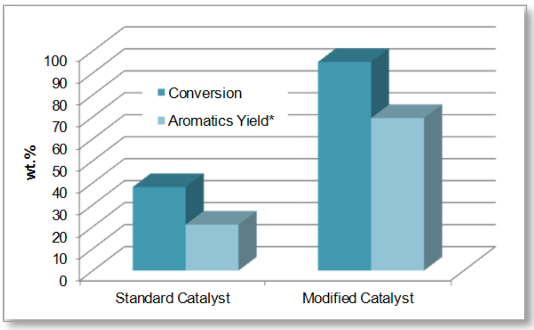


Fig 6: Improved MTA performance from modified MFI Zeolites

(= CTA) is widely discussed in China, but places with cheap gas might be good candidates for gas-based aromatics production too.

CLARIANT is on stand-by when it comes to industrialization of MTA. Owing to the company's extended experience and long-term history in the development and commercial manufacture of MTP and MTG catalysts, CLARIANT has a deeper understanding of the MTH mechanism.

Toluene methylation (TM)

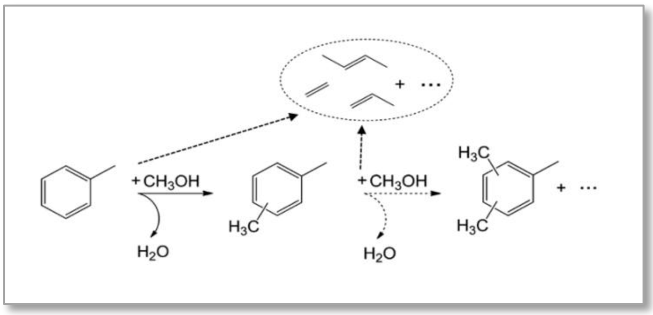


Fig 7: Toluene methylation reactions 6)

Toluene methylation (TM) uses the tendency of methanol to alkylate over MFI catalysts, and to form xylenes as primary product when reacted with toluene. Even though it looks like perfect technology, the TM process is plagued by undesirable by-products such as light olefins from MTO/MTP reactions and dealkylation of alkylated aromatics, as well as polymethylated aromatics such as trimethylbenzene (TMB) from ongoing alkylations (Fig. 7). In order to curb the side reactions, toluene is used in excess of methanol, typically 4 : 1 on a molar basis. This has an adverse effect on toluene conversion (max. 30%), however, and the fact that by-product formation can only be suppressed to a certain extent is attributed to the shape-selectivity of MFI catalysts that brings about polymethylation but also dealkylation of the polymethylated aromatics. This leads to an unavoidable level of polyalkylated aromatics and light hydrocarbons in the product 6)). However, shape selectivity of the MFI zeolite is also the reason for its superior selectivity to xylenes which makes this zeolite the best choice for TM catalysts, even more so as selectivation techniques such as silylation of the catalyst surface can be applied to raise the selectivity to paraxylene to about 90%.

It is obvious that methanol utilization is crucial for the economics of the TM process. A substantial improvement is achieved when using the TM process in conjunction with a trans-alkylation unit in an aromatics complex which receives the TMB's and converts them to additional xylenes.

In comparison with selective toluene disproportionation (STDP), the much higher PX output per ton of toluene feed (230% of STDP) sheds a favorable light on TM (Fig. 8). Furthermore, TM eliminates benzene as a co-product, a most desirable feature in a petrochemical world that is long in benzene.

