ELSEVIER

Catalysis Today 50 (1999) 73–85

CATALYSIS TODAY

Production of reformulated gasoline in the FCC unit. Effect of feedstock type on gasoline composition

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Abstract

FCC gasoline is a major component in the total gasoline pool produced in an integrated refinery, but it contains many compounds (olefins, sulfur and aromatics) which lead to harmful automobile emissions. The objective of the present study is to determine the effect of feedstock quality on gasoline composition in a range of operating variables with a constant type of catalyst. The work was carried out in an FCC pilot plant constructed and operated in CPERI. The FCC gasoline was fully analyzed in a system of GC/MS. Ten different feedstocks were used in the unit in order to investigate the feedstock physical properties which affect the gasoline yield and composition, the feed conversion and the coke yield as well. The gasoline components were measured as total hydrocarbon groups: aromatics, normal and branched olefins, normal and isoparaffins and naphthenes but special emphasis was given, in this study, for the aromatic and olefinic content of gasoline. The main conclusion of the work is that feed conversion, coke yield and gasoline yield and composition are strongly influenced by the type of FCC feedstock. It was shown that a paraffinic and an aromatic FCC feedstock produce, respectively, an olefinic or an aromatic gasoline. The hydrotreating process plays also an important role in the gasoline composition. For these feed effects detailed qualitative and quantitative information is given in the paper. Moreover, short form models were proposed for the prediction of conversion coke yield and gasoline composition as a function of the main feedstock properties. Analytical forms of these models are presented for gasoline aromatics and olefins and total conversion as well. The predictions of the models were satisfactory for all hydrocarbon groups. The models were also validated with experiments using two additional feedstocks in the pilot unit under a wide range of experimental conditions.

Keywords: FCC; Reformulated gasoline; Gasoline composition; Modeling; Feedstock properties

1. Introduction

The new regulations in USA necessitated the reformulation of gasoline composition. In order to achieve this reformulation the refineries have proceeded to changes in the various gasoline production processes. The new regulations in USA for car exhausts have as objective the reduction in the emissions of total volatile components (VOCs), NO_x and toxics. In this way the refineries must modify the components in gasoline which affects these emissions [1]. It is generally very difficult to investigate which of the gasoline compounds (and in which degree) affects the final exhaust emissions. However, some research projects were carried out mainly in USA (AQUIP) which tried to investigate these parameters [2]. Recently, a project

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0920-5861/99/$ – see front matter
PII: S0920-5861(98)00464-7

was carried out in Europe (EPEFE) [3] and the results were that changes in gasoline quality must include mainly the reduction of gasoline olefins and aromatics (and especially benzene) and the reduction of the RVP and sulfur as well. All these compounds were proved to have an effect on NO_x, VOC emissions and toxics. So an environmentally friendly gasoline must have mainly low content of olefins, aromatics, sulfur and RVP [4].

Production of reformulated gasoline affects several processes in a refinery. However, taking into account that the fluid catalytic cracking unit (FCCU) produces the highest portion of the total gasoline pool (about 50%), the 90% of the final gasoline olefins and a high percentage of aromatics, the focus is now on improving the FCC gasoline yield and composition [5]. The FCC process is a very complicated process with many variables which affect the product yield and the product selectivity. The main parameters which affect the gasoline yield and composition are: the FCC operating parameters, the type of catalyst and the type of feedstock [6]. The refineries have large databases which try to correlate FCC product yields and properties to a wide range of feedstocks, catalysts and operating conditions. However, these results are considered proprietary and therefore typically remain unpublished. Only limited results are included in literature from such studies [6–8].

The objective of the present study is to determine the effect of FCC feedstock parameters on gasoline composition using a current generation catalyst under a range of operating parameters. Feedstock has an extremely large effect on FCC gasoline composition and octane number [5]. The work was carried out, in co-operation with two Greek refineries, in an FCC pilot plant constructed and operated in CPERI. The objective is to provide guidance for the two refineries to prepare them for the new gasoline regulations. In the study a large set of experiments were performed under a wide range of operating variables using 10 different feedstocks supplied by the two refineries. The gasoline produced was fully analyzed in a system of GC/MS. The work includes the effect of various feedstocks on the total hydrocarbon groups of gasoline: *n*-olefins, iso-olefins, total olefins and aromatics. Moreover, an attempt was made to investigate the specific properties of VGO which influence these hydrocarbon groups.

2. Experimental

2.1. Description of FCC pilot plant

Based on the results from a cold model unit an FCC pilot plant was constructed in CPERI. The main parts of the FCC pilot plant are given in Fig. 1. The unit consists of a vertical reactor (riser) with 7.08 mm i.d., a fluid bed regenerator, the stripper and the lift line. The feed is injected in the bottom of the riser and it comes in contact with the catalyst flowing through a slide valve. In the riser the reactions take place and at the riser exit the mixture is entering the stripper vessel where the separation (stripping) of gases from the solid catalyst occurs. The solids flow through a second slide valve and through the spent catalyst lift line (Fig. 1) return to the reactor bottom following regeneration. The reaction products, from the stripper exit, flow through a heat exchanger for the condensation of heavier products. Then the mixture is led to a stabilizer column for better separation of liquid and gaseous products. The mixture of gasoline, light cycle oil (LCO) and heavy cycle oil (HCO) is obtained through the bottom of stabilizer. The fluid bed regenerator reactor is used to burn the carbon that covers the catalyst surface as a by-product of the cracking process. The fluidization gas (air) is introduced from the base of the regenerator and its flow rate is controlled by a mass flow controller. The regenerator exit stream passes through cyclones that remove any entrained solids. The volumetric flow rates and the compositions of the flue and cracked gases are determined by two wet test meters and two GCs, respectively. An on-line oxygen analyzer always monitors the excess of oxygen to obtain good catalyst regeneration. A more detailed description of the pilot plant is presented elsewhere [9]. The pilot plant is fully automated and the process control system of the unit is based on a special industrial computer control system. The control system collects the values of the input and drives the output signals [10].

