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Study of direct and indirect naphtha recycling to a resid FCC unit for maximum propylene production

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Abstract

To satisfy the increasing propylene demand, direct and indirect naphtha recycling schemes around an existing resid fluid catalytic cracking (FCC) unit were investigated. To this aim, light cracked naphtha (LCN), heavy cracked naphtha (HCN) and a PolyNaphtha (PN) oligomerisation product were cracked under a wide range of operating conditions over a commercial Y zeolite based equilibrium catalyst. Experimental data were acquired in three different units: a fixed bed bench scale unit, a fixed fluidised bed unit and an adiabatic circulating fluidised bed pilot plant. It was shown that FCC naphthas require high operating severities to crack, and that even then their conversion remains relatively moderate. Hence, direct recycling to the main riser does not seem a viable pathway to increase propylene product. Feeding FCC naphthas to a second reaction zone operating at high severity allows to increase the propylene yield in a significant manner. Increasing conversion, however, not only leads to higher LPG and propylene yields, but also results in very high dry gas yields. An alternative scheme was proposed, in which the olefinic C_4 and C_5 fractions are converted into a naphtha fraction through oligomerisation in a dedicated unit before being recracked in the secondary riser. As the highly olefinic oligomerised effluent mainly consist of dimerised and trimerised butenes and pentenes, this feed is more easily cracked and high conversions can be achieved. This indirect interconversion of butenes and pentenes into propylene therefore effectively allows to convert these butenes and pentenes into propylene, resulting in a significant increase in propylene yield. Each of the three main naphtha recycle options (directly to the main riser, directly to a secondary riser or indirectly via a light olefin oligomerisation unit) have been analysed and compared to a base case. In the evaluation of each of these schemes, all heat balance effects, both on the riser and the regenerator side, have been accounted for. The proposed process scheme with an indirect recycle via an oligomerisation unit enhances the already inherent flexibility of the FCC unit. The naphtha recycle can be turned on or off, the second reaction zone can be used to crack naphtha or to crack resid feed to maximise throughput, while the effluent of the oligomerisation unit can be recycled to the FCC unit for propylene production or hydrogenated and sent to gasoline and kerosene pool.

Keywords: Propylene production; Naphtha recycling; Oligomerisation; Oligomer cracking; Resid catalytic cracking

1. Introduction

Ethylene and propylene are the traditional petrochemical building blocks. The process of choice for ethylene production is steam cracking, in which propylene is a major byproduct. While the overall demand for ethylene is greater than for propylene, the growth rate of the latter has significantly outpaced ethylene's growth rate. Hence, steam-cracker derived propylene is not able to keep up with the propylene demand. To make up for this shortfall, other propylene sources are needed. On-purpose propylene technologies, such as propane dehydrogenation and metathesis, are available, but have seen only limited applicability due to the cyclic nature of the petrochemical market demand. The second most important source for propylene production is currently refinery propylene from fluid catalytic cracking (FCC) units. With the continually growing demand, operators of FCC units look increasingly to the petrochemicals market to boost their revenues by taking advantage of economic opportunities that arise in the propylene market. Refiners have hence increased propylene

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production in FCC units by optimising catalyst and operating conditions. Due to the flexibility of the FCC process, it is in a unique position to satisfy gaps in the expected increase in propylene demand.

FCC units typically produce around 3–5 wt.% of propylene, depending on the feed type, operating conditions and the nature of the catalyst. To increase the yields of light olefins, mainly propylene and butenes, in a FCC unit, several options are available. One cost-effective way to increase the propylene yield is the use of ZSM-5 based additives. Naphtha coprocessing schemes have been proposed as an alternative option, for which various configurations have been described [2]. The simplest option consists in feeding naphtha together with feed, through the same feed injectors. In a mix temperature control (MTC) system, the naphtha is fed to the riser downstream of the feed injection system [13]. Naphtha may also be injected upstream of the feed injectors, where it is cracked at higher temperature and catalyst-to-oil ratio (*C*/*O*) than in classical cracking [9,12,16]. Another method to increase propylene production is adding a second reaction zone, in which a light naphtha fraction is cracked at a higher severity (Henry et al., 2002). Finally, the C_4/C_5 fraction produced by the FCC unit can also be sent to a light olefin oligomerisation unit to produce a C_8^+ fraction, which is subsequently recycled to the FCC [6,7].

All these process schemes increase the yields of C_3 and C_4 olefins. In this work, several of these process schemes that reutilize and recycle LPG and/or naphtha fractions to a resid catalytic cracker have been evaluated and compared.

2. Experimental

2.1. Catalyst and feeds

A commercial Y zeolite based equilibrium FCC catalyst was used in this work. Its physico-chemical characteristics are given in Table 1.

For the cracking experiments, a full range cracked naphtha (FRCN), produced on a industrial unit using this catalyst, was obtained from total. This naphtha feed was split into two FCC naphthas, a light cracked naphtha (LCN) and a heavy cracked naphtha (HCN). The LCN cut concentrates the olefins, while the HCN is mainly composed of aromatics. A third feedstock was obtained via catalytic oligomerisation of C_4 olefins in a PolyNaphtha unit. PolyNaphtha units are industrially used to convert light olefins into higher value gasoline and kerosene [4,3,11,14]. Light olefin conversion is typically between 90 and 99% depending on feedstock quality and olefin distribution. The resulting PolyNaphtha product obtained from FCC C_4 cuts is very olefinic, sulfur-free and has a significantly higher RON and MON than FCC gasoline. Detailed properties of the various feedstocks are listed in Table 2.