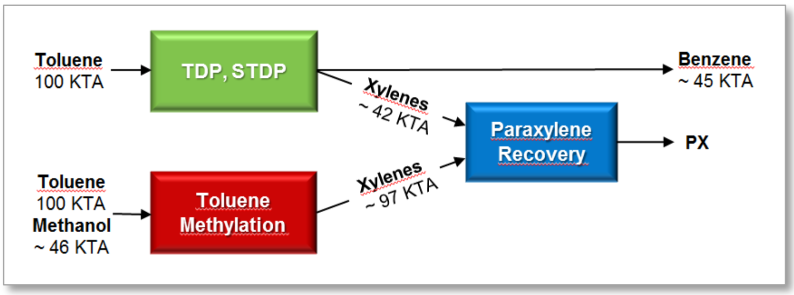


Fig 8: PX production is doubled with Toluene Methylation 7)

Last but not least, the simplicity of the process and low capital investment is worthwhile mentioning. CLARIANT's TolMeth™-101 catalyst, does not need hydrogen which keeps capital investment and operating cost at a modest level. In the end it's all about feedstock cost, and alike MTH processes, TM economics are highly dependent on methanol pricing. This suggests that TM we will not see a breakthrough as standard technology in typical aromatics complexes but its role will be confined to special environments where cheap raw materials (gas, coal) and/or methanol are superabundant.

Aromatization

Turning light olefins and/or paraffins into aromatics over MFI catalysts is industrially practiced for quite a while. Historically, this technology has been used for high octane gasoline in certain geographical areas, without aiming at maximum BTX yields, however.

Aromatization as proposed in this paper for gas-based petrochemicals can use a variety of feedstocks. C4+ olefins from an MTO/MTP plant can add value and flexibility to these methanol-conversion processes. Aromatization can handle the entire range of olefins (C4 to C8 in most cases) that otherwise would be recycled or fed to an olefin cracking stage. However, a more likely and straightforward feedstock option is propane (and/or butanes) from associated petroleum gas or shale gas, as shown in Fig. 5.

Aromatization is a multi-step reaction that involves dehydrogenation (in case of paraffins), oligomerization, cyclization and again dehydrogenation to the final aromatics product (Fig. 9). As dehydrogenation is the rate limiting step in this consecutive reaction pathway, paraffinic hydrocarbons are more difficult to process than olefins or naphthenes. Aromatization is an endothermic reaction. Reactivity is enhanced for olefins, branched and long-chain hydrocarbons. This means the highest temperatures and the longest residence times are needed for propane (Fig. 10). Depending on the feedstock, operating temperatures are in the range of 350-550°C.

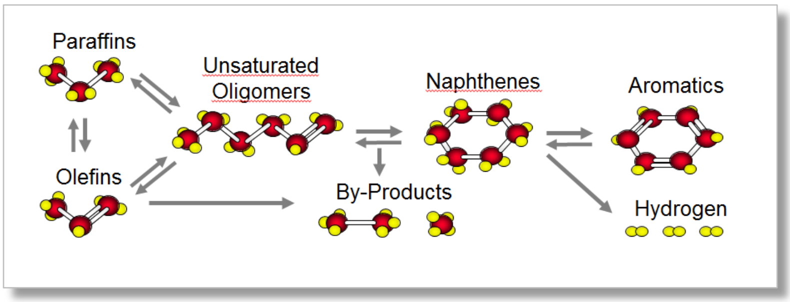


Fig 9: Dehydrocyclization (aromatization) over MFI (ZSM-5) zeolites

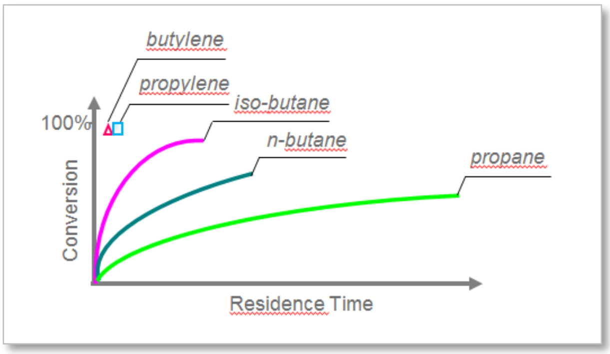


Fig 10: Ease of processing for typical components in aromatization feeds

Aromatization is subject to similar mechanisms like the MTA process, so BTX selectivity can be affected by temperature and pressure in a similar way. Depending on the feedstock, the catalysts preferably used in aromatization contain transition metals. For C3 and C4 paraffinic feeds Ga-MFI with Ga being incorporated in the zeolite framework has proven to be indispensable when it comes to achieving high conversion and aromatics selectivity 8). Modified MFI catalysts typically achieve 80-100% conversion and 55 - 60% aromatics Yields.

