

Refining/petrochemical integration – FCC gasoline to petrochemicals

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The global trend in motor fuel consumption favours diesel over gasoline, with gasoline often being in surplus. There is a simultaneous increase in demand for various petrochemicals such as propylene and aromatics. Technology providers have been successful to utilise the Fluid Catalytic Cracking (FCC) unit as a method to produce propylene by high severity operation, but the potential for other petrochemicals from these units has been neglected.

Cat-cracked gasoline contains a high level of olefins, some sulphur, and appreciable aromatics. Until now, the aromatics were not wanted due to the olefin and sulphur impurities in this stream. A novel technology is now available to separate the aromatics from FCC gasoline in order to use them directly for downstream applications. Additionally, the olefin fraction can be converted into aromatics through a simple fixed-bed reaction system. Thus all of the gasoline components are efficiently made into high-value petrochemicals. This combination of technology is much more efficient than methods that some operators use, which recycles FCC gasoline to the reforming unit.

Aromatics continues to be a fast-growing market. Petrochemicals are expected to grow significantly with aromatics global demand nearly three times the growth rate as that for gasoline from 2010 to 2024. For the next ten years, xylenes are also forecasted to be in short supply in Asia, despite the build-up of plants there.¹ Since the demand for gasoline is generally declining, and the specifications for gasoline disfavour excessive aromatics, it is logical to convert gasoline components into aromatics.

Significant amounts of aromatics can be recovered from the refinery cracked naphtha streams, and GTC offers technology to recover these aromatics for use as a petrochemical feedstock. GTC's approach also synergistically reduces the

sulphur and olefins content in the gasoline moving towards an environmentally acceptable specification. Additionally, it frees naphtha reformer capacity to accept fresh feed naphtha, thus increasing the overall aromatics production and hydrogen generation.

This presentation gives a case study of a design for an Eastern European refinery, which is re-configured to produce propylene, benzene, and paraxylene, with no gasoline. The design was enjoined with the staff of Rafo (Rafinerie Onesti), which targeted this project to earn a higher margin on crude oil processing.

High-Severity FCC

High-severity FCC is intended to increase olefin yields, driven by the fast growing global demand for npropylene. The propylene yields can be increased from 3-5% in conventional FCC to 15-28% in a high severity mode. In high-severity FCC operation, the aromatic content in the cracked naphtha is 50-70%, which is suitable for aromatics recovery, but it contains significant amounts of thiophenic sulphur impurities and is highly olefinic.

What Happens to FCC Gasoline Traditionally?

Typical FCC gasoline sulphur ranges from 1000 to 2000 ppm and is the dominate source of sulphur in the gasoline pool. FCC gasoline desulphurisation is required to meet the tight gasoline regulation. To effectively reduce the sulphur content and minimise the impact within the refinery, it is necessary to understand the olefin and sulphur distribution, olefin structure and component octane values.

Table 1 shows the sulphur distribution and type with carbon number in a typical FCC gasoline. The light ends are very low in sulphur with mercaptan being the major sulphur species, while heavy ends are very high with thiophenes

Carbon No. (boiling range)	Mercaptan %	Sulfide %	Thiophene %
C ₄	2.23	4.27	3.96
C ₅	4.16	0.67	15.02
C ₆	4.81	5.49	24.83
subtotal	11.20	10.43	43.81
C ₇	-	9.60	11.25
C ₈	-	5.34	6.66
C ₉	-	-	1.07
subtotal	-	14.94	19.00
C ₁₀	-	-	0.31
C ₁₁	-	-	0.31
subtotal	-	-	0.32
Total	11.20	25.40	63.4

Table 1

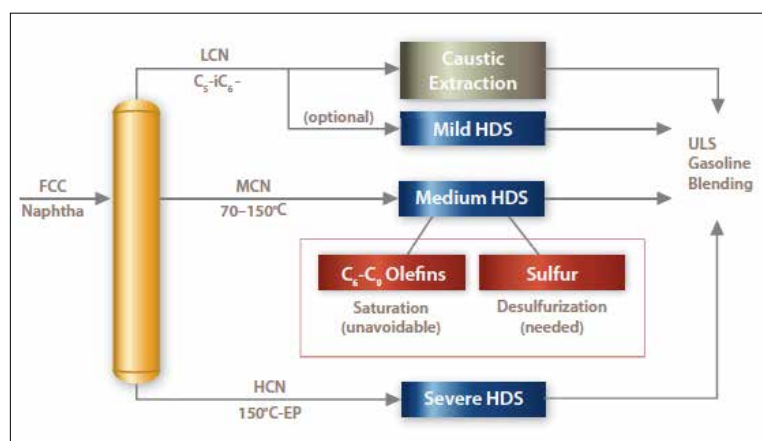


Figure 1 Traditional three stage-stage process for FCC gasoline desulphurisation

being the major sulphur species. Typically the olefins are concentrated in the light fraction, with less olefins in heavy ends.

