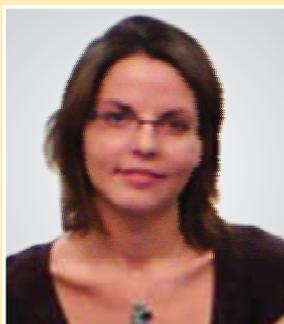


Using Technology to Increase Middle Distillate Production



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Varying constraints constantly alter the refining industry's landscape. Over the past few years, regulations on low-sulfur gasoline and diesel fuel, curbs on refinery emissions and the increase in heavy crudes have influenced the refiner's market. New forces that are altering the outlook such as improvements in light vehicle fuel economy, the widespread presence of emerging markets and the rise of shale oil and gas must now be reckoned with. This article provides an overview of market trends as well as 2020 and 2030 outlooks as the current demand for middle distillates is expected to grow in the US, Europe but also emerging markets. The second section will focus on the oligomerization technology PolyFuel, which can adjust refinery output towards middle distillates.

In 2012, global oil demand was around 89.7 Mb/d (million barrels per day) according to the latest IEA estimates (International Energy Agency, Dec. 2012), driven by growth in emerging countries. Broken down by product, global oil demand growth is driven by the middle distillates composed of kerosene and diesel, unbalancing the product slates in some regions.

World's Demand For Middle Distillates

From 2000 to 2010, world consumption growth for middle distillates exceeded the demand growth of gasoline and of total oil products: the annual average growth rates (AAGR) were 1.6%/year and 1.3%/year respectively. In 2020, continued robust global distillate demand is expected, with a growth rate still at 1.6%/year, above total oil demand growth. By contrast, gasoline demand growth is forecast to be weak with an increase of 0.7% per year. From 2020

to 2030, while global oil demand growth is expected to be restrained at 0.6%/year, middle distillates still stay a primary driver with an annual growth above oil (Figure 1).

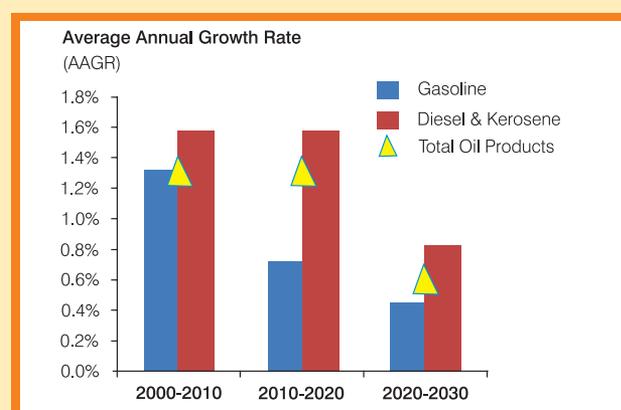


Figure 1 : World demand growth for oil products

Atlantic Basin Gasoline/ Distillates Overview

European Imbalance

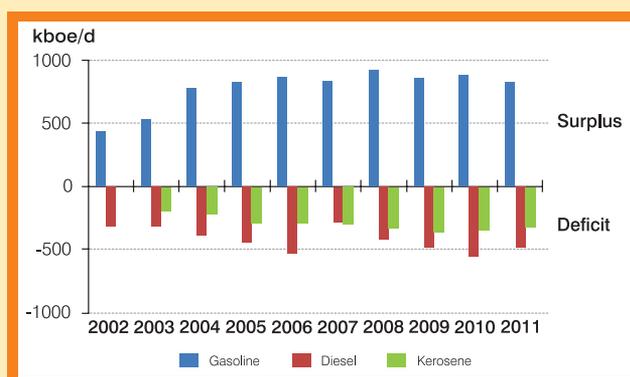


Figure 2 : European (EU-27) net exports in gasoline, kerosene and diesel (Source JODI)



Since 1998 Europe has faced excess gasoline production volumes. Much of the European excess gasoline has been exported to North America, a light vehicle gasoline market. Today, however, gasoline production within the US has increased while gasoline demand from petroleum has reduced. Consequently, European gasoline exports to the US have decreased. With a gasoline surplus exceeding 800 kboe/day (thousand barrels of oil equivalent per day) (Figure 2), European refiners have found other export destinations in Latin America, Africa and the Middle East.

