

Taking advantage of the excess of thermal naphthas to enhance the quality of FCC unit products

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ABSTRACT

Today, many European refineries finish up with excess of low-quality thermal naphthas that are hard to be marketed and, commonly, end being absorbed by catalytic naphthas at the expense of their higher quality. In this context, we propose to investigate the suitability of co-feeding thermal naphthas, i.e. visbreaker and heavy coker naphtha, with vacuum gasoil (VGO) to the conventional fluid catalytic cracking unit, without requiring revamping. A riser simulator reactor has been used in the experimentation and tested conditions have been: 500 and 550 °C; C/O mass ratio, 6 g_{cat} g_{oil}⁻¹; and, residence time, 3–12 s. Products have been lumped according to the fractionation made in refineries in: dry gas, liquefied petroleum gases, gasoline, light cycle oil and coke. The results reveal that the co-feeding of any of the naphthas hinders the over-cracking increasing the contents of gasoline and that it inhibits the condensation reactions that produce coke. Two main factors contribute to these results: (i) the competitive adsorption and reaction between the components of the naphthas and the VGO; and (ii) the shortening of the residence time caused by an increase of the flow when the naphtha is co-fed. It should be highlighted the variation in the composition of the gasoline produced with the blends,

with overall reductions of the contents of olefins and aromatics and of the gasoline octane index.

Keywords: coker; visbreaker; catalytic cracking; olefins; gasoline; BTX

1. Introduction

In recent times, oil refiners have faced important capital investments in equipment in order to fulfill the increasing strictness of environmental standards set by the governments [1]. Moreover, there is a substantial concern in the oil refining industry about the fuels market supply given the lack of any major oil field finding in the last quarter century [2]. Therefore, reaching a maximum utilization of the resources [3] and focusing on optimal process operations [4] are key goals to increase production profits and to restructure the economy of the refineries [5].

In this context, coking and visbreaking units perform a relevant role in the intensification of oils, the quality of which is decreasing since petroleum sources are becoming heavy and extra-heavy [6], as they transform heavy streams into lighter ones. Among these streams, thermally cracked naphthas are attracting special attention [7] as they consist of complex mixtures of low-quality components in the C₅–C₁₂ range [8]. Furthermore, many refineries are currently finishing up with a surplus of thermally cracked naphtha, especially in European countries [9], which is usually blended with high-quality naphthas, such as straight run naphtha, into the gasoline pool [10].

Nonetheless, thermal naphthas are also submitted to different processes within refineries in order to improve their composition prior to the blending or to focus the production on certain chemicals instead of gasoline. This way, to develop the degree of ramification and, at once, to improve the research octane number (RON) thermal naphthas are submitted to isomerization process [11,12]. However, as this process requires a hydrogen atmosphere, light olefins (ethylene, propylene and butylenes) are converted into paraffins reducing notoriously the attractiveness of this fraction [13]. On the other hand, when BTX (benzene, toluene and xylene) aromatics are the targeted products, thermal naphthas are treated on reforming units [14,15]. Reforming isomerizes paraffinic compounds to isomeric forms and dehydrogenates naphthenes into their corresponding aromatics, producing hydrogen as a byproduct but causing a volume shrinkage [16].

Even though isomerization and reforming units are commonly used to upgrade thermal naphthas, these units are not capable of managing the current surplus of thermal naphthas as the average

capacity of these units is about 5 thousand barrels per day [17]. Therefore, it would be appealing to explore the co-feeding of thermal naphthas to fluid catalytic cracking (FCC) unit according to: (i) the worldwide availability of this unit in refineries; (ii) its capacity to absorb the naphtha surplus, as a standard unit handles about 50 thousand bpd; and (iii) the promising results obtained in previous works in the catalytic cracking of pure thermal naphthas [18,19]. It is well-established the capacity of the FCC unit to handle secondary refinery streams or alternative streams (biomass, plastics) either pure or dissolved in the current FCC feedstock (vacuum gasoil, VGO) [20,21]. Moreover, recently it has been also investigated the cracking of light crude oil [22–24]. In order to assist the economy of the process, it is of special interest the flexibility of the FCC unit that allows the co-feeding of these alternative streams without requiring an expensive revamping of the unit. Corma et al. [25] have analyzed the different circumstances that suggest the modification of the catalyst or of the cracking conditions for the cracking of new feeds in the FCC unit. Among the revamping recommendations for the riser, Wang et al. [26] have proposed to co-feed FCC naphtha to a secondary riser in order to enhance the propylene production when operating above 550 °C. On the other hand, Li et al. [27] have studied a similar solution for the co-feeding of coker gasoil, avoiding the poisoning of the catalyst with the nitrogen containing compounds.

In this context, this work undertakes the co-feeding of two different thermal naphthas, i.e. visbreaker naphtha (VBN) and heavy coker naphtha (HCN), with VGO to FCC unit. Furthermore, pure VGO has been also tested to properly evaluate the effect of the blending with the naphthas on the reached conversion level and in the products distribution. Apart from the expected increase of the gasoline yield (given the nature and boiling range of the naphthas), it is interesting the assessment of the composition of the obtained gasoline fraction, as well as the over-cracking inhibition. The different composition of the naphthas (lighter and more olefinic the VBN) allows for evaluating the effect of its composition on the products distribution and composition.

2. Material and methods

2.1. Feeds

The following three feeds have been used in this study: (i) visbreaker naphtha (VBN), the lightest liquid product of the visbreaking unit; (ii) heavy coker naphtha (HCN), obtained in a delay coker unit; and (iii) vacuum gasoil (VGO), a product of the vacuum distillation tower and common feed of fluid catalytic cracking (FCC) unit. All of them provided by Repsol S.A. (Tarragona, Spain). [Table 1](#) collects their main physicochemical properties. Density, simulated distillation curves and sulfur content have been computed following the procedures described in the ASTM D4052, ASTM D2887 and ASTM D4294 Standards, respectively. On the other hand, the chemical composition has been obtained by chromatographic methods (Agilent 7890A). The separation of the compounds has been performed on a HP-PONA capillary column (50 m × 0.2 mm × 0.5 μm). The column temperature has been increased at 15 °C min⁻¹ from 30 (held for 5 min) to 235 °C and at 30 °C min⁻¹ from 235 (held for 1 min) to 320 °C (held for 20 min).

Table 1. Characterization results of the feeds.