2.2. FCC pilot unit operation

For the current experiments 10 different types of FCC feedstocks, provided by two Greek refineries, were used. One of the feedstocks was used in the unit as reference (Kuwait vacuum gas oil, code name: 372).

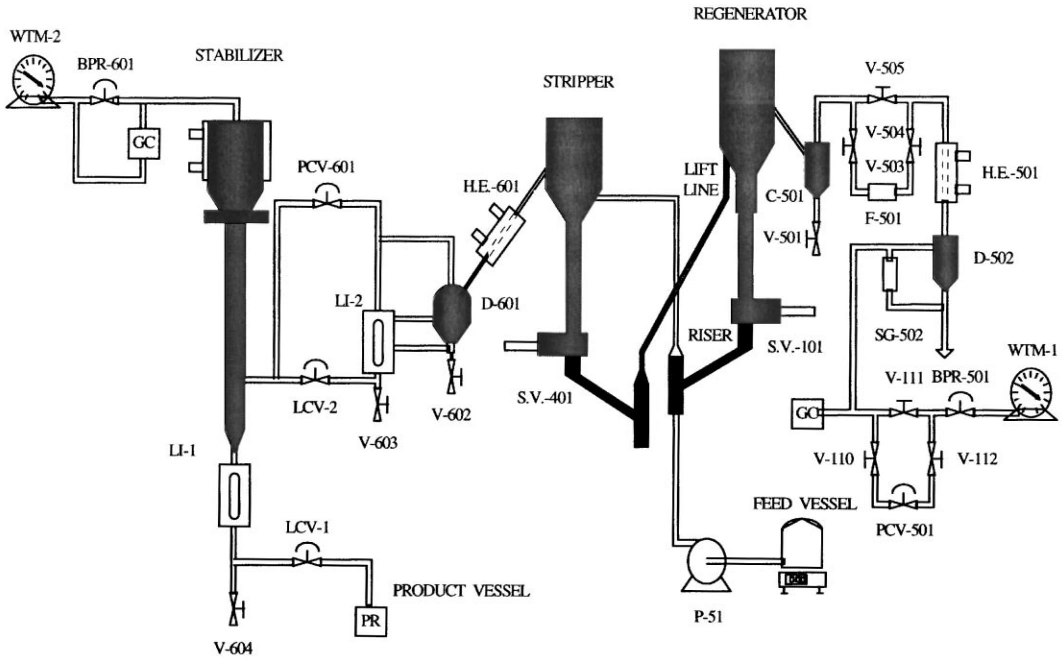

Fig. 1. Schematic view of CPERI FCC pilot plant unit.

The properties of these feeds, measured by standard ASTM procedures, are presented in Table 1. The description of the feedstocks according to its code name of Table 1 is:

feedstock 342: is a part of total FCC feedstock from refinery 2, it does not contain extracts (abbreviation: 2-no extracts)
feedstock 362: is the total FCC feedstock from refinery 2 (2-total)
feedstock 3162: a highly paraffinic feed from refinery 2 (2-paraffinic)
feedstock 3172: an aromatic feed from refinery 2 (2-aromatic)
feedstock 352: non-hydrotreated feed from refinery 1 (1-non HT)
feedstock 3122: hydrotreated feed from refinery 1 without resid (1-HT no resid)
feedstock 4112: hydrotreated feed from refinery 1 with 15% resid (1-HT-resid)

Table 1
FCC feedstock properties

Code	4112	3122	352	372	3132	342	362	3142	3162	3172
Sp. gravity	0.9189	0.9056	0.9195	0.9314	0. 913	0.9026	0.893	0.920	0.868	1.003
Sulfur (wt%)	0.66	0.175	2.127	2.98	2.036	1.82	1.31	2.722	0.803	4.686
Visc., Cst 50°C	22.17	8.96[a]	31.66	63.35	24.24	17.48	21.99	25.47	7.44[a]	221.0
Carb. residue	1.091	0.2	0.691	0.407	0.37	0.07	0.38	0.56	0.08	3.2
BN_2 (wt%)	0.035	0.033	0.05	0.033	0.029	0.024	0.027	0.05	0.003	0.05
RI, 70°C	–	1.4811	1.492	1.498	1.489	1.483	1.478	1.4955	1.4601	1.552
ASTM D1160 (°C)										
MeABP	437.3	466.4	458.6	470.9	445.1	425.4	451.6	438.1	471.0	465.0
T 20%	353.2	423	400.3	453.6	385.3	370.4	396.6	379.7	435.2	428.3
T 80%	503	517	514.6	492.5	492.1	467.8	496.0	489.2	523.1	515.0

[a] At 100°C

feedstock 3132: type of feedstock from refinery 2 (2-a)
feedstock 3142: type of feedstock from refinery 2 (2-b)

The ranges of FCC operating variables were: T=970–1040°F, catalyst/oil ratio (C/O)=4–16, weight hourly space velocity (WHSV)=40–160 h^{-1} and partial pressure of hydrocarbons (PP_{HC})=10–12 psia. The catalyst was a commercial equilibrium catalyst (E-cat) used in a Greek refinery with the following properties: MAT=70, UCS=24.26, matrix surface area=44 m^2/g, total surface area (TSA)=158 m^2/g, micropore volume=0.05 ml/g, average bulk density=0.84 g/ml, average particle size=75 μ, Al_2O_3=39.1 wt%, RE_2O_3=0.65 wt%, Ni=163 ppm, V=362 ppm.