CLARIANT's commercially-proven CPA catalyst series (CPA = Conversion of Paraffins to Aromatics) covers all feedstock options, incl. Ga-MFI for propane/butane aromatization.

Aromatics from Biomass Conversion

A detailed look into the technologies for biomass conversion to aromatics goes beyond the scope of this paper. In brief, there are two very different technologies on the verge of industrialization. GEVO's fermentation-based isobutanol to PX route converts the intermediate isooctene to PX with relatively high selectivity. A demonstration-scale paraxylene plant has been put into operation in Silsbee, TX in Aug 2013 11). Virent's

BioFormingPX® process uses a combination of Aqueous Phase Reforming (APR) and aromatization over MFI zeolite catalysts to convert oxygenates in an acid condensation reaction to aromatics. Virent intended to go commercial by 2015 [12)]. Both companies have cooperations with Coca Cola, aiming at fully renewable, non-petroleum derived PET. However, economics are questionable at this stage and marketing (image building) seems to be the main driver for commercialization.

Alternative Flow Schemes for Aromatics

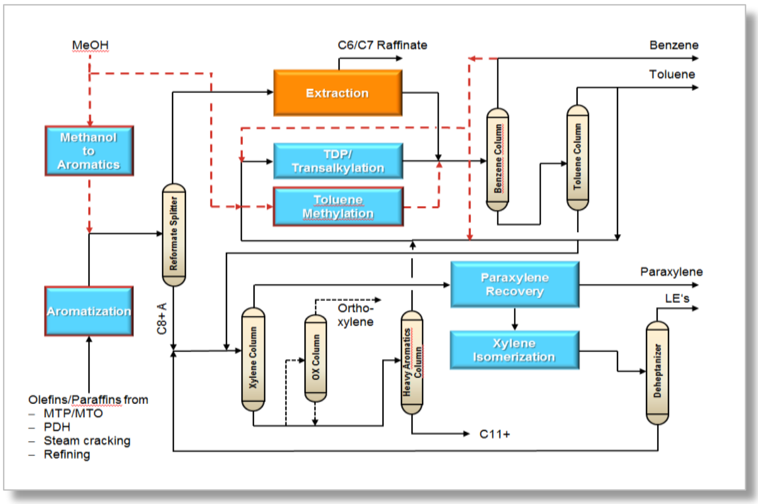


Fig 11: Alternative Process Scheme for BTX Production

Like conventional processes for BTX upgrading to paraxylene, those based on non-conventional processes cannot be used without recycle and separation environment that is typical of aromatics complexes. There are several options to design an alternative process scheme for aromatics production that is solely based on non-conventional feed-stocks. In Fig. 11, red frame boxes and dotted red lines indicate the new/alternative processes and their connections to the conventional process scheme. Replacing the naphtha reformer with an aromatization unit allows for high feedstock flexibility as paraffins and/or olefins from multiple sources can be converted to BTX. Propane and butanes from associated petroleum gas (APG) are readily available at close to zero cost. C4-C8 olefins from naphtha cracker by-product streams [10)] or from fluid catalytic cracking in refineries are also good feedstocks for aromatization. Furthermore, it is conceivable to couple Aromatization with the methanol route in feeding the C4+ olefins from MTO/MTP to an aromatization unit, as outlined in Fig. 5.

Methane steam reforming and methanol as intermediate product could be advantageous in remote areas where direct processing of natural gas liquids (NGL) to high value petrochemicals is not possible, be it for logistics or investment reasons. Methanol is easier to transport than gas and can be processed in other, technically and logistically more convenient places. In this case, toluene methylation and methanol-to-aromatics can serve as major sources of aromatics that are further processed in a conventional separation and upgrading scheme. Optionally, benzene can be fed to the TM unit where it is methylated, though not as selectively to PX as this is possible with a toluene-based alkylation process.