	VBN	HCN	VGO
Density at 15 °C (g cm ⁻³) ^a	0.7307	0.7737	0.9082
Simulated distillation (°C) ^b			
IBP-FBP	32–163	67–201	271–605
T ₅₀ –T ₉₅	120–161	152–198	447–543
Sulfur content (wt%) ^c	1.02	1.22	0.69
Chemical composition (wt%)			
paraffins	25.8	26.4	12.5
<i>iso</i> -paraffins	20.3	13.8	–
olefins	27.1	20.6	–
naphthenes	12.4	9.1	26.6
aromatics	14.5	30.1	60.9

2.2. Catalyst

The catalyst used for the runs has consisted on a commercial octane-barrel type FCC catalyst, which has been supplied by Petronor Refinery (Muskiz, Spain). The catalyst has been taken from a discarded batch, after been submitted to several reaction–regeneration cycles in the FCC unit.

Hence, prior to its use, regeneration up to 850 °C in air has been required to remove the remaining carbonaceous deposits. Its main properties are displayed in [Table 2](#).

Table 2. Catalyst characterization results.

Physicochemical property	FCC catalyst
Unitary cell size (Å) ^a	24.31
Specific surface area (m ² g ⁻¹) ^b	205
Micropore volume (cm ³ g ⁻¹) ^c	0.02
Zeolite (%) ^d	14.0
REO (wt%)	2.70
Fe (wt%)	0.35
Ni (wt%)	0.03
V (wt%)	0.12
Total acidity (mmol _{NH3} g ⁻¹) ^e	0.018
Acid strength (J mmol _{NH3} ⁻¹) ^e	145
BAS/LAS ratio ^f	3.2

^a ASTM D3942 Standard

^b BET method with N₂ adsorption

^c *t*-plot method

^d Johnson's method with N₂ adsorption [28]

^e Calorimetry with NH₃ TPD

^f FTIR spectroscopy with pyridine adsorption

2.3. Cracking reactions

A CREC riser simulator reactor designed and fabricated at the University of Western Ontario (Canada) has been used for the catalytic cracking tests. It is a mini fluidized bed reactor that mimics the industrial FCC unit [29]. A flow diagram of the unit is shown in [Fig. S1](#), while the experimental procedure followed has been well-described in the literature [30,31]. The runs have been conducted at: 500 and 550 °C; C/O mass ratio, 6 g_{cat} g_{oil}⁻¹; and residence time, 3–12 s. As the present study aims the assessment of the co-feeding of thermal naphthas to catalytic cracking unit, the following feeds have been used: (i) a blend of 20 wt% of VBN and 80 wt% of VGO

(VBN/VGO); (ii) a blend of 20 wt% of HCN and 80 wt% of VGO (HCN/VGO); and (iii) pure VGO in order to compare the results of the blends with those of the conventional FCC feedstock.

2.4. Product analysis

The fractionation commonly used in refineries has been applied to group obtained products, resulting in: dry gas (C₁–C₂), liquefied petroleum gases (LPG, C₃–C₄), gasoline (C₅–C₁₂), light cycle oil (LCO, C₁₃–C₂₀), and heavy cycle oil (HCO, C₂₁+). Cracking products have been analyzed by chromatographic means using the same equipment as in the characterization of the feeds (Section 2.1), but following a slightly different temperature profile. Thus, the GC oven has been held at –30 °C for 1 min, then it has been ramped to 235 °C at 15 °C min^{–1} where it has been held for 1 min and afterward it has been heated up to 320 °C following a heating rate of 30 °C min^{–1} and maintained at this temperature for 20 min.

A Q5000 IR TA Instruments thermogravimetric analyzer has been used to determine the amount of coke deposited on the catalyst by TPO analysis. The analyses have been carried out under a continuous 100 cm³ min^{–1} air flow in which the sample has been heated from 40 to 750 °C following a heating rate of 15 °C min^{–1}.

2.5. Reaction parameters

Conversion has been defined just as it is frequently established in the cracking studies of heavy streams [30,32,33]:

$$\text{Conversion} = \frac{(\text{LCO} + \text{HCO})_{\text{feed}} - (\text{LCO} + \text{HCO})_{\text{prod}}}{(\text{LCO} + \text{HCO})_{\text{feed}}} \cdot 100 \quad (1)$$

As an additional reaction progress measurement, the yield of each fraction has been also computed:

$$\text{Yield} = \frac{\text{mass}_{\text{fraction}}}{\text{mass}_{\text{feed}}} \cdot 100 \quad (2)$$

Additionally, several cracking performance indicators have been computed to determine the ruling mechanisms in the cracking of each feed. This way, cracking mechanism ratio (CMR), defined as the C_1+C_2/iC_4 ratio, has been computed, as it connects the monomolecular to bimolecular cracking types [34]. Hydrogen-transfer coefficient (HTC), which is defined as the ratio of butanes with respect to butylenes (nC_4+iC_4/C_4^-), indicates the hydrogen-transfer activity of the catalyst [35]. Olefinicity ($C_x^-/C_{x, Total}$) and *iso*-paraffinicity (iC_x/nC_x) parameters have been also estimated, together with the research octane number (RON) of the gasoline fraction [36].

3. Results and discussion

3.1. Product distribution

Fig. 1 shows the evolution with the residence time of attained conversion for the three feeds, i.e. VBN/VGO, HCN/VGO and VGO, at both 500 and 550 °C. As it can be seen, the blending of the VGO with the thermal naphthas noticeably modifies reached conversion. The lowest conversion levels, both at 500 and at 550 °C have been obtained for the VGO. Especially at 500 °C as a residence time higher than 9 s is required to reach a conversion above 70 %. On the other hand, in the cracking of the blends the gasoline fraction included in the naphtha co-fed contributes to reach higher conversion levels. It can be observed that at 550 °C the conversion levels follow the trend: VBN/VGO > HCN/VGO > VGO, being boosted the conversion level when increasing residence time from 3 to 12 s in the 84–88, 80–86 and 76–82 % intervals, respectively. This result could have been the expected one based on the effect of the naphtha composition on the cracking rate. Longstaff [37] has investigated the cracking of paraffinic and olefinic naphthas with the aim of producing light olefins, obtaining that at 600 °C the olefinic naphthas are clearly more reactive. Karaba et al. [8] distinguish two different fractions within the naphtha (light and heavy) based on their different reactivity in the steam cracking. Moreover, these researchers have also obtained that, in spite of not being a linear effect, both cyclic and aromatic compounds inhibit the cracking of the light naphtha. Consequently, the VBN, which is more olefinic and less aromatic (Table 1), is more reactive than the HCN. However, this statement is not fulfilled at 500 °C, as the

conversion levels reached follow the trend: HCN/VGO > VBN/VGO > VGO. The main reason can be ascribed to the complicated adsorption/reaction mechanism in the cracking of such complex mixtures of compounds. Nevertheless, it should be also taken into account that the co-feeding of naphtha causes the expansion of the reaction medium (with the subsequent increase of flow), because of its lighter composition. The lighter composition of the VBN with respect to that of the HCN will bring a bigger increase of flow and a consequent shorter residence time. This effect will be predictably higher at 500 than at 550 °C due to the slower cracking rate and the highest incidence of the residence time (Fig. 1).