Table 1
Physico-chemical characteristics of the commercial equilibrium catalyst

Skeletal density (kg/m^3)	1362
Bulk density (kg/m^3)	903
Average particle diameter (μm)	57
Specific surface area (m^2/g)	156
Rare earth content (wt.%)	1.61
Ni content (wt ppm)	689
V content (wt ppm)	1070

2.2. Equipment

In this work, three different units were used to crack the feedstocks under various conditions: a fixed bed bench scale unit, a fixed fluidised bed unit and an adiabatic circulating fluidised bed pilot plant.

To assess the reactivity of the PolyNaphtha (PN) product, it was first cracked in a fixed bed bench scale unit. The reactor was loaded with 2 cc of equilibrium catalyst. The liquid feed is pumped to the reactor and diluted with a nitrogen flow to attain typical hydrocarbon partial pressures. An eight-loop sample storage valve was used to collect samples throughout the duration of the test. Blank tests using a reactor filled with only 50 μm diameter SiC have been carried out to verify the absence of thermal cracking both in the reactor and in the different sample storage loops. The effluent was analysed on-line on a gas chromatograph equipped with a PONA column and a FID detector. The temperature profile applied in the oven of the gas chromatograph starts at −60 °C to ensure a baseline separation for propane and propylene, and ramps until 280 °C so as to quantify the heavy hydrocarbons produced.

The LCN, HCN and PN feeds were also cracked in a fixed fluidised bed short contact time-resid test unit (SCT-RT). Before injection, feed is circulating through a system that includes a supply vessel, pump, and six-way port valve. Feed injection takes place by switching the six-way port valve for 1 s toward the reactor. At that moment, relatively cold feed is injected into a hot fluidized catalyst bed, causing a fast fluidized-plug flow regime for a short period of time. At the top, the catalyst particles are retained by a porous filter-plate mounted in the reactor head through which cracked products are evacuated. The cracked products are condensed in a liquid product receiver, the permanent gases are collected over water in a gas collection bottle. In the meanwhile, the catalyst is stripped with nitrogen. Further details on the SCT-RT reactor design and modes of operation can be found elsewhere [1,18,10].

To evaluate the combined effect of catalyst circulation and operating temperature on the yield structure, the feeds were also cracked in a continuous adiabatic circulating pilot plant. The pilot plant unit comprises a feed injection system, a 5.7 m high riser reactor, a catalyst stripper with disengaging section, a first regenerator, a lift line to the second regenerator, a second regenerator and catalyst transfer line from the second regenerator to riser (Fig. 1).

Table 2
Feedstock properties

	FRCN	LCN	HCN	PolyNaphtha
Specific gravity at 15 °C	0.7592	0.7209	0.8435	0.7385
Average molecular weight (g/mol)	101.8	89.4	137.4	125.2
Hydrogen content (wt.%)	13.37	14.21	11.79	14.42
Sulfur content (wt ppm)	1530	550	3370	0
Mercaptan sulfur (wt ppm)	54	67	29	0
Nitrogen content (wt ppm)	–	16.6	–	0
Basic nitrogen content (wt ppm)	45.3	12.5	107.0	0
Bromine index (g/100 g)	67	89	25	–
PIONA analysis (wt.%)				
Paraffins	4.80	5.88	2.77	0.07
Isoparaffins	18.94	22.08	13.03	2.99
Olefins	38.46	49.49	17.76	96.88
Naphthenes	6.51	7.67	4.33	0.06
Aromatics	31.29	14.88	62.11	0.00
ASTM D2887 distillation (°C)				
IBP	−6	−6	70	71
5%	19	14	126	109
10%	31	24	145	113
20%	56	38	168	116
30%	81	55	177	118
40%	102	71	188	118
50%	125	87	194	119
60%	146	100	203	125
70%	167	115	209	153
80%	189	136	221	191
90%	210	149	230	198
95%	226	164	240	224
FBP	258	183	258	269

The hot regenerated catalyst flows through the standpipe from the second regenerator to the bottom of the riser, where preheated finely atomised hydrocarbon feed is injected onto the hot catalyst through a proprietary nozzle with nitrogen as the feed atomisation medium. Vaporisation and cracking generates a significant expansion that lifts the catalyst up the riser. At the end of the riser, a riser termination device rapidly separates hydrocarbon vapours and catalyst particles to reduce further thermal and catalytic cracking [17]. The catalyst is sent to a stripper, in which nitrogen is used to remove most of the entrained hydrocarbon vapours in a counter-current dense phase stripper bed. The stripper contains two cyclones in series to ensure an efficient separation of the entrained catalyst particles. The stripped spent catalyst flows through a catalyst slide valve into the first fluidised bed regenerator, where air is injected through a bottom grid plate. The first regenerator acts as a mild precombustion zone that removes 40–70% of the coke on the catalyst [8]. The partially regenerated catalyst leaves the regenerator with less than 0.5 wt.% coke and is lifted to the elevated second regenerator by means of nitrogen injection. In the second regenerator, complete regeneration is achieved with slight air excess. Finally, the hot regenerated catalyst is returned to the riser bottom via a 6.6 m long standpipe.