The most important work in this study is the analysis of gasoline obtained from the different FCC pilot plant experiments. However, the determination of gasoline composition is difficult because of the presence of many compounds in different amounts. CPERI has applied a methodology for this analysis based on a system of GC/GC–MS. With this method the gasoline can be analyzed not only as a function of the different components group (n-paraffins, isoparaffins, normal olefins, branched olefins, diolefins, saturated naphthenes, unsaturated naphthenes, naphtheno-aromatics, aromatics) but also as a function of carbon atoms in each one of the various groups. With the same method the benzene content can be calculated since benzene analysis is suffering from the presence of interfering compounds like 1-methylcyclopentane [11].

3. Results and discussion

3.1. Effect of feedstock type on gasoline yield

The effect of each one of the FCC feedstock properties on the gasoline composition is difficult to be studied since there are no feedstocks which vary only in one physical property and keep all other properties constant. For this reason many studies are described in literature where model compounds or artificially prepared gas oil feedstocks were used for the experiments [12–15]. Corma and Woijciechowski [13] and Corma et al. [14] have used model compounds for the investigation of some physical or chemical properties of the feeds on catalytic cracking. The more simple approach for a prediction of gasoline composition (as total paraffins, naphthenes and aromatics) was based on the lump methodology developed in Mobil [15]. The problem with the lump models is that the relative concentrations of the species making up individual kinetic lumps can change as the reaction proceeds and thus these models cannot be extrapolated to new conditions or feedstocks and they are specific for the feedstock, catalysts and operating conditions used. For this reason, Liguras and Allen [16,17] have presented a new class of lumped kinetic models providing a mechanism for utilizing pure compound data in an advanced structural model which describe the entire catalytic cracking reactions network. This model represents an oil mixture by a distribution of pseudo-components. Recently, Joshi et al. [18] presented a computer assisted modeling for FCC based on large mechanistic kinetic models and a stochastic approach to obtain a molecular representation of FCC feedstocks. All these advanced models can indeed predict gasoline composition and FCC product selectivity but require detailed mass spectral data, extensive compound kinetic data base and computational power which sometimes are not available.

Considering the difficulties mentioned above about the effect of each feedstock property on FCC products, the changes in gasoline yield and composition are examined, in this work, as a function of total FCC conversion (wt%). In this way the effect of conversion on the gasoline yield is presented in Figs. 2 and 3 for seven feedstocks from the two refineries. These seven feedstocks are selected both for the simplicity of the figures and since they cover some extreme cases in the quality of all the 10 feeds of this study. Fig. 2 shows that the total hydrotreated FCC feed with 14% resid (feed 4112) gives the lowest gasoline yield. The addition of 14% atmospheric resid causes a high decline in gasoline yield in relation to the similar feedstock but without resid (3122). This result can be easily explained by the fact that the introduction of resid into the feed increases mainly the concentration of condensed aromatics. It is well known from the mechanism of catalytic cracking [15–17,19,20,22] that these compounds cannot be cracked to produce compounds in the gasoline boiling range but they are mainly coke precursors. Indeed, although it is not

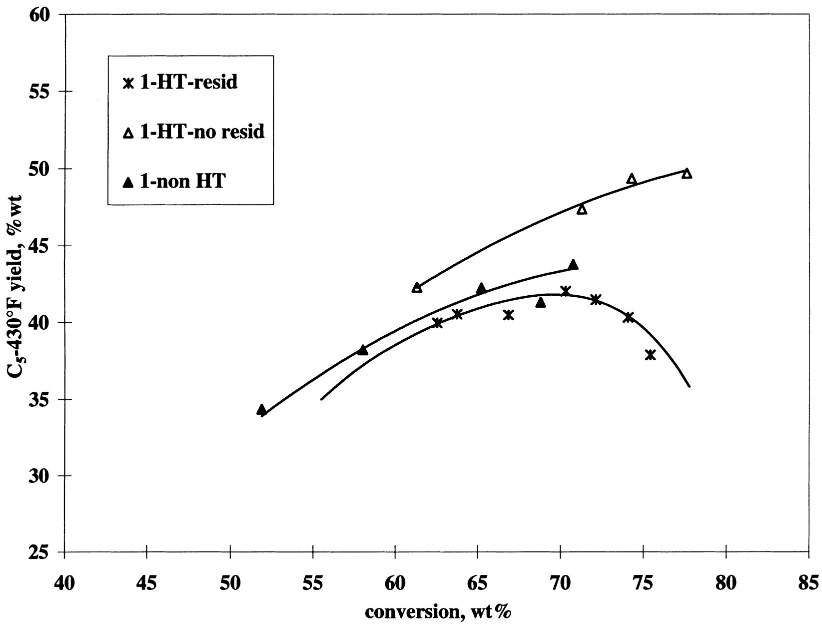

Fig. 2. Effect of various FCC feedstock from refinery 1 on gasoline yield.