Paying closer attention to the effect of the residence time and the temperature is evident that the effect of both parameters is closely linked. This way, residence time has a marked effect at low temperatures (500 °C), as obtained conversions increase at least a 10 % when increasing residence time from 3 to 12 s. However, at 550 °C the effect of residence time is attenuated leading to an increase of 7 % in conversion at most.

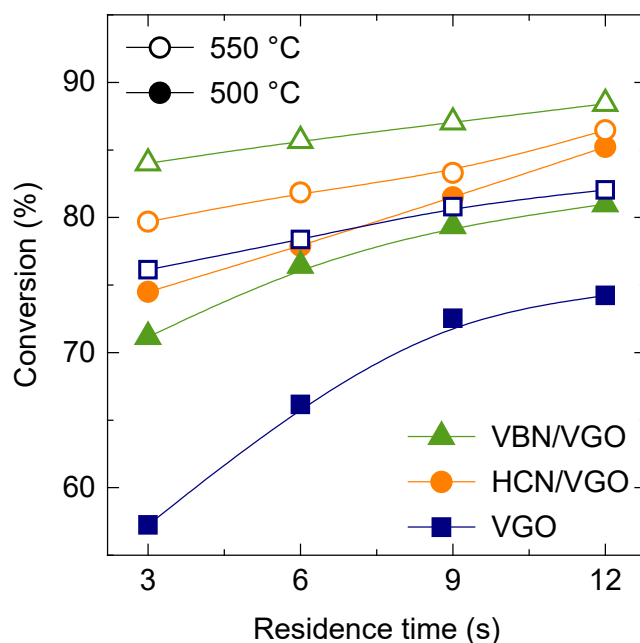


Fig. 1. Conversion as a function of the residence time for the catalytic cracking of the different feeds at 500 and 550 °C. Symbols: solid (500 °C); hollow (550 °C); VBN/VGO (▲); HCN/VGO (●); VGO (■).

The yields of the fractions obtained at both temperatures in the cracking of the VBN/VGO and HCN/VGO blends and of the pure VGO have been depicted in Fig. 2. Note that the fractions have been separated in two different subfigures (Fig. 2a and b for 500 °C and Fig. 2c and d for 550 °C) for clarity purposes. Additionally, the results of Fig. 1 and Fig. 2 have been tabulated in Tables S1 and S2 in order to offer a global view of obtained results. Attending to the results obtained with the VGO, the dry gas, LPG, gasoline and coke yields increase with conversion at both temperatures, whereas that of LCO decreases. With regard to gasoline fraction, it can be seen that at low conversion levels, the yield obtained at 500 °C (Fig. 2a) is smaller than that obtained at 550 °C (Fig. 2c). However, at high conversions the gasoline fraction obtained at 550 °C over-cracks forming gaseous products. Hence, higher gasoline yields are obtained at 500 °C for high conversion values. Because of the over-cracking of the gasoline fraction at 550 °C, higher yields of the gaseous products are obtained at this temperature (Fig. 2d). Furthermore, the promotion of cracking reactions at 550 °C leads to lower concentrations of LCO and HCO fractions, as the cracking of their components progresses with the reaction extent [38]. The small increasing slope observed in the yield of coke exposes that it is formed at very short residence times (< 3 s) and that it grows quite slowly [39]. Moreover, the temperature seems to have a minor effect on the yield of coke, even though it increases slightly with temperature. This small effect is a consequence of the mutual neutralization of the condensation and cracking reactions of coke precursors, as both are promoted at high temperatures [40].

The addition of any of the thermal naphthas, i.e. VBN or HCN, to the conventional feedstock (VGO), produces important variations in the yields of the fractions (Fig. 2). However, the trends obtained for the different fractions are quite similar for all the feeds, meaning that both the residence time and the temperature have a similar influence on all of them. Thus, higher gasoline yields are obtained with both HCN/VGO and VBN/VGO blends, accompanied by lower yields

of gases. Therefore, it can be said that the co-feeding transforms in a more effective way carbon into gasoline fraction suppressing its over-cracking (especially when HCN is co-fed), which is consistent with literature [41,42]. Comparing both blends, VBN/VGO blend behaves more similarly to pure VGO than HCN/VGO one, as VBN is formed by lighter compounds harder to crack, as it can be seen in the simulated distillation results (Table 1). This fact is in concordance with the almost steady evolution with the conversion of the gasoline fraction obtained with VBN/VGO blend both at 500 and at 550 °C (Fig. 2a and c, respectively).

The content of coke (Fig. 2b and d) obtained with both blends is also lower than that obtained with VGO at the whole range of studied operating conditions. Meaning that apart from the coke catalytically formed by dehydrogenation and condensation reactions, additive coke is also formed from the multiring aromatics already present in the VGO [43]. Consequently, the blending of the VGO with any of the naphthas free of these heavy molecules will lead to a reduction of the amount of coke deposited. The lesser formation of coke must be considered in the heat balance of the unit and will require either a higher preheating temperature of the feedstock or modifications in the operation of the regenerator [44].