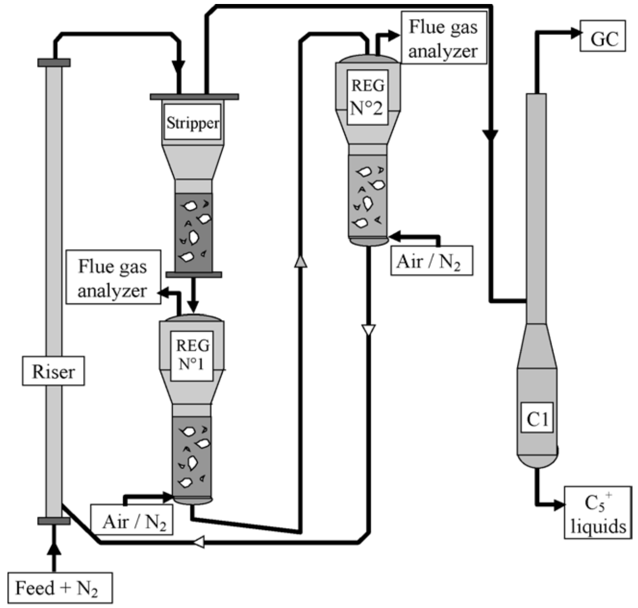

Fig. 1. Schematic of the adiabatic circulating fluidised bed pilot plant unit.

The circulating R2R pilot plant at IFP allows to investigate cracking of hydrocarbon feeds over a wide range of operating conditions (Table 3). In order to correctly reproduce the adiabatic operation of a commercial FCC unit, the pilot plant is equipped with a sophisticated heat loss compensation system combined with a complex control system. True adiabatic operation of the pilot plant unit is achieved by means of electrical surface heaters that eliminate heat transfer

Table 3
FCC pilot plant operating limits

Feed flowrate (kg/h)	4–15
Quench flowrate (kg/h)	0–10
Catalyst flowrate (kg/h)	20–200
Catalyst to oil ratio (kg/kg)	2–20
Catalyst inventory (kg)	30–70
Total catalyst residence time (min)	15–60
Maximum pressure (bar abs)	3
Maximum temperature (°C)	
Riser	650
Stripper	650
Regenerator 1	740
Regenerator 2	840

through the vessel walls. As for industrial units, the feed flow rate is fixed and the catalyst flow rate is adjusted to obtain the required riser outlet temperature by controlling the pressure difference between the second regenerator and the stripper. The pilot plant has been validated through a comparison of pilot plant results with industrial unit data using identical feed and catalyst [5]. These tests showed that the pilot plant provided realistic simulations of commercial FCC units, both in terms of conversion level and *C*/*O* ratio for a given riser outlet temperature and in terms of yield structure. A more detailed description of the pilot plant and its operation can be found elsewhere [5].

During all tests, the mass balances were all between 95 and 105 wt.% of feed injected, with 97–100 wt.% being the more typical range. In order to compare the yield structure of the different feeds on a similar basis, the conversion used in this work is defined as the conversion of the C_5^+ fraction into non-liquid products, i.e. as the sum of the dry gas, LPG and coke yield.

3. Results and discussion

3.1. Cracking of naphtha fractions

The three feeds (HCN, LCN and PN) were cracked over a wide range of operating conditions. Figs. 2 and 3 illustrate the evolution of the dry gas, propylene, butenes, total LPG, gasoline (C_5–220 °C), LCO (220–360 °C), slurry (360 °C+) and coke yield as a function of the C_5^+ conversion during the HCN cracking experiments. As can be noticed, the HCN feed is difficult to recrack under typical FCC conditions (ROT = 520 °C and *C*/*O* = 6 t/t). Even at severe operating conditions (ROT = 600 °C and *C*/*O* = 11 t/t), conversions remain low. This is mainly due to the fact that the feed mainly consists of aromatics and only contains a relatively low amount (<20 wt.%) of olefins, the most reactive species. In all conditions, over 58 wt.% of the effluent remains in the gasoline fraction. The main reaction products are a LCO fraction of 14–18 wt.%, and an olefinic LPG fraction, whose olefinicity grows from 61 to 77% with increasing severity. The propylene yield increases from 3 wt.% at 520 °C to over 6 wt.% at 600 °C. When the cracking severity is increased, the dry gas yield rapidly increases, going from 1.4 wt.% to almost 5 wt.%. Only small amounts of slurry are formed, while the coke yield amounts to about 3 wt.% and does not vary significantly with increasing severity.

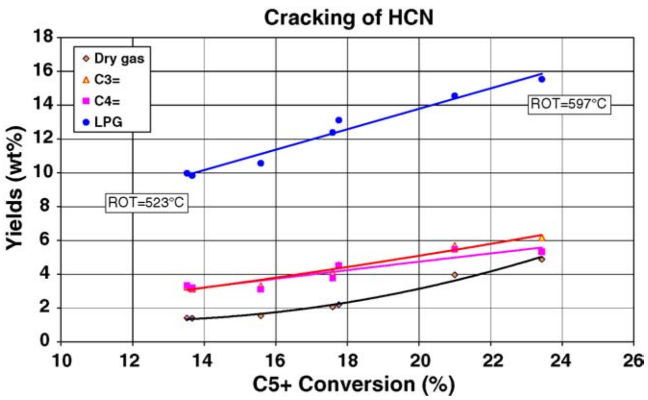

Fig. 2. Evolution of the dry gas, propylene, butenes and total LPG yield as a function of the C_5^+ conversion during the HCN cracking experiments.

