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Integration of the Total Petrochemicals-UOP olefins conversion process into a naphtha steam cracker facility

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Abstract

Integration of the Total Petrochemicals-UOP olefins conversion process (OCP) into a conventional naphtha steam cracker allows maximizing the propylene to ethylene yield ratio while converting olefinic feedstocks such as Raf 2, Raw C4s, HT Raw C4s and light FCC gasoline.

Comparisons are made between the product yields obtained from these olefinic streams through conventional steam cracking, and the combined yields when the olefinic feedstocks are first converted on an OCP process and the C4+ product further processed on a steam cracker furnace

OCP as a feed-pretreatment for steam cracking of olefinic feedstocks allows shifting the P/E ratio in the global product slate to values well outside the normal ranges observed on SR naphtha. In an existing steam cracker that is furnace limited, the concept may permit to increase the propylene yield dramatically. The highest potential is observed when the plant has no other option than to recycle crack the Raw C4s.

Keywords: Olefins conversion process; Naphtha; Olefinic

1. Introduction

Total Petrochemicals Research Feluy (formerly Fina Research S.A.) started in 1995 a development aiming to produce propylene at high selectivity and of ‘‘chemical grade’’ (>94% purity) by catalytic conversion of C4 raffinates and olefinic gasolines originating from steam crackers, FCC units, coker and visbreaker units [1].

The catalyst that was developed for this purpose has many similarities with propylene booster type additives commonly used on FCC units. The particular challenges that needed to be resolved were:

- minimal hydrogen transfer capabilities in order to enhance the propylene purity, to reduce the paraffin, aromatics and coke production;
- hydrothermal stability during regeneration cycles;
- Precise control of density and strength of acid sides.

A medium scale process demonstration unit (~2 tonnes/day) was installed in the Total Antwerp Refinery, and extensive data have been collected for several years on various refinery streams. In 2003, a formal alliance with UOP was announced at the Paris EMEA Conference [2] and since then, the OCP process has been widely presented at symposia [3–5] and several basic engineering studies have been launched for industrial projects.

Fig. 1 summarizes the main chemical reactions occurring over the catalyst. C4 olefins can only be converted to propylene via an oligomerization/cracking mechanism. Interestingly, experiments demonstrate that even ethylene will convert to a significant extend to propylene and higher olefins. As illustrated in Fig. 2, an OCP process can be designed with various recycle options in order to increase the overall yield of propylene.

More recently, it was also confirmed that long chain paraffins do convert into olefins under the typical OCP operating conditions.

2. Steam cracking of naphtha and alternative feedstocks

It is generally recognized that the demand for propylene will increase at a higher pace as compared to ethylene. On a

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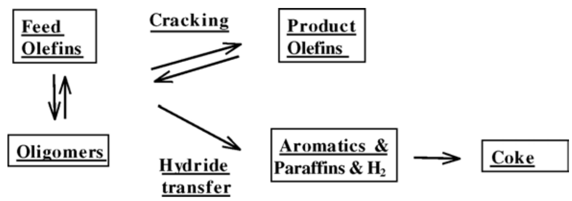

Fig. 1. OCP main chemical reactions.

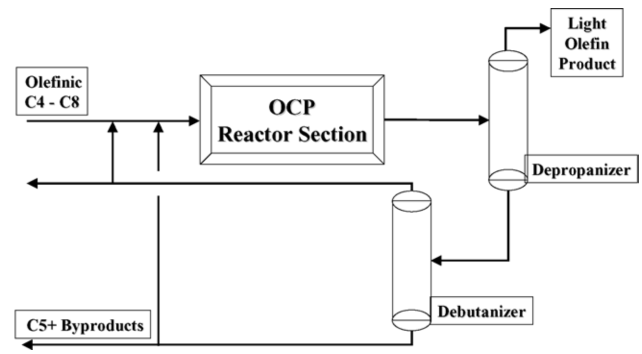

Fig. 2. OCP simplified process scheme.