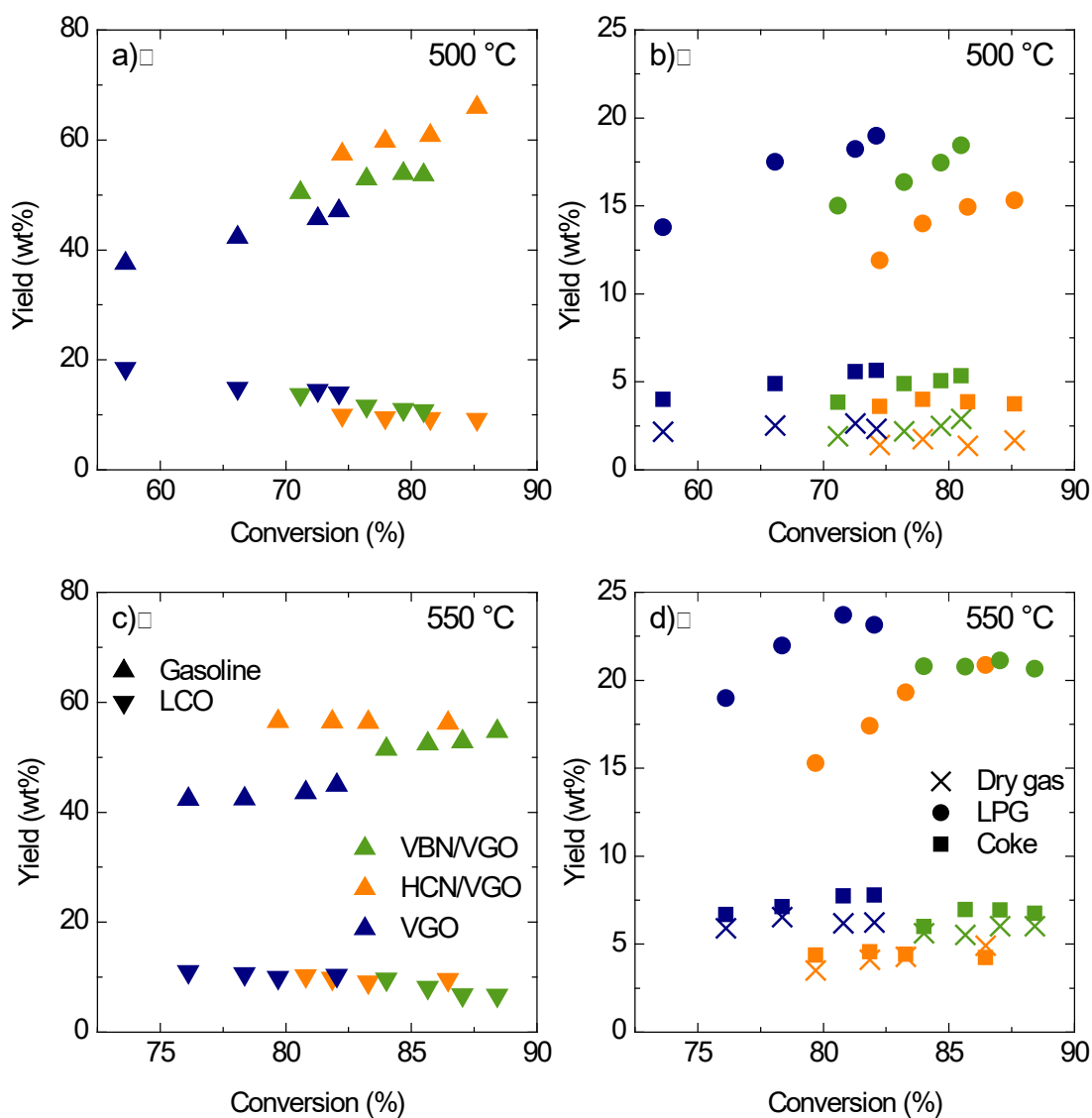


Fig. 2. Yields of the fractions as a function of the conversion of HCN/VGO, VBN/VGO and VGO feeds at 500 (a and b) and 550 °C (c and d). Symbols: dry gas (×); LPG (●); gasoline (▲); LCO (▼); coke (■).

Furthermore, the content of coke obtained with HCN/VGO blend is even lower than the content obtained with VBN/VGO blend, because of the different composition of the feeds. Thus, attending to the results collected in [Table 1](#), HCN has a higher concentration of aromatics than VBN (30.1 vs. 14.5 wt%, respectively), but lower of olefins (19.8 vs. 27.1 wt%, respectively). On the other hand, two main coke formation mechanisms are predominant in catalytic cracking

processes [40]: (i) the first one in which aromatics react successively with olefins on the Brønsted acid sites of the catalyst forming heavy polyaromatics; and (ii) the second one in which two aromatics react between them ending in the formation of pyrenes or bulkier heavy molecules after several consecutive steps. Therefore, as the content of coke obtained with HCN/VGO blend is lower (Fig. 2) in spite of its higher content of aromatics (Table 1), it can be considered that coke is mainly formed by the first mechanism, in which the concentration of olefins plays a key role.

The distribution of the yields obtained in the cracking of the pure naphthas has been summarized in Fig. S2. These results have been extracted from our previous works [18,19]. By comparing the results obtained with the pure streams with those obtained with the blends it can be obtained a complete idea on the effects of co-feeding thermal naphthas to FCC unit. Comparing the VBN and its blend with VGO, as it could have been expected the former offers yields of gasoline much higher given its lightest nature (Table 1). The yields of the dry gas, LPG and coke fractions are higher for the blend than for the pure naphtha, meaning that the VGO contributes to the formation of these fractions. However, it must be highlighted that no LCO fraction is obtained in the cracking of the pure VBN. With regard to HCN and HCN/VGO blend, similar differences have been observed than those aforementioned for the VBN and its blend with VGO. Nevertheless, a small concentration of LCO has been obtained for the pure HCN.

3.2. Characterization of the gaseous products

The yields of the different gaseous products, which include dry gas and LPG fractions, obtained with all the feeds at 500 and 550 °C have been displayed in Table 3. It can be seen that the main components for all the studied feeds and temperatures are propylene and *iso*-butane. Note that the yields of butylenes also reach quite high values, but it must be considered that the different C₄ olefinic isomers (α -butylene, *cis*- β -butylene, *trans*- β -butylene and *iso*-butylene) have been grouped under this name. Overall, dry gases, i.e. methane, ethane and ethylene, are mainly formed at high temperatures, given the endothermic nature of the cracking reactions that produce them [45]. This increase is more pronounced for the VGO and the VBN/VGO blend given their higher

tendency to over-crack (Fig. 2), as the production of C₁–C₂ compounds is commonly attributed to thermal cracking reactions, which are responsible for the over-cracking [46]. The yield of the LPG components also follows increasing trends with temperature, with the exception of that of *iso*-butane when VBN is co-fed. The same unconventional decreasing trend in the yield of *iso*-butane has been obtained by Passamonti and Sedran [47] in the catalytic cracking of VGO when increasing the temperature from 500 to 550 °C.