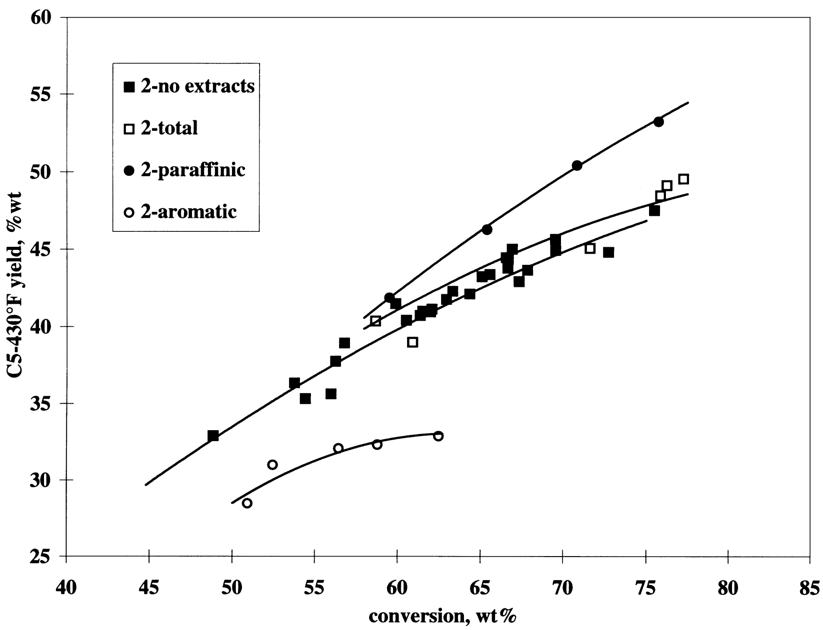

Fig. 3. Effect of various FCC feedstock from refinery 2 on gasoline yield.

presented in figures, this type of feedstock produces the highest coke yield. The above effect of FCC feedstocks with resid in gasoline is in agreement with [19,20].

The hydrogenation of VGO has also a major effect on gasoline yield. The hydrotreated feed (3122) gives higher gasoline than the non-hydrogenated (352). The delta yield in gasoline for the two feedstocks is about

+6 wt% and this value is in accordance with results presented in [22,23]. It is remarkable from Table 1 that the hydrotreating process reduces not only the sulfur and nitrogen content but it mainly affects the chemical structure of the feeds as it is reflected from the reduction in the refractive index (RI) and specific gravity (SG) (Table 1). The hydrotreated feed has less aromatic carbons (lower RI) and more paraffinic carbons. For refinery 2 (Fig. 3) the highly aromatic feed (3172) gives the lowest gasoline yield while the highly paraffinic feed (3162) gives the highest yield. The two feeds with and without extracts (362, 342) give about the same gasoline yield.

3.2. *Effect of feedstock type on gasoline composition*

The effect of various feedstocks on gasoline composition is also depicted using the conversion as independent variable. In the following, the gasoline hydrocarbon groups are presented in wt% on FCC feed basis. The gasoline aromatics yields are presented for the seven feeds in Fig. 4. The highly paraffinic feed (3162) produces the lowest aromatics yields while the feed with the resid (4112) gives the highest yields. High aromatics yields are also obtained with the non-hydrotreated feed (352). The aromatics molecules produce higher octane and thus the high aromatic content of gasoline from the non-hydrotreated feeds can lead to higher RON for this gasoline in relation to the hydrotreated gasoline [19,21]. The aromatic feed (3172) gives more aromatics than the paraffinic (3162) but because this feed (3172) produces low gasoline yield this moderates the production of the aromatics (Fig. 4). The feedstocks with the higher amount of aromatics make the higher amount of aromatics in the gasoline product. This happens because the aromatic rings with an attached substituent group undergo reaction such that the substituent group reacts to give aromatic ring which belongs to the gasoline fraction due to the resultant lowering of boiling point [15,19,20]. For all feeds the gasoline aromatics increase with increasing conversion (Fig. 4). This is a result of the mechanisms of the reactions (primary and secondary) which take place in catalytic cracking and lead in the production of increased refractory aromatics with feed conversion. Increasing the process severity (higher conversions) the olefins (and naphthenes) can be converted, via hydrogen transfer reactions, to aromatics. Thus, for the production of a

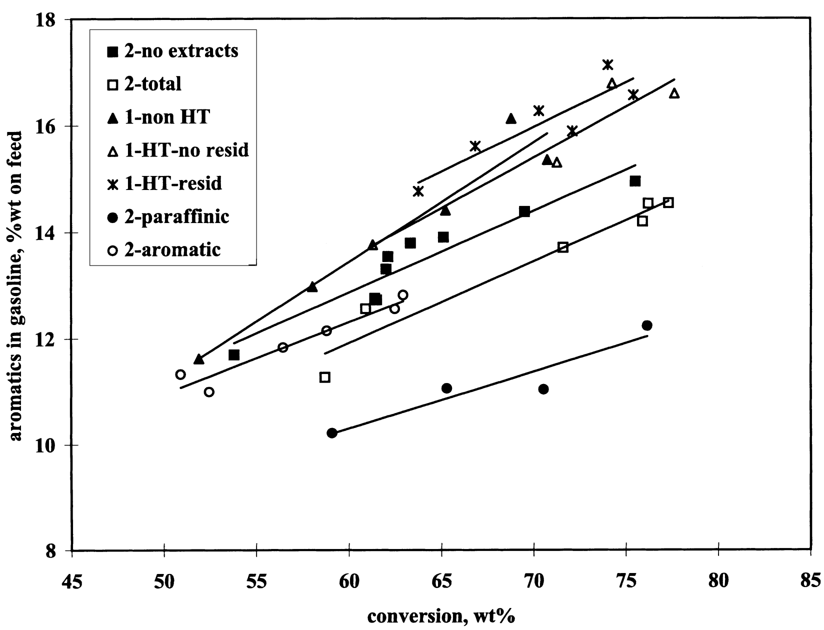

Fig. 4. Effect of FCC feedstocks on gasoline aromatics.

reformulated FCC gasoline with less aromatics the FCC unit must operate at more moderate than for conventional conversion level. This conversion level can be found from Figs. 2–4 taking into account the available aromatics from the other gasoline components and of course the aromatic content which will be defined by the new regulations for the reformulated final gasoline pool. Figs. 2–4 can also give to refineries guidelines for an optimum feedstock (or an optimum mixing of feedstocks) in order to achieve future aromatics in gasoline. Generally, for the same conversion the lower the aromatic content in the feed, the lower the production of gasoline aromatics. The same behavior, as for total aromatics, is observed (not presented in figure) for a very important (for environmental reasons) aromatic compound, the benzene. Benzene yield increases also with conversion. The results for total aromatics and for benzene are in agreement with the result from [5,6,11].