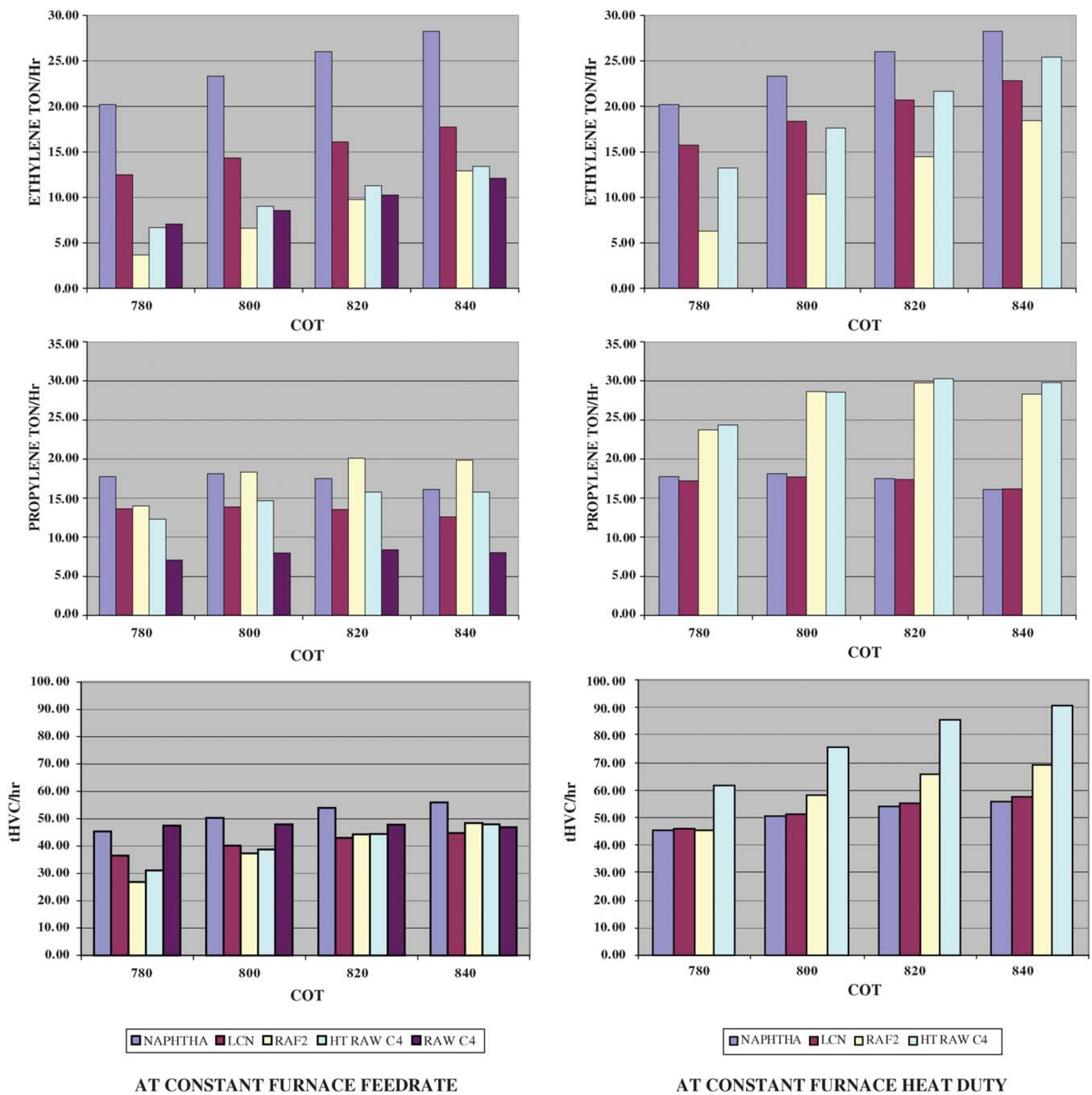

Fig. 3. Steam cracking of straight run naphtha and olefinic feedstocks.

naphtha steam cracker, the propylene to ethylene product ratio (“P/E”, often referenced as “severity”) typically ranges from 0.4 to 0.7 by weight. The product slate and olefin productivity on feed basis also depend on the feed flexibility that is accounted for in the design, and the integration with upstream and downstream processing units. A nearby refinery will facilitate seasonal imports of butanes, MTBE C4 raffinate (“Raffinate 2”), FCC off gas, etc. Downstream units – or their non-existence such as a butadiene extraction process – can force a cracker to recycle crack Raw C4s, Raffinate 1, C5 pyrolysis gasoline after the first stage hydrogenation, etc. In a region, such as NW Europe that is long in gasoline, steam cracking of light FCC

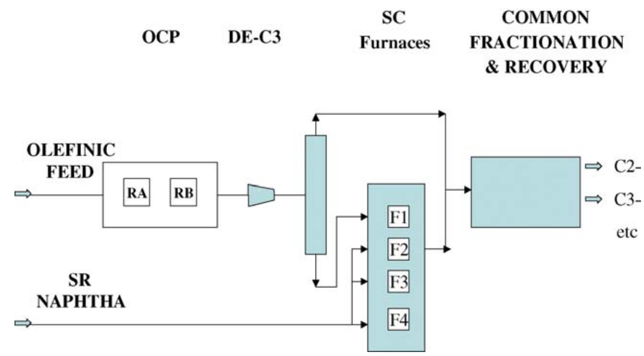

Fig. 4. OCP/steam cracker integration scheme.