Figs. 4 and 5 show the evolution of the yield structure in terms of dry gas, propylene, butenes, total LPG, gasoline, LCO, slurry and coke yield during the LCN cracking experiments. At typical FCC conditions (ROT = 520 °C and *C*/*O* = 6 t/t), the conversion into non-liquid products remains low, at around 16 wt.%. Increasing the severity of the operating conditions rapidly allows to obtain more important conversions, up to 40 wt.% at the most severe operating conditions (ROT = 600 °C and *C*/*O* = 11 t/t). This illustrates that it is possible to recrack the olefins, which are mainly C_5, C_6 and C_7 compounds, and isoparaffins of the LCN fraction. In the LCN cracking experiments, however, the liquid fraction mainly consists of gasoline, as less than 3 wt.% of LCO and slurry are produced. The slurry yield represents less than 0.5 wt.%, a value less than half of the slurry yield obtained during the HCN cracking experiments. The coke yield is also much lower and varies between 1.5 and 2.5 wt.% with increasing severity. The main reaction product is the LPG fraction, which is even more olefinic

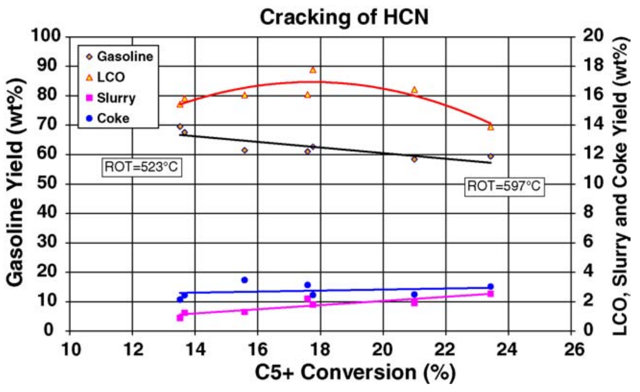

Fig. 3. Evolution of the gasoline, LCO, slurry and coke yield as a function of the C_5^+ conversion during the HCN cracking experiments.

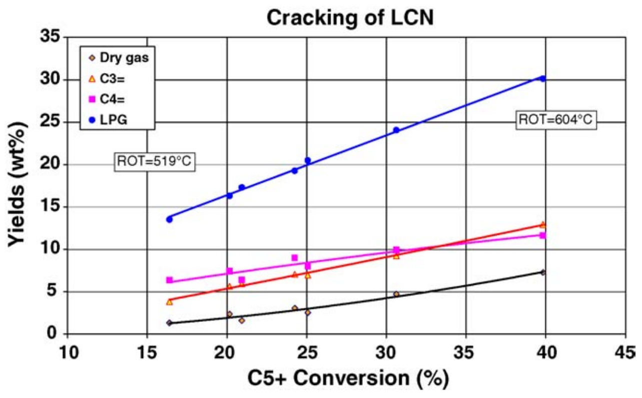

Fig. 4. Evolution of the dry gas, propylene, butenes and total LPG yield as a function of the C_5^+ conversion during the LCN cracking experiments.

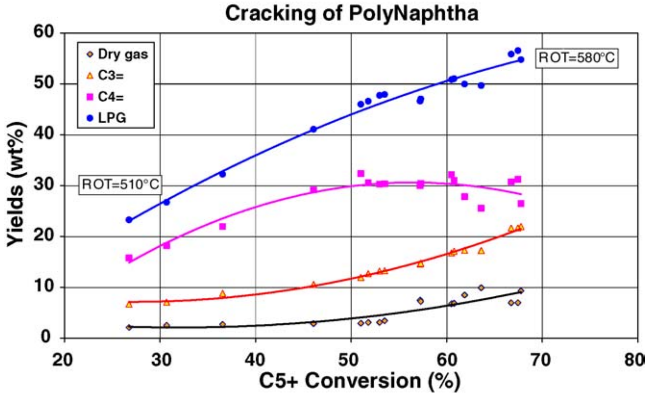

Fig. 6. Evolution of the dry gas, propylene, butenes and total LPG yield as a function of the C_5^+ conversion during the PN cracking experiments.

(71% at 520 °C up to 82% at 600 °C) than in the HCN cracking experiments. The propylene yield increases from 3.8 wt.% at 520 °C to almost 13 wt.% at 600 °C. Due to the higher olefin content (≈50 wt.%) of the LCN feed, not only are higher conversions attained, but the product distribution also favours higher propylene yields. Again, when the cracking severity increases, the dry gas yield rapidly increases, going from 1.3 to 7.3 wt.%.

Fig. 6 presents the evolution of the yield structure in terms of dry gas, propylene, butenes and total LPG, during the PN cracking experiments. As can be seen, very high conversions are obtained, even though the operating conditions are somewhat less severe than during the LCN and HCN cracking. This clearly illustrates the high reactivity of the branched olefins, which are mainly C_8 compounds, of the PN towards cracking. At the most severe conditions, almost 70 wt.% of the PolyNaphtha product is transformed into dry gas, LPG and coke. The remaining liquid fraction is essentially gasoline type material, for which the C_5 to C_6^+ ratio is close to 1 at conversions between 50 and 70 wt.%. As for LCN cracking, the main reaction product is again the LPG fraction. Its olefinicity varies between 86% and 96%, while the propylene yield increases from 6.7 wt.% at 510 °C up to 22 wt.% at 580 °C. At high severity, almost all olefins are converted and their selectivity towards propylene and butenes is very high. With the PN feed, high amounts of dry gas are produced, varying between 2.1 and 10 wt.% depending on severity. Finally, the coke yield increases from 1.4 to 2.9 wt.% with growing severity.