The effect of feedstock quality on the olefins produced in the FCC gasoline is presented in Figs. 5 and 6 for normal and branched olefins, respectively (in a wt% on feed basis), as a function of conversion. Fig. 5 reveals that for the same conversion the highly aromatic feedstock (feed 3172) gives the lowest *n*-olefins yield, while the highly paraffinic feedstock the highest (feed 3162). The same trend is valid for the branched olefins as well (Fig. 6). This behavior is attributed to the production mechanism of olefins. According to carbenium ion chemistry the olefins are the primary products from the catalytic cracking of paraffins. Thus, paraffinic feedstocks produce more primary olefins than aromatic feedstocks. Although olefins participate in many secondary reactions (hydrogen transfer, isomerization, etc.) since paraffinic feedstock is more crackable than aromatic it requires lower severity (lower C/O) to obtain the same conversion as the aromatic feedstock. This lower C/O favors also the lower extent of bimolecular hydrogen transfer reactions. In contrary the high severity required for the highly aromatic feedstock (to obtain the same conversion) favors hydrogen transfer reaction and thus the decrease in olefins yield.

Resid in feedstocks (4112) decreases the olefins yield in relation to feedstock without resid (3122). This happens for both types of olefinic compounds (Figs. 5 and 6) and is due to the higher gasoline selectivity of the feedstock without resid than the corresponding with resid. The hydrotreated feed (3122) gives more olefins (normal and branched) than

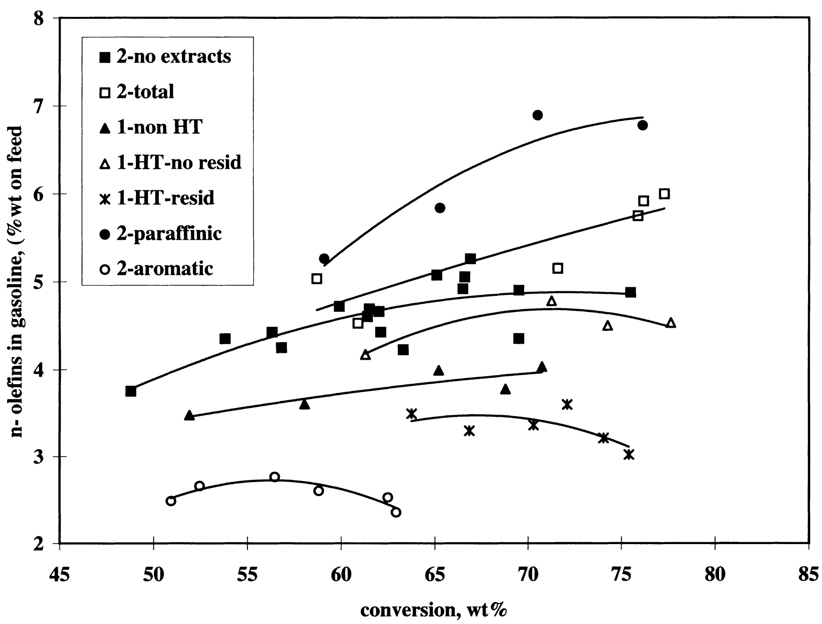

Fig. 5. Effect of FCC feedstocks on gasoline *n*-olefins.

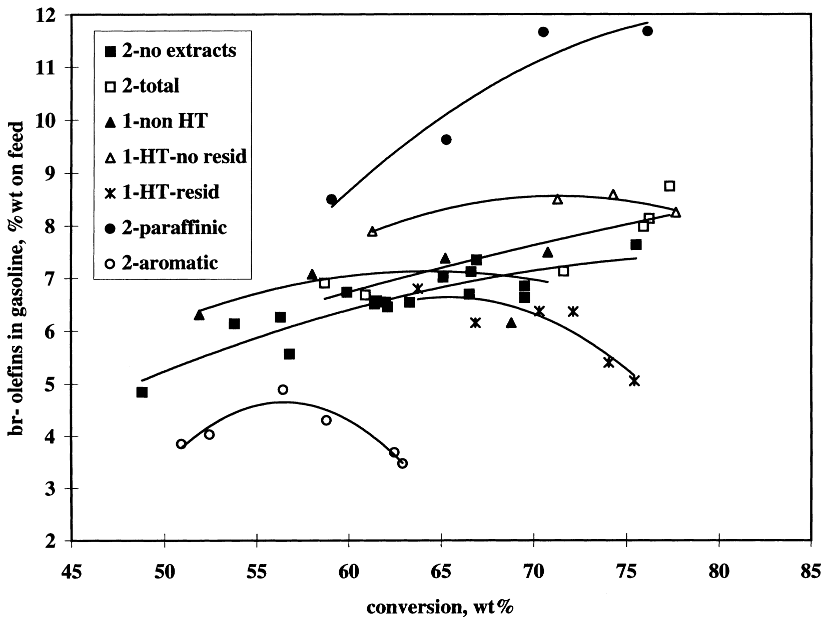

Fig. 6. Effect of FCC feedstocks on gasoline branched olefins.