Accounting for half of total oil demand, diesel remains the principal product consumed in Europe (EU-27) mainly due to the transportation sector. The mismatch between gasoline and diesel supply and demand increases the pressure on European refineries which cannot satisfy their market. As a result, net diesel imports remain significant reaching a maximum of 560 kboe/day in 2010, originating mostly from the CIS and the US. Furthermore, Europe is short of kerosene with a strong and stable deficit of around 300 kboe/day, heightening the European thirst for middle distillates (Figure 2).

North American Refining "Metamorphosis"

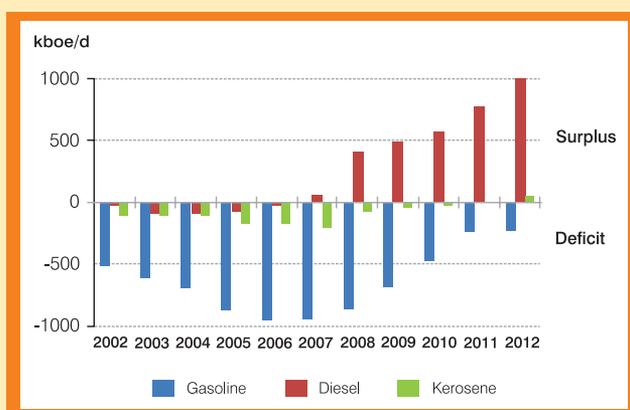


Figure 3 : North America net exports in gasoline, kerosene and diesel

The North American situation is completely different (Figure 3):

- US diesel net exports have considerably increased since 2008 reaching more than 1 Mboe/d in 2012,
- kerosene imports and exports are balanced and
- North America gasoline imports have reduced by 75% when compared to 2006 and should be about 230 kboe/d in 2012.

With world growth in middle distillates and reduced domestic demand for gasoline, the US refiners have developed diesel exports over the past few years, increasing distillate yields by changing distillation

cut-points or adapting their refinery units' operation mode with small capital investment.

US petroleum based gasoline imports have collapsed since 2011 due to reduced finished motor gasoline demand, which has been declining by 1.6%/year since 2007 because of economic conditions and improved engine energy efficiency for new light duty vehicles (CAFE standards) and ethanol blending requirements.

On the crude supply side, a game changer is also modifying the US refining dynamics; the rapid growth in shale oil production. US crude production is surging in states where shale oil is available, the Bakken field in North Dakota and Eagle Ford field in South Texas are the largest but many other finds are spread across the country. This development has transformed the US refining industry. Refiners in the US Gulf Coast - where 44% of the US refining capacity is located, benefit from this cheap crude.

Yet there are some disparities; refiners on the East Coast struggle and experience closures. In PADD 1, refiners cannot easily access the new shale oil supplies; they remain dependent on crude imports and face competition from European gasoline imports. Nevertheless, imports of crude and oil products are collapsing and the US has become a net exporter of oil products. Furthermore, US Gulf coast refineries which run shale oil will produce more light products due to this light sweet crude supply and natural gas liquids (NGLs) associated with shale production will increase in the coming years. All of these factors will weigh on the whole light ends complex and may lead to naphtha surplus in the US.

Non-OECD Economies Spur Growth in Global Oil Demand

Predictions point to non-OECD oil demand share rising from 48% to 60% in 2030, mostly concentrated in Asia, the Middle East and Africa (Figure 4).