Comparison of the results obtained by cracking these three feeds over a wide range of severities clearly shows that the reactivity of a naphtha fraction is mainly determined by its olefin content. Looking at the conversion of the individual chemical families at a LCN C_5^+ conversion of 30 wt.%, 78% of the olefins, 47% of the naphthenes and 24% of the paraffins have been transformed. Hence, the aromatics content of gasoline remaining in the liquid effluent has substantially increased. Detailed gas chromatographic analysis of the composition of the remaining gasoline showed that olefins with seven or more carbon atoms are almost totally converted. The C_6 olefins were not completely transformed, however, while less than 43% of the C_5 olefins were cracked. These results are similar to those reported by Corma et al. [2] and are fully consistent with carbenium ion chemistry. Indeed, cracking a C_5 olefin through β-scission necessarily involves the formation of a primary carbenium ion, which significantly reduces its overall reaction rate. C_6 olefins will crack more easily, as this reaction will proceed via a secondary–secondary β-scission pathway. From the C_7 olefins onwards, the more favourable secondary–tertiary or tertiary–secondary β-scission mechanisms will come into play, leading to an almost complete conversion of these higher carbon number olefins. The same holds for naphthenes with seven carbons or more, as is confirmed by the analytical results showing that the higher carbon number naphthenes react to a large extent. Similarly, the conversion of the alkanes also increases with carbon number, even though their reactivity is much lower rate than olefins and naphthenes with the same carbon number.

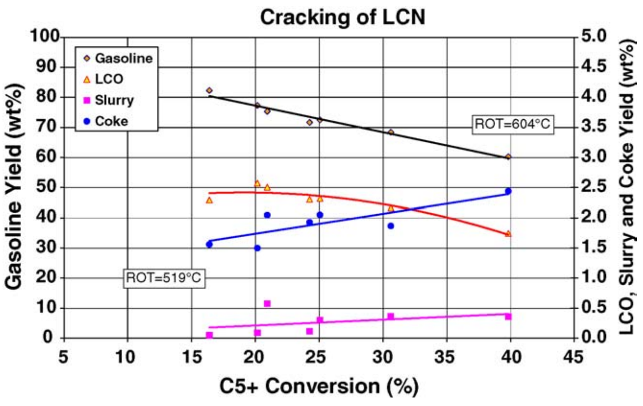

Fig. 5. Evolution of the gasoline, LCO, slurry and coke yield as a function of the C_5^+ conversion during the LCN cracking experiments.

3.2. Evaluation and comparison of various process schemes

The base case in this study was taken from an industrial R2R resid FCC unit with a catalyst cooler on the second regenerator. Its feed is an unhydrotreated atmospheric resid with a specific gravity of 935 kg/m^3, a weight average boiling point of 503 °C, a hydrogen content of 12.06 wt.%, a sulfur content of 1.67 wt.%, a nitrogen content of 0.15 wt.% and a Conradson carbon content of 5.7 wt.%. The operating conditions of the industrial unit and its yield structure are listed in Table 4 as case a. The unit runs at a ROT of 525 °C and a *C/O* ratio of 6.3 t/t. Since the feed is very heavy, the coke yield amounts to 8.7 wt.%, which required the installation of a catalyst cooler on the unit to decrease the regenerator temperatures. The gasoline yield amounts to 43.1 wt.% and the LPG yield is at 13.9 wt.%, with a base case propylene yield of 4.2 wt.% with respect to the fresh feed.

In order to increase the propylene production on this FCC unit, a number of process schemes were proposed, evaluated and compared. To correctly evaluate a process scheme, the heat and mass balances of the FCC unit need to be solved simultaneously. Indeed, fluid catalytic cracking is an integrated reaction-regeneration process where the heat produced in the regeneration zone is transported by the catalyst to the reaction zone to vaporise the liquid feed and to promote endothermic reactions. This very specific characteristic implies that the catalyst flowrate in the reactor does not only depend upon the reaction requirements, but also upon the adiabatic requirements of the process. Hence, a modification in the heat balance of the unit will modify the catalyst circulation and the reaction zone performance.

Table 4
Configuration, operating conditions and yield structure for various LCO, FCC naphtha and PolyNaphtha recycle schemes