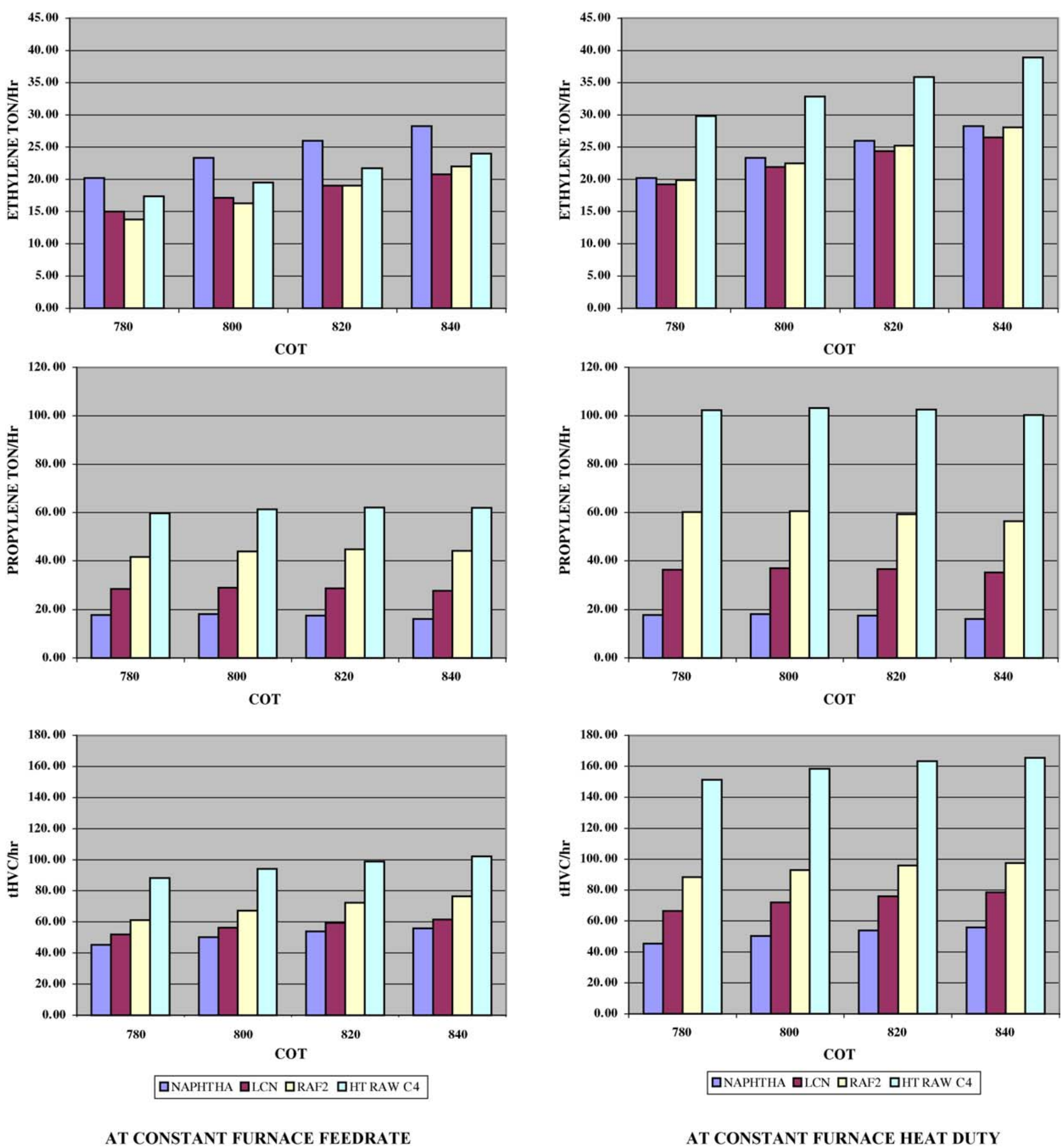

Fig. 5. OCP integration into a steam cracker.