The most important gaseous products are ethylene, propylene, *iso*-butane and butylenes given their industrial interest. However, the yield obtained for each component with the different feeds does not provide information for a proper comparison among the feeds. Therefore, there have been computed several cracking indicators (Table 3) to offset the lack of appropriate information. Focusing on the olefinicity of C₃ and C₄ compounds, they both increase with temperature for all the feeds. It suggests that primary cracking reactions of heavy molecules (within gasoline fraction) that produce olefins are selectively promoted instead of hydrogen-transfer ones that would have converted these olefins into paraffins within LPG fraction [48]. The olefinicity of C₃ compounds is about 0.80 for all of the feeds, being slightly smaller the values obtained with VBN/VGO blend (averagely 0.77). The olefinicity of C₄ compounds, in turn, is highly influenced by temperature. Thus, at 500 °C values about 0.44 are obtained with all the feeds. However, at 550 °C the following increasing trend can be established between the feeds: HCN/VGO < VBN/VGO < VGO, perhaps due to a continuously increasing contribution from thermal cracking given their tendency to over-crack [49].

CMR denotes the relative importance of monomolecular versus bimolecular cracking pathways [50]. As expected, the obtained values strongly depend on reaction temperature, as well as on the composition of the feed. This way, the values for CMR obtained at 550 °C triplicate those obtained at 500 °C, meaning that temperature promotes protolytic cracking instead of β-scission reactions of branched products. Attending to the values obtained with each feed, higher values are by far obtained with VGO (0.52 and 1.88 at 500 and 550 °C, respectively), being intermediates those of VBN/VGO blend (0.51 and 1.59) and the lowest the values of HCN/VGO blend (0.39

and 1.00). This indicator once again exposes the higher tendency to over-crack of the VGO and, in a lesser extent, of the HCN/VGO. On the other hand, the effect of the temperature on products distribution is in concordance with the well-established mechanisms for the cracking of the individual components [51,52]. This way, high temperatures promote the extent of the cracking reactions, but inhibit the effect of the bimolecular hydrogen-transfer ones.

Table 3. Yields of the gaseous products and main cracking indicators obtained with HCN/VGO, VBN/VGO and VGO feeds at 500 and 550 °C for a residence time of 6 s.

	VBN/VGO		HCN/VGO		VGO	
	500 °C	550 °C	500 °C	550 °C	500 °C	550 °C
Dry gas	1.59	4.98	1.11	2.75	1.40	4.65
methane	0.73	1.57	0.42	1.23	0.57	2.21
ethane	0.56	1.83	0.42	1.08	0.48	1.80
ethylene	1.03	3.15	0.69	1.67	0.92	2.85
LPG	16.2	19.7	14.2	17.6	13.9	22.5
propane	1.65	1.72	1.09	1.64	1.12	1.93
propylene	4.66	6.95	4.79	6.12	4.64	8.11
butane	1.06	1.09	0.78	1.03	0.72	1.13
<i>iso</i> -butane	4.56	4.14	3.87	3.97	3.79	4.17
butylenes	4.29	5.80	3.66	4.80	3.70	7.18
Indicator						
CMR	0.51	1.59	0.39	1.00	0.52	1.88
HTC	1.31	0.90	1.27	1.04	1.22	0.76
C ₃ ⁼ /C ₃	0.74	0.80	0.81	0.79	0.81	0.82
C ₄ ⁼ /C ₄	0.43	0.53	0.44	0.49	0.45	0.57

HTC exposes the hydrogen-transfer reaction degree, which is helpful to reduce the content of olefins in naphtha or gasoline fractions. The general trend is that the HTC decreased with temperature, given the exothermic nature of the hydrogen-transfer reactions [53]. With regard to the values obtained with the different feeds, the blending of the VGO with any of the naphthas has a subtle effect at 500 °C. However, at 550 °C the addition of the naphthas has a notorious

effect, as the following increasing trend for the HTC has been obtained: VGO (0.76) < VBN/VGO (0.90) < HCN/VGO (1.04).

3.3. Characterization of the gasoline fraction

The gasoline fraction has been characterized by gas chromatography and the results obtained for each feed at 500 and 550 °C for a residence time of 6 s have been plotted in Fig. 3. Once again, it can be seen how determinant is the blending of the VGO with any of the naphthas. This way, the gasoline fraction obtained with the VGO is mainly *iso*-paraffinic (35.9 wt%) and aromatic (31.0 wt%) at 500 °C (Fig. 3a), but their main compounds at 550 °C (Fig. 3b) are olefins (34.6 wt%) and aromatics (32.5 wt%). It is remarkable the low concentration of n-paraffins obtained with the VGO at both temperatures (3.9 and 4.3 wt% at 500 and 550 °C, respectively). When the HCN is co-fed, main compounds of the gasoline fraction obtained at 500 °C do coincide with those obtained with the pure VGO, i.e. *iso*-paraffins (29.7 wt%) and aromatics (28.3 wt%). However, at 550 °C these families remain the most abundant ones (26.3 and 33.2 wt% of *iso*-paraffins and aromatics, respectively) in the gasoline fraction obtained with the HCN/VGO blend, unlike to that obtained with the VGO. Finally, the blending with VBN produces at 500 °C a gasoline, mainly composed of *iso*-paraffins (31.6 wt%), but with important concentrations of olefins and aromatics (21.3 and 23.9 wt%, respectively). Its composition at 550 °C is significantly modified, as the concentration of *iso*-paraffins, olefins and aromatics are equilibrated reaching values of 25.2, 25.5 and 27.0 wt%, respectively. On the other hand, the concentration of naphthenes is quite low (< 10 wt%) in all cases, which supposes a significant reduction in their concentration, comparing with the initial ones (Table 1) in spite of their moderate reactivity [54].