The sulphur content can be reduced considerably by hydrodesulphurisation (HDS), but some of the olefins are consequently saturated, causing octane loss and hydrogen consumption. Figure 1 is a traditional FCC gasoline desulphurisation configuration to remove sulphur. FCC naphtha is commonly separated into three fractions by distillation. Since the primary sulphur content in the light cut naphtha (LCN) is mercaptan, a caustic extraction process is very effective to remove those types of components. Alternatively, mild HDS can be used.

Therefore, a high octane number for light fractions is mostly retained. For middle cut naphtha (MCN), due to increased content of thiophenic

sulphur, medium-severity HDS is required to remove this sulphur, which will also cause unavoidable saturation of C₆-C₉ olefins contained in this stream, and consequently octane loss. Heavy naphtha (HCN) goes through a severe HDS, but due to low olefin content in this stream, octane loss is minimal.

Some refiners process the FCC gasoline through a naphtha reformer, to “yield more aromatics.” In theory, reformed FCC gasoline does have a high aromatic content, but this material is not a good reformer feed. The contained-aromatics simply take a free ride through the unit, while the olefins will consume hydrogen in the naphtha hydro-treater unit before being reformed. Fresh naphtha on the other hand, will create more aromatics and hydrogen through the reformer unit.

GT-BTX PluS® – A New Value Proposition

Aromatics cannot be directly recovered at high purity by conventional distillation because of the close-boiling components and azeotropes which form with

other components. 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.

Until recently, refiners did not consider recovering aromatics from FCC gasoline, because the extraction technology would not function with olefinic or sulphur impurities in the feed. The GT-BTX PluS technology is designed specifically to make this operation by extractive distillation, which permits the direct recovery of aromatics, while rejecting the olefin-rich fraction as raffinate. The sulphur species are also extracted into the aromatic fraction (ie. -PluS), 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 a conventional one, and can be a simple design. The raffinate from the GT-BTX Plus unit can be used directly in the gasoline.

GT-BTX Plus is optimally installed on the FCC middle cut naphtha stream. FCC gasoline in the C₆-C₈ range is routed to the GT-BTX Plus, where the aromatics plus sulphur species are separated from the olefinic raffinate. The aromatics fraction goes to simple hydrosulphurisation and BTX fractionation. Figure 2 shows a simple scheme for the GT-BTX Plus process.

The reformer can take in additional fresh naphtha to generate more aromatic molecules and more hydrogen, than it would if the FCC gasoline were included in the feed mix. The olefin-rich nonaromatics fraction can be directly routed to gasoline.

Is it possible to make better use of this olefin rich stream, particularly to convert this stream into BTX? The answer is yes, by the addition of an aromatisation technology using olefin-containing feedstock. GTC offers aromatisation technology for this purpose.

Aromatisation Process

The aromatisation 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 many olefinic components in the C₄-C₈ range as feed to produce the aromatics. By-products are light paraffins and LPG off gases.

The aromatisation reaction takes place in a fixed bed reactor; the reactor operates in a cyclic mode of regeneration (Figure 3). The operation is very simple and it requires no recycle

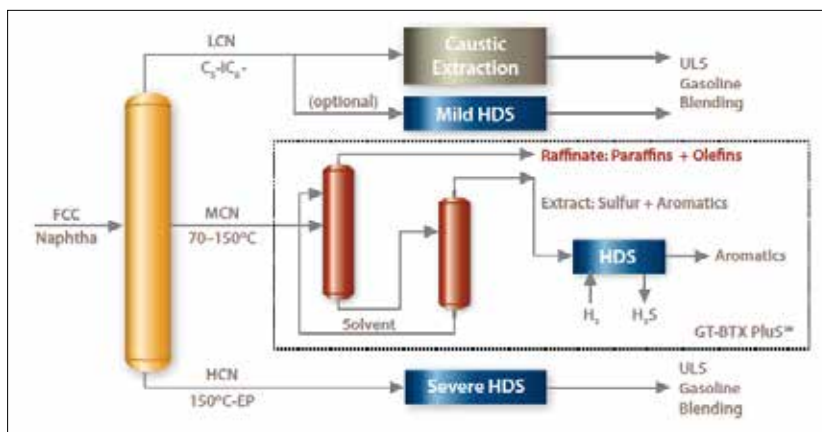


Figure 2 Simple GT-BTX Plus® process

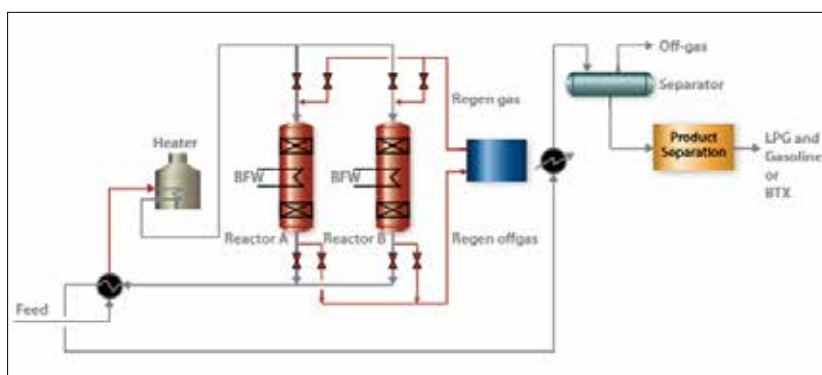


Figure 3 Simplified process scheme for Aromatisation technology

compressor or hydrogen consumption. The reactor is operated at 460-540 °C and the pressure is 1-4 bars. The liquid yield (aromatics) is 47-55% depending on feedstocks. By-products are dry gas and LPG off gases.