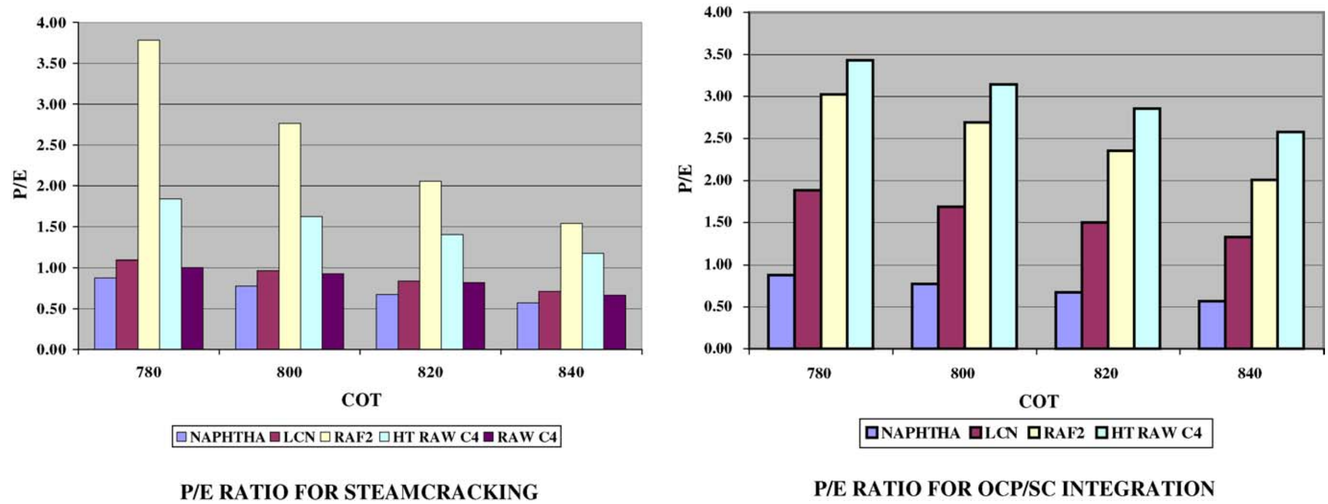

Fig. 6. Propylene to ethylene ratios.

gasoline can become economically attractive in spite of the poor ethylene yields.

The endothermic heat of reaction for the pyrolysis of olefinic feedstocks is significantly lower than for straight run naphtha. This implies that for a given heat duty of the fire box, the feedrates for olefinic feedstocks can – at least conceptually – be increased in order to reduce the gap in light olefins productivity. Fig. 3 summarizes some of the main simulation results. All reported simulations have been made for 500 ms of residence time and a coil outlet temperature (COT) ranging from 780 to 840 °C. For simulations at constant feedrate, the feedrates have been arbitrarily set at 100 MT/h, simulations at constant heat duty refer to the furnace duty of 100 MT/h of SR naphtha at the corresponding COT. In these simulations, the furnace geometry was kept unchanged and as a consequence, the coil pressure drop increased accordingly while the residence time decreased. The main observations are:

- Olefinic feedstocks produce significantly lower yields of ethylene, comparable or lower amounts of propylene, but higher yields of butadiene and benzene. The sum of these is often referred to as high value chemicals (HVC).
- At constant feedrate, the P/E is dramatically shifting to extreme ratios in particular for Raffinate 2 and hydrotreated Raw C4s.
- At constant heat duty, the same observations are confirmed but the productivity of HVC is very much recovered.

Simulated coking rates are acceptable, but it is obvious that cycle times will become shorter. Reducing the COT favors in all cases the propylene selectivity and will alleviate the coke lay down in the coils.