non-hydrotreated feed (352) at the same conversion. As it was mentioned above hydrotreated feeds contain more paraffins and less aromatics than the non-hydrotreated feeds. Important differences in the olefins yield do not exist for the two feedstocks of refinery 2 (with and without extracts: 362, 342, respectively). The above effect of feedstock type (hydrotreated or not) on gasoline olefins has a similar explanation as above for the paraffinic and aromatic feeds. Generally, the olefinicity of the gasoline is higher for more paraffinic feeds. A very important type of olefins is the diolefins which although are in small quantities they are significant for environmental reasons and moreover they contribute to the gasoline color and stability since they create gums (polyolefins). The effect of feedstock type on diolefins yield is presented in Fig. 7 for some feeds. The main conclusion of this figure is that there is a strong effect of feed quality on diolefins yield. Paraffinic feeds (3122, 3162) produce higher yields than aromatic feeds (3172, 4112). It must be also pointed out that in contrast to other olefins the hydrotreated feed 3122 gives the highest diolefins yield. Diolefins are referred in literature to be a product of thermal cracking and sometimes the diolefins content of the gasoline is used as monitoring tool of thermal coking reactions [19]. Brevoord and Wilcox [19] using an Arco pilot unit concluded similar results for the high diolefins yield from paraffinic feedstock and give a possible explanation of diolefins reactions. The effect of conversion on the gasoline olefins yield is different from that of aromatics. Olefins are intermediate and not stable products and they decompose at high conversion levels (high severity). Depending on the type of feedstock the olefins yield increases up to a certain value of conversion and after this value (higher conversion levels) the olefins decrease (Figs. 5–7). Although limited literature results exist for the effect of feedstock on various type of olefins the present results are in agreement with [5,12,15,19].

3.3. *Modeling of the feedstock effects on gasoline composition*

For the development of short form models for the effect of FCC feedstock properties on gasoline composition the following methodology was applied. For a constant feed and the same catalyst the effect of FCC operating variables was determined. The independent variables taken into account were: C/O, WHSV, *T*.

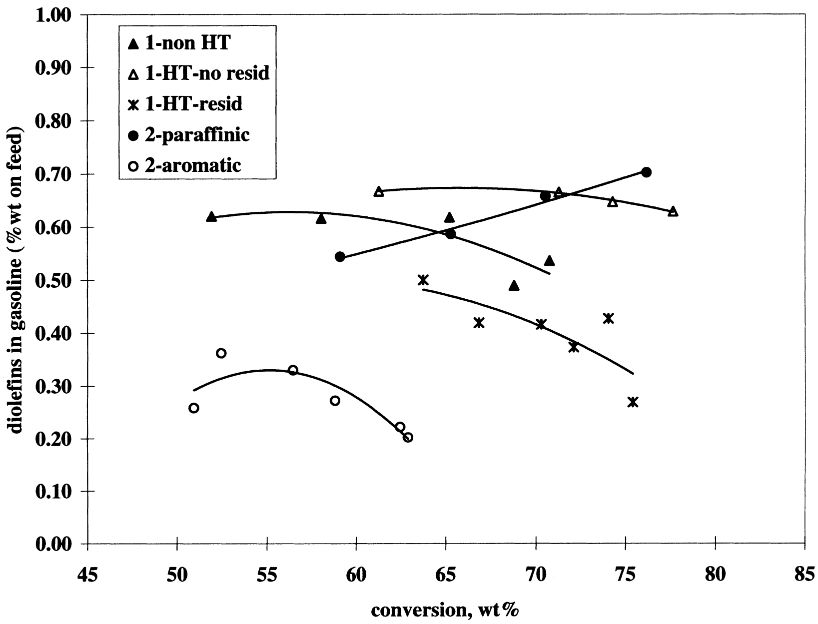

Fig. 7. Effect of FCC feedstocks on gasoline diolefins.

Detailed results of the effect of these operating conditions on gasoline composition will be presented in a future work. Following this, for the same catalyst and for the eight different feedstocks, the effect of FCC feedstock properties was determined. From an extensive literature review in CPERI [6–8,19–22,24], it was concluded that the independent feedstock properties which affect gasoline composition and which can be measured on a daily basis in any refinery laboratory are: the mean average boiling point (MeABP), the wt% sulfur, the specific gravity (SG), the refractive index (RI) and the basic Nitrogen (BN_2). For the parameter determination of the short form models, regression analysis studies were performed and a suitable software was developed based on the Levenberg–Marquard algorithm. It is clear that this attempt depends on the choice of the function which will be used. In this study many different mathematical functions were applied but linear functions were finally selected since they were adequate and more simple than the non-linear models. For the determination of the parameters only the statistically significant variables were considered while for the best model selection the F-test were applied at 95% confidence level. In this way for the prediction of gasoline components, functions as below have been proposed:

$$\text{component } i \text{ (wt\%)} = f_i(\text{feed}) \times z_i(\text{oper})$$

The component i concerns the following gasoline hydrocarbon groups: n-paraffins, i-paraffins, normal olefins, branched olefins, total olefins, aromatics, naphthenes and they are referred as yields on feedstock basis. In addition to gasoline composition, models for the total conversion and coke yield were also developed based on the work of Wollaston et al. [8]. The functions f and g are functions of feed quality (f) and operating conditions (z). The functions of feed quality include the VGO physical properties which, as mentioned above, are easily determined in a refinery. It must be pointed out that each one of gasoline components is not affected by all feedstock physical properties. In the following the short form models for the conversion, aromatics and olefins in gasoline are discussed since they are more interesting for the production of reformulated gasoline.

As far as the total conversion is concerned it was concluded in the present study that it is a strong function of three feed properties: MeABP, SG and BN_2. All other properties do not influence significantly the total conversion (for the range of feedstock properties used in the present study). The following equation was obtained:

$$\text{conversion (wt\%)} = [\text{C/O}^{0.6} \times \text{WHSV}^{0.4} \times \text{DEXP}(-17650/1.987 \times T)] \times [4820.8 + 9.19 \times \text{MeABP} - 11900 \times \text{SG} - 0.2472 \times \text{BN}_2],$$

where MeABP is in °F, BN_2 in ppmw and T in R.