	Case								
	a	b	c	d	e	f	g	h	i
Recycle									
LCO (220–360) ≥ Riser 1 (%)	0	0	0	0	0	0	0	0	50
Gasoline (C$_6$–220) ≥ Riser 1 (%)	0	70	70	0	0	0	0	0	0
Gasoline (C$_6$–220) ≥ Riser 2 (%)	0	0	0	70	70	0	0	70	75
C$_5$ cut ≥ Riser 2 (%)	0	0	0	0	70	0	0	0	0
C$_5$ cut ≥ PolyNaphtha unit (%)	0	0	0	0	0	0	100	100	100
C$_4$ cut ≥ PolyNaphtha unit (%)	0	0	0	0	0	100	100	100	100
Yield structure									
Dry gas (incl. H$_2$S) (wt.%)	4.41	10.25	5.65	6.67	7.29	4.67	4.96	7.93	10.86
C$_3$= (wt.%)	*4.21*	*9.17*	*6.01*	*7.58*	*8.74*	*5.13*	*5.96*	*10.82*	*14.12*
LPG (wt.%)	13.94	26.63	18.84	22.39	24.60	10.71	11.94	19.67	24.24
C$_5$–220 (wt.%)	43.14	31.97	34.48	30.02	26.35	45.69	44.02	30.70	29.50
220–360 (wt.%)	15.85	13.87	16.88	16.33	16.64	16.04	16.16	16.82	12.36
360–400 (wt.%)	3.60	1.77	3.66	3.70	3.71	3.62	3.60	3.62	2.94
400+ (wt.%)	10.39	4.92	10.50	10.71	10.70	10.46	10.37	10.44	7.95
Coke (wt.%)	8.66	10.59	9.99	10.18	10.72	8.81	8.95	10.82	12.15
Spent catalyst coke content (wt.%)	1.37	0.96	1.59	0.84	0.71	1.24	1.15	0.69	0.58
Flow rates									
Fresh feed to Riser 1 (t/h)	294.0	294.0	294.0	294.0	294.0	294.0	294.0	294.0	294.0
Recycle LCO to Riser 1 (t/h)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	36.3
Recycle gasoline to Riser 1 (t/h)	0.0	126.0	158.8	0.0	0.0	0.0	0.0	0.0	0.0
Recycle gasoline to Riser 2 (t/h)	0.0	0.0	0.0	121.9	141.7	0.0	0.0	137.2	155.6
Recycle C$_5$ cut to Riser 2 (t/h)	0.0	0.0	0.0	0.0	39.0	0.0	0.0	0.0	0.0
Feed to PolyNaphtha unit (t/h)	0.0	0.0	0.0	0.0	0.0	31.0	68.5	105.3	120.8
Recycle PolyNaphtha to Riser 2 (t/h)	0.0	0.0	0.0	0.0	0.0	18.4	33.8	53.3	62.4
Main fractionator (t/h)	268.5	388.8	423.4	385.9	443.2	286.5	301.5	452.7	512.6
Operating conditions									
Cat circulation Riser 1 (t/min)	31.0	53.8	30.9	30.9	30.9	30.9	31.1	31.5	39.0
Cat circulation Riser 2 (t/min)	–	–	–	28.8	42.8	3.9	7.2	45.1	63.0
C/O Riser 1 (t/t fresh feed)	6.33	10.98	6.30	6.31	6.31	6.30	6.34	6.43	7.95
C/O Riser 2 (t/t)	–	–	–	14.17	14.21	12.65	12.79	14.22	17.34
Feed temperature (°C)	200	200	200	200	200	200	200	200	200
Riser outlet temperature Riser 1 (°C)	525	525	525	525	525	525	525	525	525
Riser outlet temperature Riser 2 (°C)	–	–	–	600	600	600	600	600	600
Stripper temperature (°C)	521	521	522	553	560	528	533	561	563
Regenerator 1 temperature (°C)	659	627	726	666	668	661	661	666	652
Regenerator 2 temperature (°C)	713	673	801	713	713	714	712	710	690
Catalyst cooler duty (Mcal/h)	55000	55000	25500	20000	0	49000	44500	0	0
Regenerator 1 air rate (t/h)	217.6	266.2	251.1	255.9	269.3	221.3	224.8	271.8	305.5
Regenerator 2 air rate (t/h)	92.6	113.2	106.8	108.8	114.6	94.1	95.6	115.6	129.9

Consequently, a change in the unit yield structure, and especially of the coke yield, will modify the riser heat balance and the regenerator temperatures, which will in turn influence the *C*/*O* ratio needed to maintain a given riser outlet temperature. This adjusted *C*/*O* ratio alters the operating severity in the riser, leading to a new yield structure. The evaluation of the various process schemes was therefore based on rigorous representation of this set of heat and mass balances, both for the regenerator and riser sections.

Concerning the yield structures, a FCC model based on the work of Saraf et al. [15] was tuned to the industrial data and used to simulate the effect of the operating conditions on the fresh feed conversion and yield structure. For the LCN, HCN and PN cracking, a first order rate equation was derived from the experimental data presented above to predict the C_5^+ conversion of each naphtha fraction as a function of operating conditions (*C*/*O* ratio and reaction temperature). The detailed yield structure was subsequently calculated by interpolating the yield profiles that were experimentally obtained. The lines in Figs. 2–6 illustrate this approach. For each process scheme, the final yields, expressed as weight percent produced with respect to the fresh feed, have been determined from the flow rates to storage.

Starting from base case, various streams can be recycled from the main fractionator to the inlet of the riser, as illustrated in Fig. 7a. The number of possible cases that can be examined is tremendous, however. Indeed, one cannot only vary the type of recycle (HCO, LCO, FRCN, HCN, LCN or a C_5 cut), but also its flow rate. Moreover, the operating severity (ROT and *C*/*O* ratio) can be varied by modifying the ROT setpoint, the feed preheat temperature and/or the catalyst cooler duty. Over 200 combinations have been simulated, but only a limited number of cases will be illustrated in this work. For the sake of clarity and to ease the comparison between cases, it was decided to show cases with a similar operating severity, as characterised by the ROT and *C*/*O* ratio, in the resid feed riser resulting from an adjusted the catalyst cooler duty.

3.2.1. Recycling catalytically cracked gasoil and gasoline to the FCC unit

The simplest option for naphtha recycle processing in a FCC unit, recycling a cracked naphtha fraction directly to the feed injection system, will be studied first. Case b in Table 4 shows that adding the naphtha recycle to the main riser increases the catalyst circulation, and hence the *C*/*O* ratio, owing to additional heat removal by vaporization and to a lower average coke content on the spent catalyst. The latter results in regenerator temperatures that are too low to ensure proper catalyst regeneration. This case was only added to illustrate the complex behaviour of the process schemes, even though the results are not technically achievable. As mentioned above, it was decided to adjust the catalyst cooler duty in order to maintain a similar ROT and *C*/*O* ratio in the resid feed riser. In case c, the catalyst cooler duty was lowered until a *C*/*O* ratio of 6.3 t/t was obtained. Even though the naphtha recycle ratio is very high (54% with respect to the fresh feed), recycling a cracked naphtha fraction directly with the resid feed only shows a slight improvement in yield structure, due to its low reactivity at classical operating conditions. The resulting propylene yield is about 50% higher than in the base case.