The existence of synergistic effects on the cracking of the blends has been also checked in order to perform a proper assessment. To do so, gasoline composition has been estimated considering the mixing ratio of the blends (20 wt% of naphtha and 80 wt% of VGO) and assuming no interaction between feeds [55]. Finally, estimated composition has been compared with the experimental data (Table S3). The data on the composition of the gasoline fraction obtained in

the cracking of the pure naphthas have been summarized in Fig. S3, but a full description of them is available in our previous works [18,19]. This way, attending to the results collected in Table S3 it can be seen the existence of synergistic effects that at 500 °C enrich in linear paraffins and in naphthenes the gasoline fraction obtained with both blends. At 550 °C, similar but different effects are observed for each of the blends. The gasoline obtained with the both blends has higher contents of paraffins (both linear and ramified) and naphthenes than estimated, but with the HCN/VGO blend, also the content of aromatics is higher than the estimated one.

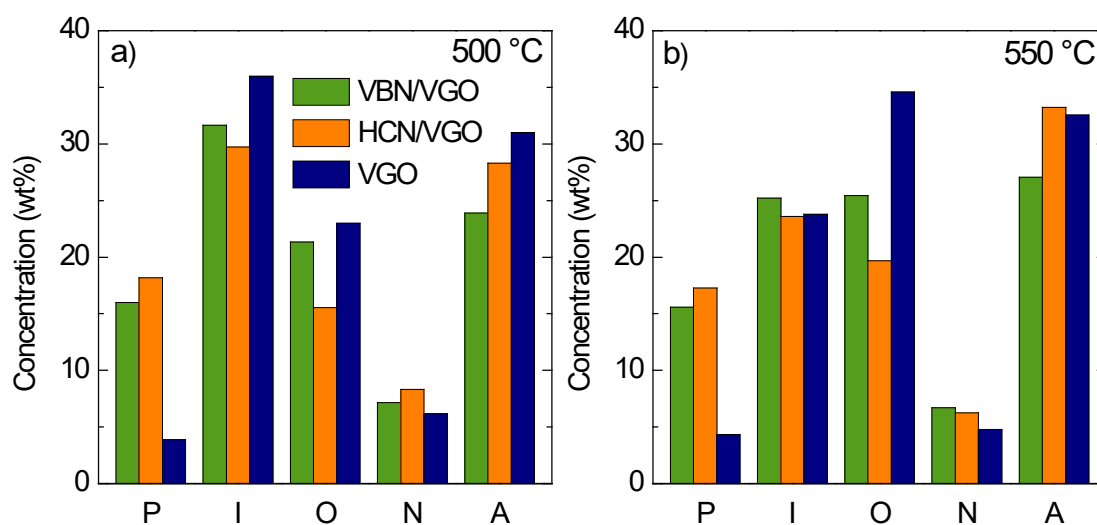


Fig. 3. Chemical nature of the gasoline produced in the cracking of VBN/VGO, HCN/VGO and VGO at 500 (a) and 550 °C (b) for a residence time of 6 s. Key: P, paraffins; I, *iso*-paraffins; O, olefins; N, naphthenes; A, aromatics.

The gasoline composition is clearly influenced by the temperature, as the concentrations of linear and ramified paraffins and of naphthenes decrease with temperature, but those of olefins and aromatics increase. These are expected trends, as condensation and cracking reactions that produce aromatics and olefins, respectively, are boosted at high temperatures. At low temperatures, hydrogen-transfer reactions are more significant and they promote the formation of saturated compounds, i.e. n-paraffins, *iso*-paraffins and naphthenes. However, the increasing or decreasing rate of each family of compounds is quite different depending on the feed. This way, the concentration of *iso*-paraffins decreases notoriously in the blends (about a 20 wt%), but in a

greater extent (34 wt%) in the VGO. In the case of olefins and aromatics, something similar occurs. The concentrations in the blends increase averagely a 23 wt% and a 15 wt% for the olefins and aromatics, respectively, whereas in the VGO they increase a 50 and a 5 wt%, respectively. Hence, these significantly different rates expose the strong influence of the molecules distribution and nature of each feed.

In order to obtain more detailed information of the composition of the gasoline fraction, its chemical nature has been deeply analyzed (Figs. 4 and 5). The distribution of the n-paraffins (Fig. 4a and b) is highly influenced by the feed used, whereas temperature has a subtle effect on it. This way, the distribution obtained in the cracking of the VGO follows a decreasing order from the lowest to the highest number of carbon atoms. Note that C₁₁ and C₁₂ n-paraffins have been grouped causing that the concentration of C₁₁₋₁₂ n-paraffins is lightly higher than that of C₁₀. However, the distribution of the n-paraffins obtained with HCN/VGO and VBN/VGO blends goes through an intermediate maximum, as it has been obtained in the cracking of low-quality naphtha [18]. Thus, the gasoline fraction obtained with the HCN/VGO reaches its maximum concentration for molecules of 6 carbon atoms, while it is displaced to molecules of 9 carbon atoms with VBN/VGO blend.

On the contrary, the concentration of *iso*-paraffins (Fig. 4c and d) shows a decreasing distribution from the lowest to the highest number of carbon atoms for all the feeds. Furthermore, temperature plays an important role in this family as the concentration of these compounds, especially those of C₅–C₇ compounds, are significantly reduced when increasing temperature up to 550 °C. It exposes the high reactivity of this family of compounds that are highly cracked at high temperatures. Moreover, their formation through hydrogen-transfer reactions is inhibited at high temperatures given the thermodynamic restrictions of this reaction [56].