From the above equation it seems that by increasing MeABP the conversion increases but increasing SG the conversion decreases. The MeABP is an indication of the boiling range and types of molecules in the FCC feed [21]. The effect of increasing MeABP on the conversion is related to the increased carbon number of the components present in FCC feedstocks. It has been now accepted that increasing the carbon chain length (carbon atoms in the hydrocarbon) the cracking activity increases. This fact has been related with the statistical number of cracking possibilities in the *n*-alkane molecules and to the increase in the adsorption when increasing the hydrocarbon chain length [14,16,17,21]. The negative effect of SG on the total conversion is related to the amount of aromatics in the FCC feedstock. Aromatics with the same boiling point are more dense than paraffins and then the measure of a higher SG (or API) indicates a more aromatic feed. Although specific gravity by itself shows a weak correlation with conversion [7] its combination with other properties can give satisfactory predictions of total conversion. Moreover, SG is the easiest parameter to measure on any feed. The same negative effect for total conversion is observed when the BN_2 increases in a feedstock. The participation of nitrogen compounds in the actual FCC cracking process is limited but the negative effect of basic nitrogen compounds as reversible poisons for the FCC catalysts is well known [7,22,25–28]. Basic nitrogen compounds are strongly adsorbed on catalyst acid sites and so they deactivate the catalyst and decrease the conversion of FCC process. The degree of catalyst deactivation depends on the degree of poisoning of the available catalyst acids sites which also depends on the proton affinity of nitrogen compounds [26,27]. The model predicts a decrease of about 1 wt% conversion for an increase of about 200–300 ppmw in basic nitrogen. This result is in agreement with literature results [21,28].

In contrast to the effect of feedstock quality on gasoline, coke yield is influenced strongly by feedstock RI. Increasing the aromatics of feedstock the coke yield increases. The aromatics are the main coke precursors and their condensation reaction leads to more coke while dry gases are also produced [15,20,22]. Although the actual effect of FCC feed sulfur content on conversion was found above negligible, sulfur content seems to increase the coke production. Probably sulfur has a deactivation mechanism that involves blockage of the active site than a chemical reaction [21]. Generally, sulfur impurities are associated with heavier feedstocks. It is reported in [22] that a portion (3–28%) of the sulfur compounds initially present in the feedstock is deposited in coke. These compounds are the uncracked thiophenic sulfur compounds with two or three rings. The fraction of sulfur ending up in coke is related to both sulfur type and conradson carbon in feed as well as coke yield. Thus, always the sulfur in feed has a positive effect on the coke yield. The results of the present study for the effects of the feedstock properties predicted by the models on each of gasoline hydrocarbons and for conversion and the coke yield are in agreement with results from [6–8].

The gasoline aromatics are influenced by MeABP, RI, SG, BN_2 and sulfur content as follows:

$$\text{gasoline aromatics (wt\% on feed)} = [-7.45 - 0.0435 \times \text{WHSV} + 0.0171 \times T] \times [11.585 - 0.000557 \times \text{MeABP} + 7.799 \times \text{SG} - 0.0829 \times S - 11.551 \times \text{RI} + 0.000399 \times \text{BN}_2],$$

where MeABP is in °F, BN_2 in ppmw, S in wt%, T in R and RI at 70°C.

From the above equation it is clear that although the MeABP has strong positive influence on the total conversion (proportionality factor 9.18) this influence is relatively small for the aromatics and also the increasing of MeABP gives lower aromatic yield. This result concludes that feedstocks with higher MeABP are suitable for the production of reformulate gasoline since they give high conversion without increase in the aromatics content of gasoline. For example feedstock 362 (Figs. 3 and 4) can be a suitable FCC feedstock which can control the gasoline selectivity along with the low aromatics production. Although RI seems to increase the aromatics (Fig. 4) it reduces much more the gasoline yield and so the overall increase of RI reduces the aromatics yield. In contrast SG (which along with RI can determine the aromatic content of FCC feedstock) influences positively the production of aromatics. The effect of sulfur on the aromatics is negative since sulfur is related to the production of coke and the lost of catalyst activity. BN_2 causes an increase in the aromatics yield although the basic components have a negative effect on total conversion. However, basic components influence the hydrogen transfer reactions which lead from the olefins to aromatics [24,25]. These results show that for less aromatics in gasoline the BN_2 content of FCC feedstock must be minimum.

The derived equation for the total olefins in the gasoline (wt% on feed basis) is

$$\text{gasoline olefins (wt\% on feed)} = [-5.352 - 0.1826 \times \text{C/O} - 0.0506 \times \text{WHSV} + 0.0165 \times T] \times [0.00161 \times \text{MeABP} - 4.1764 \times \text{SG} + 0.0824 \times S - 0.00038 \times \text{BN}_2 + 0.2868 \times K_\text{w}],$$

where MeABP is in °F, BN_2 in ppmw, S in wt% and T in R, K_w is the Watson factor.

The total olefins yield in gasoline is affected by the MeABP and mainly by the K_w of FCC feedstocks. K_w in an index of paraffinicity and thus increasing the paraffins in the FCC feedstock more olefins are produced from the primary cracking. The effect of increasing the MeABP is similar to that of total conversion according to the explanations given above. The increase of SG in FCC feedstock implies an increase in aromatic content which cannot lead to more olefins. The model predictions of the effect of BN_2 on gasoline olefins is opposite (and more severe) with that on gasoline aromatics. The basic nitrogen components affect the gasoline olefins which are intermediates in the entire reaction network and gives more paraffins and aromatics [26,27].