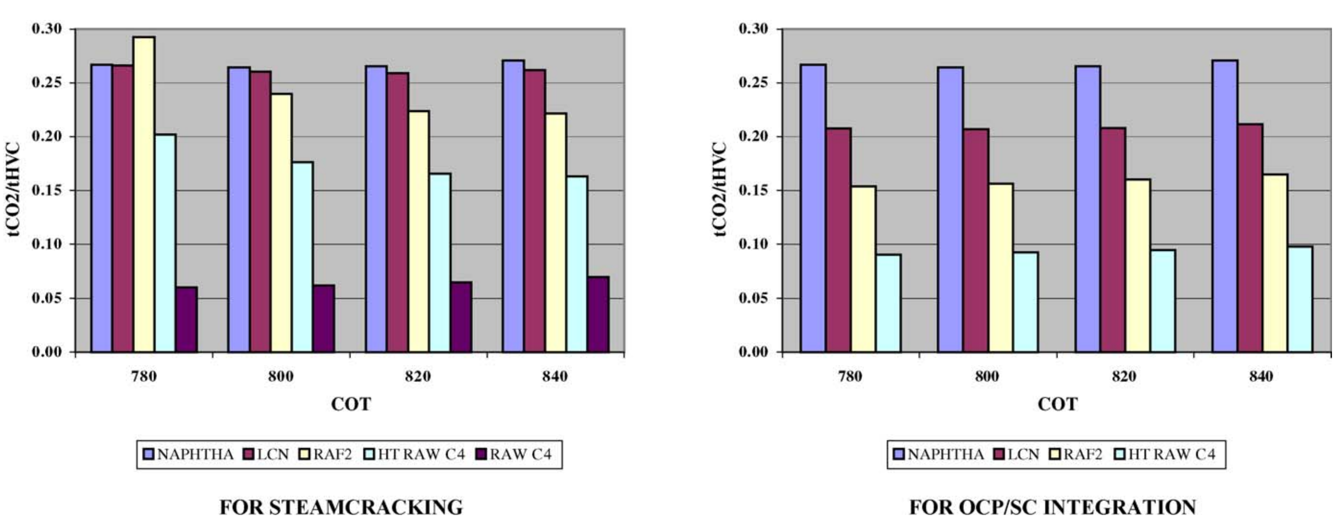

Fig. 7. CO_2 emissions per tonnes of HVC.

3. OCP integration into a steam cracker

One can imagine various ways to integrate an OCP into a naphtha steam cracker [6]. Feedstock availability, grass roots versus debottlenecking, local conditions and capital expenditure will impact the optimal design. In all cases, the justification is logically to favor the propylene productivity. Fig. 4 illustrates an integration concept where olefinic feedstocks that can be recycle streams from the steam cracker (hydrotreated Raw C4s, Raffinate 1) or imported feedstocks from a refinery such as light FCC gasoline (LCN), are introduced into an OCP. The effluent is compressed and depropanized, the overhead is routed to the product recovery section, while the bottom stream is fed to one or more dedicated steam cracking furnaces. In many steam cracker plants, one will find furnaces of different vintages, and certain furnaces may be more appropriate to receive olefinic feedstocks. As already suggested in Section 2, it may be beneficial to run these dedicated furnaces at lower COTs. Another option could be to co-crack the olefinic streams with the straight run light naphtha.

Fig. 5 summarizes the same comparisons as made in Section 2:

- either the furnace operates at the same feedrate as per the base case (SR naphtha);
- or the comparison is made at the furnace duty of the SR naphtha at the same COT.

The product yields given in Fig. 5 are this time the combined yields of the OCP and the steam cracker furnaces and these are significantly higher since overall, more tonnes of feed materials are introduced to the complex. It is clear that for an existing steam cracker, the cracked gas compressor and the recovery section will determine the amount of SR naphtha that can be substituted by the olefinic feedstocks. Very noticeable is the reduction of the production of fuel gas (H_2 and CH_4) on the furnaces that will help to unload the cracked gas compressor.

Fig. 6 compares the propylene to ethylene product rations for steam cracking as opposed to the OCP/SC integrated scheme. While ‘‘Raffinate 2’’ produces propylene at high selectivity under conventional steam cracking conditions, all olefinic feedstocks strongly favor the production of propylene in the OCP/SC integrated process, at a relatively moderate loss of ethylene (for constant furnace feedrates) or an ethylene gain (at constant furnace duty).

Fig. 7 compares the CO_2 emissions per ton of HVC for constant steam cracker feedrates, with the OCP integration the comparison accounts for the OCP energy consumption. These emissions have been derived from the endothermic heats of reaction and do not account for dilution steam generation.

4. Conclusions

Integration of OCP into a naphtha steam cracker allows shifting significantly the product slate in favor of propylene production. C4 and higher olefins contained in C4 raffinates or olefinic gasolines are converted selectively into propylene and to a minor extent into ethylene. The olefins content of the non-converted fraction of these feedstocks is substantially reduced such that these streams can be readily converted on a conventional steam cracking furnace. The pyrolysis of these streams produces a product slate that is substantially better then if these olefinic feedstocks were steam cracked as such.

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