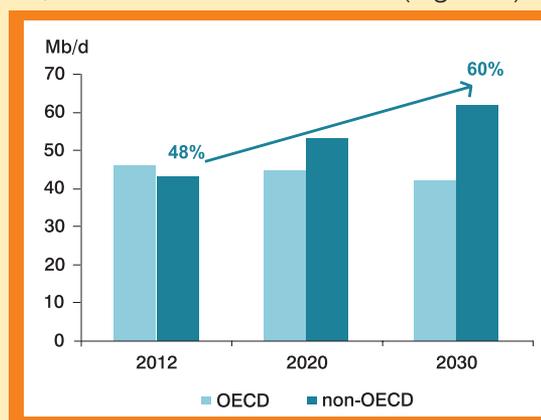


Figure 4: OECD and non-OECD total oil demand from 2012 to 2030



Emerging countries are forecast to dominate middle distillate demand growth, particularly in non-OECD Asia, with a significant shift towards diesel in the passenger vehicle market in India and a demand growth driven by commercial freight in China.

In conclusion, with a global surplus of gasoline reducing the export opportunity and a growing deficit in middle distillates regionally, either in OECD countries or emerging economies, refiners are led to rebalance their product slates. New technologies are needed to respond to these trends, producing more middle distillates and compensating for a gasoline demand reduction in OECD countries and a potential oversupply of light products and gasoline in the US.

PolyFuel Technology Review

Optimizing refining product slate around the FCC

As the demand for middle distillates is growing faster than that of gasoline increasing interest in process options to shift the ratio of diesel to gasoline production has been registered. This trend has been seen in Fluid Catalytic Cracking (FCC) units along with an increased demand in propylene from the FCC to help satisfy the much faster growing petrochemicals demand. An underlying theme has been increased regulation to sharply reduce the sulfur content of both gasoline and diesel and limit the olefin content in gasoline.

An increasingly popular technology option to address the fuels imbalance and product flexibility requirements is olefin oligomerization. Reactive olefins can be oligomerized mainly into dimers and trimers to increase the size of the molecules and shift the product slate towards heavier components. A well proven technology to convert C_3 - C_4 olefins into gasoline and diesel range components has been in commercial operation since 1986 under the trade name of Polynaphtha™. Unlike older polymerization technology oriented to gasoline production based on solid phosphoric acid catalyst, Polynaphtha uses a regenerable catalyst with the ability to produce gasoline and distillate fuels. Polynaphtha offers a low cost alternative to alkylation and an alternative outlet for propylene, particularly when recovery is not economic.

When distillate production is favored, an extension of this concept can be used to convert C_5 - C_9 gasoline olefins into distillate in a simple, low cost PolyFuel™ process. A generic block flow diagram

of the PolyFuel process is shown below:

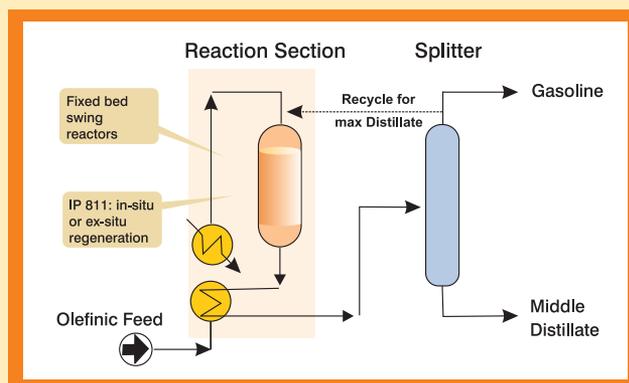


Figure 5 : PolyFuel™ Process General Flow Diagram

In the PolyFuel process, light olefins are oligomerized catalytically in a series of two fixed bed reactors. Conversion and selectivity are controlled by reactor temperature adjustment while the heat of reaction is simply removed by feed-effluent heat exchange (Figure 5). The reactor section effluent is fractionated producing gasoline depleted in olefins and middle distillate fractions. The gasoline fraction is partly recycled to the reaction section to enhance middle distillate production. The distillate fraction is typically sent to existing kerosene and diesel hydrotreating directly.