Separation of liquid aromatics products can be accomplished in the existing BTX recovery post-fractionation unit.

The unit can take the FCC C₄ and C₅ cuts along with the GT-BTX-Plus C₆-C₈ raffinate as feed to add another aromatics increment. This option has the synergistic effect of removing olefins from the gasoline pool and increasing aromatics production for petrochemical use.

Case Study – GT-BTX Plus® and Aromatisation

The case study is part of a recent design prepared for Raffinerie Onesti. This particular European refiner considered the competitive challenge in the industry to be of a serious nature, and chose a refinery configuration to make a very high proportion of products as

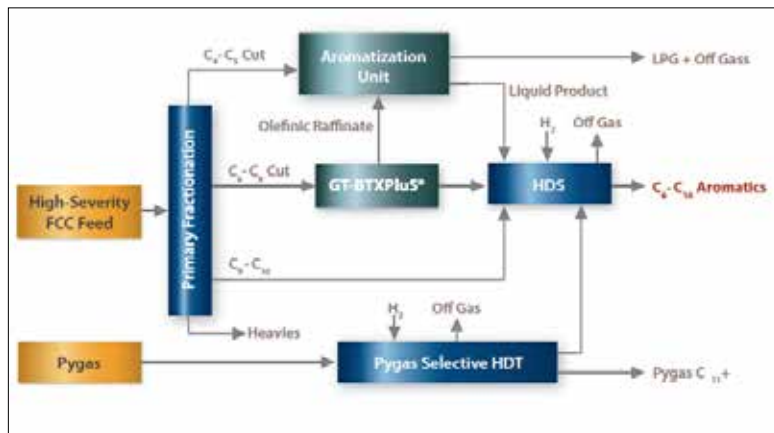


Figure 4 GT-BTX PluS® and Aromatisation implemented for Rafinerie Onesti

C ₆ -C ₉ AROMATICS	KG/HR	TPA
INDIGENOUS FCC	11,427	97,126
PYGAS	8,029	68,245
AROMATIZATION	26,525	225,471
TOTAL	45,981	390,842

Table 2

petrochemicals with no yield of gasoline.

In the configuration (Figure 4), the primary fractionator separates the high-severity FCC products into light, heavy, and gasoline-range products. The heavy fraction is routed to the diesel pool.

The middle fraction is processed in the GT-BTX PluS unit, which separates the aromatics plus sulphur from the olefins. The aromatics are desulphurised in a simple HDS unit. Since there are no olefins in this fraction to saturate, the hydrogen uptake is minimal and the octane remains unchanged. Additional pygas is imported and processed through a selective hydrotreating unit and the HDS unit to increase BTX production.

The non-aromatic raffinate fraction, rich in olefins, along with the C₄/C₅ fraction (also rich in olefins) is processed through an aromatisation unit. This fixed-bed process yields a highly-enriched aromatic fraction, concentrated in toluene, xylenes, and C₉ aromatics that are ideal for producing paraxylene.

The hydrotreated GT-BTX PluS effluent and the aromatisation product are fed to the aromatics complex for benzene and paraxylene recovery. A global BTX balance for the case

study is presented in Table 2. The total C₆-C₉ aromatics incremental capacity is 225 TPA with the addition of the aromatisation unit. Thus, Rafo gained enough aromatics to supply a world scale project for paraxylene manufacture without building costly catalytic reforming capacity.

Another option for the olefinic raffinate stream is to recycle to the FCC unit itself, then generate more propylene, as olefinic components have a high cracking yield of propylene.

Conclusion

In conclusion, GTC Technology has processes available now that can significantly improve aromatic feedstock availability, while maintaining current refinery capabilities with increased asset utilisation.

- GT-BTX PluS for direct extraction of aromatics from FCC gasoline or other cracked stock, which helps to rebalance gasoline surplus in some regions
- GT-BTX PluS in conjunction with the Aromatisation process for additional aromatics production from cracked gasoline olefinic species to meet market demand
- GT-BTX PluS is an enabling technology that permits different uses for the olefinic stream from which aromatics have been removed

The demand profile for motor gasoline is declining, yet petrochemical demand is increasing. The combination of GT-BTX PluS and Aromatisation will give better economics than the traditional approach to produce aromatics solely through catalytic reforming or pygas extraction.

References

1. IHS 2014 World Petrochemical Conference – www.ihs.com

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