Adding the naphtha recycle to a separate MTC feed nozzle downstream of the feed injection system leads to an almost similar yield structure, but has the advantage of creating a higher temperature zone that improves the vaporisation of the resid feed. Injecting the naphtha recycle upstream of the feed injectors allows for higher severity to convert the naphtha fraction. However, although this option may be interesting when treating gas oil feeds, cooling down the catalyst before it contacts the heavy feed degrades the overall performance of the resid FCC unit. Hence, the latter case was not simulated due to technical constraints on the operation of the unit.

Cracking naphtha in a separated riser reactor allows to operate a second reaction zone at a higher severity to effectively crack the naphtha recycle, while maintaining the main riser at classical cracking conditions (Fig. 7b). As

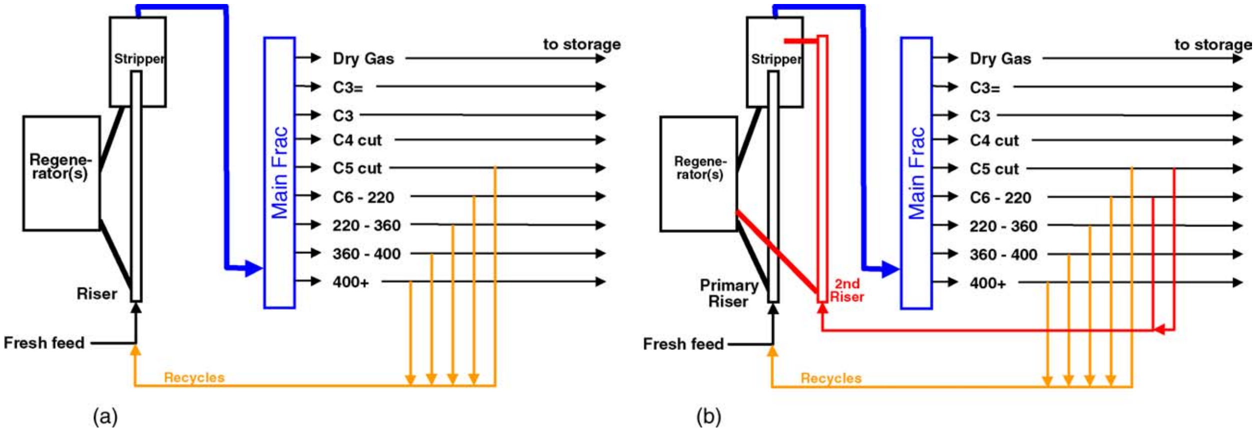

Fig. 7. (a) Representation of classical recycle options and (b) representation of a dual riser system with recycles.

illustrated in the experimental section, cracking LCN at a ROT of about 600 °C and *C/O* of 12 t/t leads to a LPG selectivity of 65%, while the propylene yield is 12.9 wt.%. In such a scheme, the propylene production can be significantly increased. Moreover, as the coke content on the catalyst leaving the secondary riser only amounts to 2.4 wt.%, the average coke content on the catalyst entering the regeneration section is lower, leading to lower regenerator temperatures. Hence, cracking a naphtha stream in a secondary riser will therefore have a similar effect on the heat balance of the unit as a catalyst cooler. This effect could be used to treat even heavier feedstocks in the main riser. In case d of Table 4, 70% of the C_6–220 °C fraction coming from the fractionation tower was recycled to the secondary riser and the catalyst cooler duty was reduced to reach a *C/O* ratio of 6.3 t/t. Operating this second reaction zone at high severity results in an additional propylene yield of 3.4 wt.%, which is 80% higher than the base case. In case e, 70% of the C_5–220 °C fraction coming from the fractionator was recycled to the second riser. The spent catalyst coke content further decreases and the catalyst cooler is shut down in order to maintain the primary riser conditions. The propylene yield is now more than twice the yield obtained in the base case. However, the significant reduction of the overall gasoline output rate counterbalances the economics of this extra yield. Moreover, the dry gas and coke yields are also significantly higher than in the base case. In case e, 18 wt.% of the fresh feed is converted into dry gas and coke.

From the various cases investigated, it can be concluded that the dual riser resid FCC alone can not maintain its gasoline and gasoil production level while co-producing propylene. Morever, moving the FCC unit into high conversion also increases the dry gas yield and the coke yield significantly. Hence, such a dual riser resid FCC unit can only be economically viable if the refiner accepts to give up part of its fuel market to enter the petrochemical business.

3.2.2. Dual riser resid FCC scheme with a PolyNaphtha unit

Since the C_4 and C_5 fractions are highly olefinic, they can also be sent to a light olefin oligomerisation unit in which dimerisation and isomerization are promoted. As mentioned before, such a unit converts the C_4 and C_5 olefins into an olefinic fraction in the gasoline and kerosene boiling point range. This naphtha type fraction can then be recycled to the secondary riser, where the dimers and trimers are recracked (Fig. 8). Since propylene is not recycled, the butenes and pentenes are indirectly transformed into propylene. Moreover, as for LCN cracking, the secondary riser will again have a catalyst cooler effect on the heat balance of the unit.

Compared to a traditional olefinic FCC gasoline, PolyNaphtha effluent contains over 95 wt.% of olefins (Table 2). As shown from the experimental data, this naphtha fraction is cracked much more easily in a FCC reactor, even at lower severity. Furthermore, the C_3 cut obtained from PolyNaphtha cracking has a high purity (typically around 94 wt.% of propylene) compared to the 86 wt.% purity of the C_3 cut obtained through LCN cracking.