The reaction section uses swing reactors to allow for continuous operation with on-stream catalyst regeneration or replacement. The management of the reactors is optimized to maximize catalyst run-length. With the objective to produce high quality distillate, the PolyFuel process utilizes the IP 811 catalyst which can be operated at high severity to maximize the middle distillate fraction thanks to its high activity and stability. Typically the middle distillate yield exceeds 70% as compared to feed olefins. The IP 811 catalyst can undergo multiple regeneration cycles with over 95% activity recovery demonstrated. Catalyst regeneration can be performed in-situ or ex-situ.

Like Polynaphtha, PolyFuel produces a high quality jet A1 fraction after hydrotreatment to saturate olefins. The smoke point exceeds 35 mm which is far above the Euro V specification.

Feedstock selection for PolyFuel depends on the availability of olefin-rich streams and the refinery-specific product requirements. When distillate is more favored than gasoline, portions of the FCC gasoline product are logical feeds. In principle PolyFuel can accept the full range of C_5 - C_9 gasoline



cut produced from the FCC unit. The C₅-C₆ portion contains the highest concentration of reactive olefins. The heavier C₇₊ portion contains less olefins and can have a high content of contaminants (sulfur, nitrogen and oxygenates) which reduce catalyst cycle length. As an illustration a typical gasoline olefins and sulfur profile as a function of boiling point is shown in Figure 6.

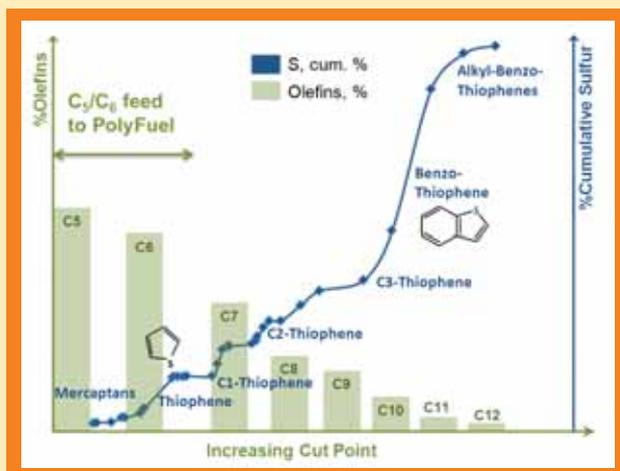


Figure 6 : Typical FCC gasoline olefins and sulfur profile

Based on these observations, Axens has identified the C₅-C₆ olefin-rich cut as the preferred feed to be processed in the PolyFuel to reach the highest profitability by:

- maximizing the amount of the oligomer product,
- maximizing catalyst run-length,
- minimizing the feed pretreatment,
- significantly reducing the olefin content in the remaining gasoline product.

The previous point on olefins reduction in the remaining gasoline pool can be significant in regions where olefins content is tightly regulated. Typically the olefins in the C₅-C₆ cut are reduced by over 80% as compared to the C₅-C₆ PolyFuel feed. When the FCC is operated at high severity to maximize propylene, the concentration of C₅-C₆ olefins is very high in the gasoline and may result in an off-spec gasoline pool. As a result, PolyFuel can help both to satisfy the need for increased distillate and to improve the gasoline pool properties.

In order to prepare the feedstock to the PolyFuel unit, one can take advantage of existing FCC gasoline selective desulfurization unit design. The most widely selected technology is the Prime-G+™ process with 214 licensed units as of January 2013.

The Prime-G+ first step, which consists of a Selective Hydrogenation Unit (SHU) on the Full Range Cracked Naphtha (FRCN) with a downstream splitter, provides an ideal feed pre-treatment by removing the diolefins and by reducing the sulfur content of the light C₅-C₆ cut. In refineries which include the Prime-G+, a PolyFuel unit can easily be installed on the Light Cracked Naphtha (LCN) from the splitter top thereby minimizing pretreatment cost of the process (Figure 7).