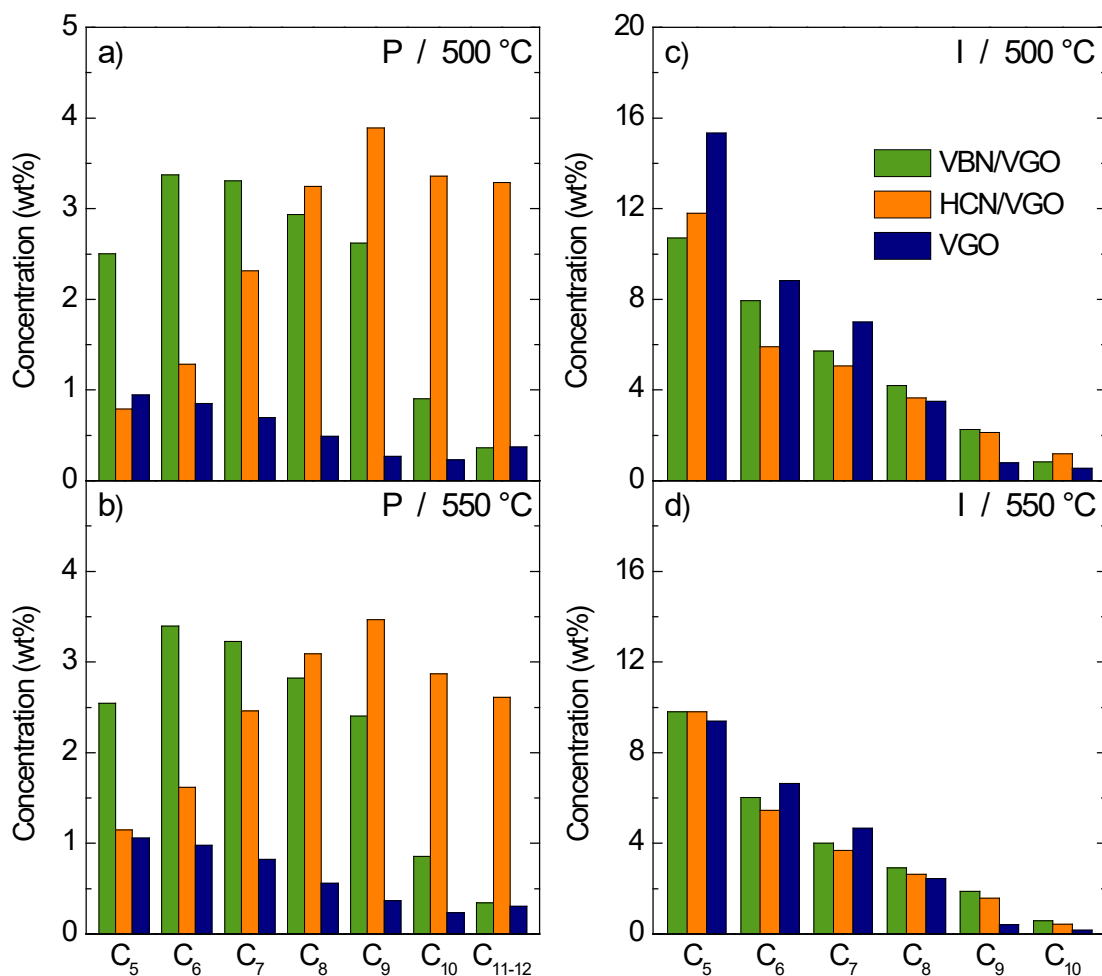


Fig. 4. Comparison of the concentration of n-paraffins (graphs a and b) and of *iso*-paraffins (graphs c and d) in the gasoline fraction obtained with the three feeds and grouped according to their number of carbon atoms at (graphs a and c) 500 °C and (graphs b and d) 550 °C. Key: P, n-paraffins; I, *iso*-paraffins.

The distribution of the olefins (Fig. 5a and b) is also affected by the thermodynamics of the hydrogen-transfer reactions causing a considerable increase of their concentration at high temperatures. Furthermore, this increase is more accused for C₅–C₇ olefins that are formed in the cracking of heavier olefins within LCO and HCO fractions, but also within the gasoline fraction that co-form light olefins.

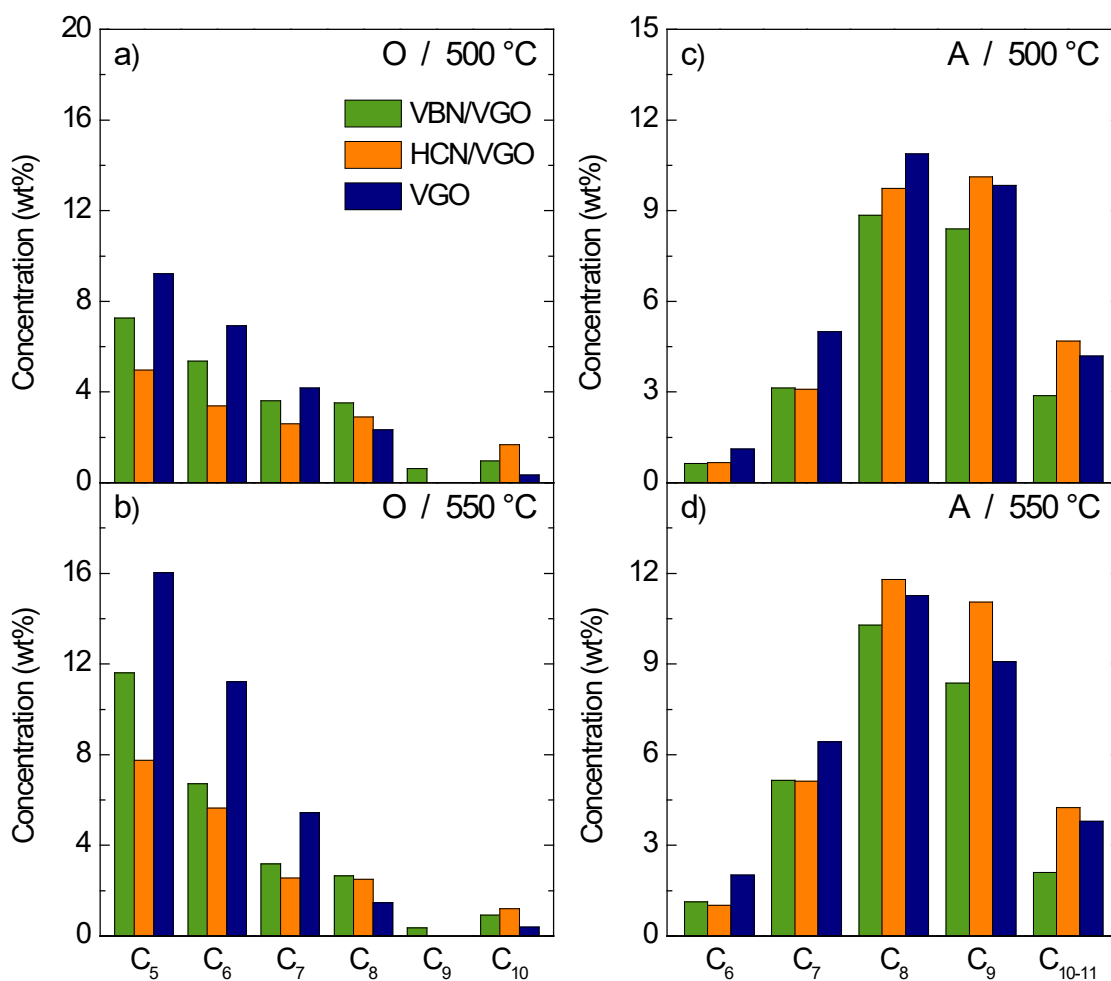


Fig. 5. Comparison of the concentration of olefins (graphs a and b) and of aromatics (graphs c and d) in the gasoline fraction obtained with the three feeds and grouped according to their number of carbon atoms at (graphs a and c) 500 °C and (graphs b and d) 550 °C. Key: O, olefins; A, aromatics.