CLARIANT Catalysts and Adsorbents for Aromatics

CLARIANT’s catalyst business goes back to the former Süd-Chemie, a world leading catalyst supplier, taken over in 2011 as part of CLARIANT’s strategy to achieve profitable and sustainable growth. Aromatics is part of CLARIANT’s growth strategy in petrochemicals, and the company’s expertise in zeolite catalysts & adsorbents is fundamental to this venture. A complete portfolio of products for conventional and non-conventional aromatics processing is offered to the industry, comprising catalysts, adsorbents and clay treating (see table below). In addition, customers take advantage of CLARIANT’s close partnership with GTC Technology LLC of Houston (TX), on process technology, engineering, licensing and equipment.

Application	CLARIANT Catalyst	GTC Licensed Process
Adsorptive PX Recovery	ZeoSorb® PX-200	AdsorbPX℠
Xylene Isomerization	ISOXYL® MPH	GT-IsomPX℠
Toluene Disproportionation	TransMax® 301	GT-TransAlk℠
C9+A Transalkylation	TransMax® 501	GT-TransAlk℠
Toluene Methylation	TolMeth™ 101	GT-TolAlk℠
Aromatization	CPA Series	GT-Aromatization℠
Methanol-to-Aromatics	MTA-xxx	Future option

CLARIANT and GTC Technology offer complementary technologies that provide comprehensive solutions to the industry based on technology packages. These are unmatched in the industry in terms of the varieties customers can choose from.

Conclusions

Aromatics from non-conventional feedstocks can become a real option, especially for gas-based economies. New catalysts and processes are available for toluene methylation, aromatization and methanol-to-aromatics that allow for the gas/methanol-based production of aromatics. These new technologies have the potential to impact aromatics production as they unlock new feedstock potential in an increasingly tight supply situation, leading to unprecedented feed and process flexibility. Though technically viable, biomass-based BTX is further down the road due to lack of cost competitiveness at this stage. Zeolite catalysts with MFI structure are key to most aromatics-selective conversion processes. They play a dominant role in conventional as well as non-conventional BTX production and upgrading. CLARIANT, based on its long-term commercial experience in zeolite catalysts, offers a complete portfolio of advances zeolite catalysts and adsorbents, incl. process technologies in alliance with GTC Technology, both for naphtha-based conventional and gas-based non-conventional aromatics technologies.

References

1) International Energy Agency 2012
2) IHS Chemical Week, April 8/15, 2013
3) ICIS 2013
4) M. Stöcker, Microporous and Mesoporous Materials 29 (1999) 3–48
5) G.F. Froment et al., Zeolite catalysis in the conversion of methanol into olefins, Catalysis: Volume 9, 1992, 9, 1-64
6) J.H.Ahn et al., Methanol usage in toluene methylation with medium and large pore zeolites, ACS Catal. 2013, 3, 817−825
7) J. Gentry, New Routes to Paraxylene, 8th Russia & CIS Petrochemicals Technology Conference (RPTC), September 22 & 23, 2013, Moscow
8) M. Guisnet, N.S. Gnep, Mechanism of short-chain alkane transformation over protonic zeolites. Alkylation, disproportionation and aromatization, Appl. Catal. A: General, 146 (1996) 33-64.
9) Flaring Up - Companies pay high costs to be green on www.oilandgaseurasia.com
10) J.Weller et al., Unlocking value potential from naphtha cracker by-product streams, Chemical Industry Digest, July 2013, 69-74
11) Gevo opens renewable paraxylene plant in Texas, Hydrocarbon Processing, http://www.hydrocarbonprocessing.com/
12) Paraxylene, ICIS Chemical Business, 35, Aug 13-26, 2012