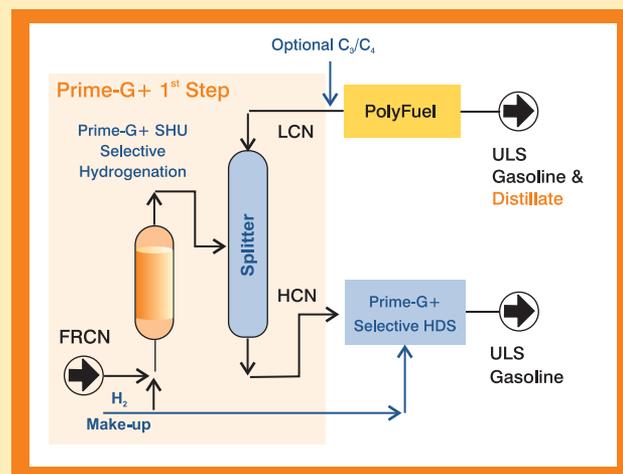


Figure 7 : Prime-G+ integration with PolyFuel for contaminant control

To maximize refinery profitability the feedstock can also include olefinic C₃ and/or C₄ fractions depending on the refinery objectives and economics. Olefin-rich feed components may come from any cracking process such as FCC, Coking, Steam Cracking or any other olefin sources such as effluent from paraffin dehydrogenation or alcohol dehydration. Specific pretreatment options are adapted depending on feed origin and contaminants level.

An attractive FCC-based refinery configuration to maximize middle distillates consists of mixing available LPG with a C₅-C₆ LCN cut and feeding the blend to a PolyFuel unit. Available sources of LPGs in a refinery may be:

- C₃s when not sent to petrochemicals,
- C₄s when no C₄ cut upgrading processes are present,
- or excess C₄s in case of existing C₄ cut upgrading processes bottleneck (alkylation unit, ...).

The relative amounts of LPG and C₅-C₆ cuts and the operating severity of the PolyFuel unit can be



optimized to adjust the distillate product rates in accordance with the market demand while reducing the gasoline surplus.

In summary, the PolyFuel technology addresses the gasoline/middle distillates imbalances by selectively converting unwanted olefinic streams in the C₃-C₆ range into distillate fuels while meeting increasingly tight product specifications. A PolyFuel unit can be designed to operate over a wide range of LPG and/or C₅-C₆ olefinic feed compositions and with the flexibility to adjust the gasoline/middle distillates product ratio to regional requirements.

In addition to a stand-alone configuration, PolyFuel can also be applied within the FlexEne™ concept which is Axens' innovative combination of FCC and oligomerization processes. This combination enhances product flexibility by controlling the balance of propylene, gasoline and middle distillates production with a low additional capital investment to the FCC complex. This flexibility is achieved via selective oligomerization of light FCC olefins into heavier fractions and recycle of undesired oligomer cuts for further cracking in the FCC thus increasing the desired product slate - often an increase in propylene and distillate.

A typical distillates oriented flow scheme of PolyFuel integrated in the FlexEne concept is presented in Figure 8. The operation of the FCC, selection of feedstock cuts to the PolyFuel, operating severity of the PolyFuel and oligomer product cut recycled to the FCC are all parameters subject to optimization depending on product demand and pricing.

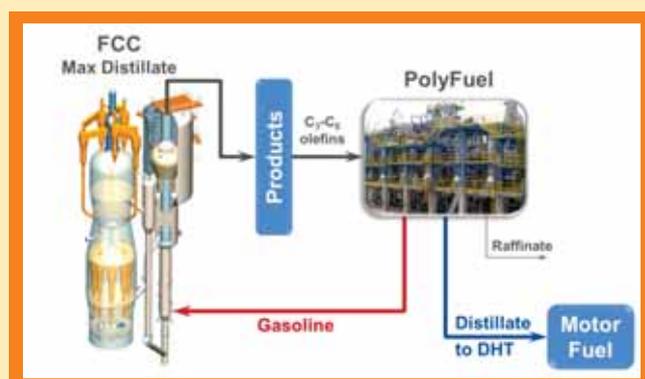


Figure 8 : PolyFuel in a FlexEne configuration oriented to distillates production