Finally, the distribution of aromatics (Fig. 5c and d) is barely affected by the blending of the naphthas and by the reaction temperature. Thus, the distribution goes through a maximum at C₈–C₉ molecules, which are the main products of the Diels-Alder reactions of the olefins as obtained by Passamonti et al. [57] and Al-Sabawi et al. [58] in the cracking of VGO. Moreover, the aromatic fraction contains important concentrations of C₆–C₈ molecules (about 50 and 60 % at 500 and 550 °C, respectively). Hence, these gasoline fractions can be used as a source of BTX (benzene, toluene and xylenes) aromatics, given their high commercial interest [59].

The quality parameters collected in [Table 4](#) offer a wider perspective of the gasoline fraction produced and of the effect of the temperature on it. Thus, *iso*-paraffinicity parameter, which gives information about the isomerization degree of the C₅ and C₆ molecules, can be related to a certain extent with the RON of the gasoline fraction. As a global trend, it can be established that the higher the temperature, the lower the *iso*-paraffinicity parameter. It means that cracking reactions that consume the *iso*-paraffins are boosted at high temperatures. Moreover, this reduction is more marked for C₅ than for C₆ molecules. However, the magnitude of the change significantly depends on the feed used. This way, biggest modifications have been obtained in the case of the VGO both for C₅ and C₆ molecules. On the contrary, VBN/VGO is the feed less sensitive to a temperature change.

Olefinicity parameter, in turn, increases with temperature. Commonly, this parameter follows opposite trends to those of *iso*-paraffinicity because of the inhibition at high temperatures of the hydrogen-transfer reactions that produce *iso*-paraffins from olefins. Comparing the feeds, it can be observed that there are no significant differences among them, being the olefinicity obtained with VGO both for C₅ and C₆ molecules the one most modified with temperature.

RON is the most meaningful parameter when characterizing gasoline lump as marketed automotive fuels must have a RON of 95 or 98 to comply with the current legislation. Therefore, the feed that offers the closest values to those established by the administration is the VGO with values of 95.1 and 99.1 at 500 and 550 °C, respectively. The co-feeding of the naphthas decreases the values of the RON obtained, especially when adding the VBN as the values obtained at 500 and 550 °C have been 85.0 and 87.2, respectively. The attenuation suffered by the addition of the HCN is less marked obtaining values about 88.5 at both temperatures. Even though these results may appear as a drawback, the RON of the gasoline fraction obtained with the blends can be easily increased by supplementing it with an additive that acts as a quality octane booster [60]. Equally, the gasoline fraction produced must be added to the gasoline pool of the refinery and be submitted to the common reforming and hydrodesulfurization processes in order to comply with the environmental legislation.

Table 4. Effect of the temperature on the quality parameters of the gasoline fraction produced in the catalytic cracking of the VBN/VGO, HCN/VGO and VGO for a residence time of 6 s.

Quality parameter	VBN/VGO		HCN/VGO		VGO	
	500 °C	550 °C	500 °C	550 °C	500 °C	550 °C
<i>iso</i> -paraffinicity						
iC ₅ /nC ₅	4.28	3.85	14.9	8.53	16.2	8.89
iC ₆ /nC ₆	2.35	1.78	4.61	4.52	10.3	6.80
olefinicity						
C ₅ ⁼ /C ₅	0.35	0.48	0.28	0.41	0.36	0.61
C ₆ ⁼ /C ₆	0.31	0.39	0.30	0.41	0.39	0.54
RON	85.0	87.2	88.5	88.4	95.1	99.1

4. Conclusions

The blending of thermal naphthas, i.e. visbreaker naphtha (VBN) and heavy coker naphtha (HCN), with VGO has a notorious effect on the conversion and products distribution obtained in the catalytic cracking under industrial conditions. Overall, the blending with any of the thermal naphthas attenuates the cracking of the heavier compounds of the VGO. The preferential adsorption and reaction of the components of the naphtha and the shortening of the residence time caused by the increase of flow do contribute to this effect. Hence, thermal naphthas can be considered as product distribution controllers being their main effects the ones detailed below.

The yields the gaseous fractions are reduced with the blends, meaning that over-cracking reactions of the compounds within the gasoline fraction are significantly reduced. This reduction is more accused when HCN is the naphtha co-fed. The yield of gasoline fraction is also maximized with the blends, especially with HCN/VGO blend. Furthermore, the conversion of the heaviest fractions, i.e. LCO and HCO, is barely affected by the co-feeding, whereas the yield of coke is lower than that obtained for the VGO, expanding the life cycle of the catalyst. As naphthas are gasoline range fraction, their co-feeding implies a deep modification of the composition of the

gasoline fraction fed. The composition of the thermal naphtha co-fed has a great incidence on the composition of the gasoline product. This way, the blending with HCN increases the concentration of n-paraffins, naphthenes and *iso*-paraffins and reduces that of olefins. On the other hand, the co-feeding of VBN reduces the concentration of aromatics, olefins and *iso*-paraffins causing an increase in the concentration of n-paraffins and naphthenes, but also a decrease of the RON of the gasoline fraction with respect to that obtained in the cracking of the VGO. Even though the total content of aromatics is the less affected one, their distribution shifts to compounds within the C₆–C₈ range, which are known as BTX aromatics and are considered as highly important for the petrochemical industry. Temperature also has a marked effect on the composition of the stream of products. This way, raising temperature up to 550 °C promotes the cracking reactions while inhibits the bimolecular hydrogen-transfer reactions.

Therefore, obtained results in the 500–550 °C range reveal that the co-cracking of the thermal naphthas and VGO in FCC units is an interesting way of alleviating their current surplus. Thus, thermal naphthas can be co-fed to industrial FCC units without causing any operational issue. The proposed strategy aims for valorizing thermal naphthas in current FCC units without requiring any revamping of the unit. However, if revamping of the unit is an affordable option, the injection of the thermal naphthas before the conventional feedstock avoids the reduction of the RON of the gasoline fraction.

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