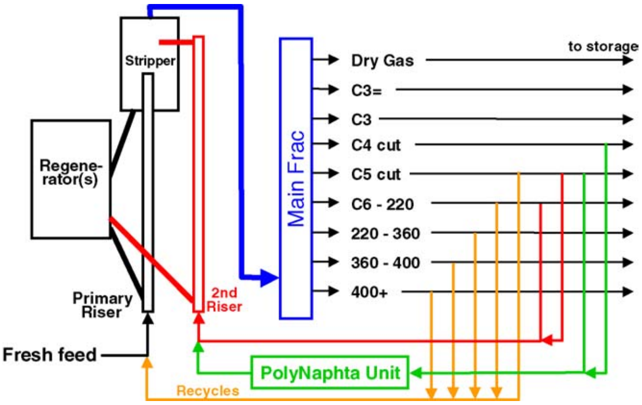

Fig. 8. Representation of a dual riser resid FCC scheme with a PolyNaphtha recycle.

In case f of Table 4, the C_4 cut is fed to the PolyNaphtha unit and the C_5^+ oligomerate of this unit is then sent to the second riser operating at 600 °C. This option leads to a propylene yield of 5.1 wt.%, which is almost 1 wt.% higher than in the base case. The catalyst circulation in the second riser remains very low, however. To further increase the propylene yield, the C_4 and C_5 cuts can both be sent to the PolyNaphtha unit (case g). Here, the yield structure is quite similar to that of the base case in terms of LPG, gasoline and distillate yields. The overall gasoline to distillate ratio is almost the same, but the propylene yield is increased by 75% through the indirect conversion of C_4 and C_5 olefins into propylene. Moreover, the main fractionator load is only increased by about 12%. Compared to case c, the same propylene yield is obtained, but much less coke and gas are formed. It should also be noted that in cases f and g, the catalyst cooler duty was only slightly affected.

In case h, 100% of the C_4 and C_5 cuts are sent to the PolyNaphtha unit to produce an oligomerate that is recycled to the secondary riser together with 70% of the produced gasoline. To maintain the same conditions in the primary riser, the catalyst cooler was shut down. A significantly higher propylene yield of almost 11 wt.% is achieved. However, the naphtha recycle to the additional riser also leads to a 70% increase of the FCC main fractionator load. Therefore, such a high gasoline recycle may lead to uneconomical energy consumption.

To illustrate the complexity of optimising these process schemes, a 75% gasoline recycle to the second riser is combined with a 50% LCO recycle to the main riser (case i). As the catalyst cooler was already shut down, the very low spent catalyst coke content can no longer be compensated for, resulting in lower regenerator temperatures than the base case. Hence, the severity of both risers increases, leading to a propylene yield of more than 14 wt.% of the total resid feed. Adding a LCO recycle to primary riser while cracking naphtha in the second reaction zone allows increasing the propylene yield further, while restoring part of the gasoline production. Recycling LCO therefore gives the dual riser resid FCC additional degrees of freedom to adjust the distillate to gasoline balance.

It should be emphasised that the presented yield structures are based on experiments with an equilibrium FCC catalyst that does not contain any ZSM-5 additive. Hence, if a permanent propylene production at a high yield is needed, ZSM-5 addition should also be applied into a dual riser resid FCC with PolyNaphtha system, as in classical FCC applications.

Finally, it should also be stressed that the process scheme of Fig. 8, in which a light olefin oligomerisation unit is added to a FCC complex, also allows to enhance gasoline production, thus giving a higher operation flexibility to the refiner. In the latter case, partial or total hydrogenation of the oligomerate is needed to meet the olefin level requirements of the gasoline pool. Moreover, a kerosene boiling point product will also be obtained, which will be on specification after total hydrogenation.

4. Conclusions

Each of the three main naphtha recycle options (directly to the main riser, directly to a secondary riser or indirectly via a PolyNaphtha unit) have been illustrated and compared to the base case. For the evaluation of each of these schemes, all heat balance effects, both on the riser and the regenerator side, have been accounted for, while naphtha cracking experiments were carried out in order to evaluate the crackability of the feed in FCC units and its selectivity towards propylene. It was shown that FCC naphthas require high severities to crack, and even then, their conversion remains relatively moderate. Hence, to increase the propylene yield significantly, a second reaction zone operating at high severity is necessary. An alternative scheme has been proposed, in which the olefinic C_4 and C_5 fractions are converted into a naphtha fraction through oligomerization in a PolyNaphtha unit before being recracked in the secondary riser. As the PolyNaphtha oligomerate is highly olefinic, high conversions can be achieved. This indirect interconversion of butenes and pentenes into propylene allows to achieve a significant increase in propylene yield. Moreover, cracking light feeds in a dual riser system significantly reduces the average coke content on the catalyst, leading to lower regeneration temperatures. Hence, the *C/O* ratio of the primary riser can be increased, leading to a higher conversion of the resid feed and to a better yield structure. Thus, cracking a light feed in a secondary riser will therefore have a similar effect on the heat balance of the unit as a catalyst cooler and allows to treat even heavier feedstocks in the main riser. In addition, the propylene production can be increased further by adding a ZSM-5 additive to the catalyst inventory.

The main drawback of these schemes resides in the fact that pushing the FCC unit into high conversion mode also increases the dry gas yield and the coke yield significantly. This does not only have a negative effect on the economics of these process schemes, but also imposes important constraints on the unit in terms of air blower, wet gas compressor and gas plant capacity. A significant question concerning the right economic optimisation of the complete process scheme therefore remains and will be addressed in future work.

Finally, it is also interesting to note that the proposed process schemes preserve the inherent flexibility of the FCC unit: the naphtha recycle can be turned on or off, the second reaction zone can be used to crack naphtha or can be fed with the main resid feed to maximise throughput, while the effluent of the PolyNaphtha unit can be recycled to the FCC unit for propylene production or hydrogenated and sent to gasoline and kerosene pool.

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