Reaching Refining/Petrochemical Integration

When the refinery is integrated with a petrochemicals complex there are further opportunities to share feed and product streams to improve profitability. The

oligomers from the PolyFuel unit can be entirely recycled to the FCC to maximize propylene production, and the paraffinic raffinate sent to the steam cracker to produce more petrochemicals or gasoline blend stock.

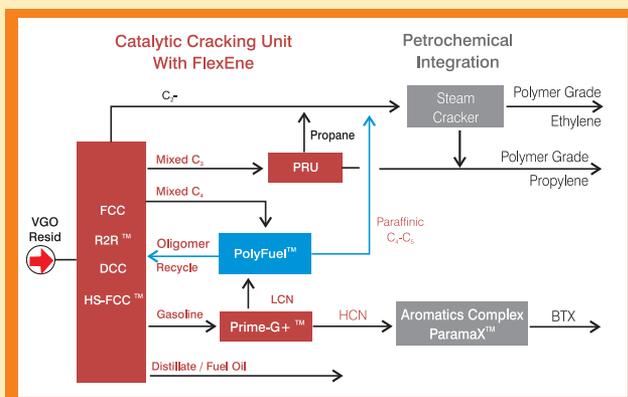


Figure 9 : Refining and Petrochemicals integration with FlexEne and PolyFuel

As indicated in the name, the FlexEne concept utilizing FCC with PolyFuel provides great flexibility to optimize the production of propylene, gasoline, and distillates according to the market demand.

In the context of faster worldwide growth in demand for distillates and propylene than for gasoline but with regional disparities, Axens has developed a new PolyFuel process with the flexibility to:

- process lower valued olefinic feeds in the C₃-C₆ range from a variety of sources,
- maximize distillate production and reduce gasoline production according to market demand,
- further optimize distillate or propylene production when integrated with FCC in a FlexEne configuration,
- improve the overall refinery economics as feed and product prices fluctuate.

Conclusion

With the world market for middle distillates growing and a reduced demand for gasoline in certain regions, the new PolyFuel process for olefinic gasoline oligomerization allows the refinery scheme to be adapted to a maxi distillate mode.

It is particularly in Europe where the difference between the refinery yield structure and market demand is critical, especially since the conventional refining tools do not have the flexibility to reduce excess gasoline production and to increase the amount of middle distillates. Moreover, with

European refineries having increasing difficulties in finding an export market for their excess gasoline and given the tensions in middle distillate supply, PolyFuel should fulfill a primordial role in adjusting the gasoline-distillate production to better fit market demand.

In other regions, new tendencies such as shale oil

and shale gas are revolutionizing the US market, providing additional light products and consequently influencing market balance and prices.

The flexibility of PolyFuel offers many advantages to the refiner and particularly the ability to anticipate market needs in different regions with as constraints evolve.

Snippets

Money involved in banks writing- off bad loans to corporates between 2000-01 and 2012-13, rarely mentioned or debated: ₹ 1,00,000 crore

Average age of billionaires in USA, Germany and Brazil, in years: 67/66/64

- Average age of billionaires in India, UAE and China, in years: 63/57/53

- Percentage of Chinese billionaires that are self-made, highest such proportion worldwide: 90

- Percentage of Indian billionaires that are self-made: 47

Percentage increase in global CO₂ emissions in 2012: 1.1

- Rank of China, USA, European Union and India among world's largest emitters: 1,2,3,4

- Percentage change in CO₂ emissions in India and

China between 2011 and 2012: 7&3

- Percentage change in CO₂ emissions in USA and EU between 2011 and 2012: -4 & -1