Using the short form equations developed in this study, satisfactory results were obtained for all the gasoline components. The models were validated with many experiments in the pilot unit using two feedstocks (3132, 3142) under a range of operating conditions. In Figs. 8 and 9 the predicted vs. experimental results are quoted for two main gasoline hydrocarbon

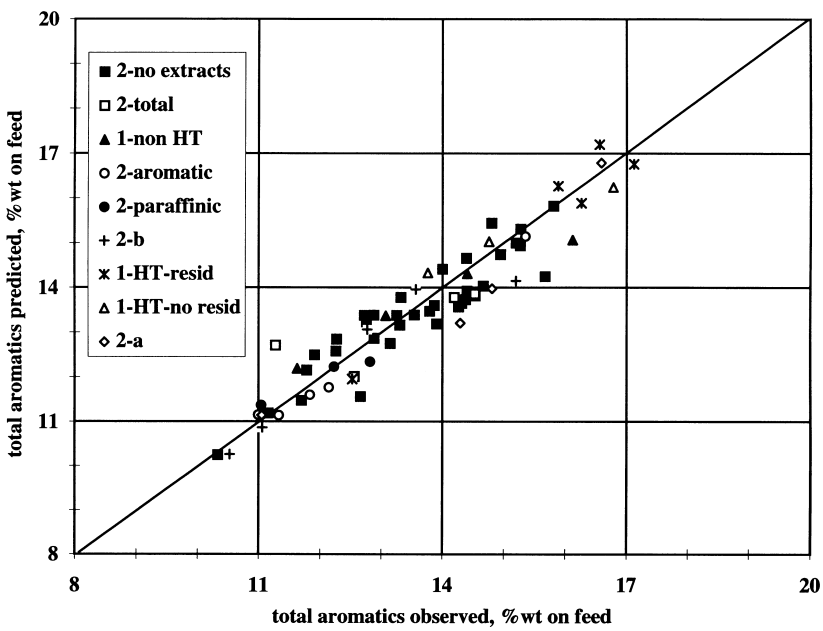

Fig. 8. Model predictions on gasoline aromatics.

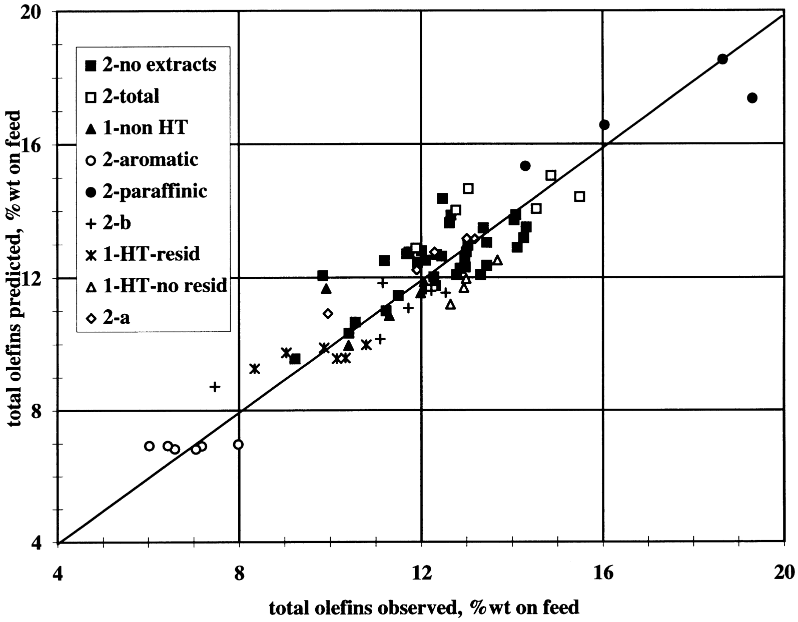

Fig. 9. Model predictions on gasoline total olefins.

groups (aromatics and total olefins). The results are satisfactory for all gasoline components: aromatics, normal olefins, branched olefins, isoparaffins, normal paraffins, saturated naphthenes and unsaturated naphthenes. In general the relative standard deviations of model predictions are below 12%.

4. Conclusions

The FCC pilot plant of CPERI was used for the investigation of the effect of FCC feedstock properties on gasoline composition, on gasoline and coke yield and on the feed conversion. The gasoline composition is referred to total hydrocarbon groups: normal paraffins, isoparaffins, normal olefins, branched olefins, diolefins, aromatics and naphthenes. In this work special emphasis was given for the aromatics and the olefins in gasoline since these compounds are interesting for environmental reasons. It was concluded that feedstock quality affects strongly the gasoline yield and composition. Thus, resid in VGO, aromatic feedstocks and non-hydrotreated FCC feedstock produce lower gasoline than paraffinic or hydrotreated FCC feed. The aromatics in the gasoline are favored at high conversions. Moreover, the addition of resid causes an increase in gasoline aromatics yield while high aromatics are also produced with aromatic and non-hydrotreated feedstocks. Normal, branched and diolefins in gasoline were also studied as a function of feedstock quality. It was concluded that the aromatic feeds give the lowest olefins while paraffinic feedstock the highest. Hydrogenation of VGO increases the production of olefins in the FCC gasoline. Gasoline olefins in contrast to gasoline aromatics start to decompose at high conversion levels.

In addition to the qualitative analysis, an attempt was also carried out for a quantitative prediction of gasoline composition (and coke yield and conversion as well) as a function of feedstock properties. Taking into account the FCC feedstock properties which are easily measured in a refinery, short form models were developed for the gasoline composition. It was proved that the specific gravity, the refractive index, the basic nitrogen, the mean average boiling point and the Watson factor are the parameters which influence the gasoline composition. Each one of these parameters has a different effect on the gasoline compounds. For example feed conversion is affected by

MeABP, SG and BN_2. The functions proposed were finally validated with experiments using two additional feedstocks in the pilot unit under a range of experimental conditions. The predictions of the model were satisfactory for all gasoline hydrocarbon groups.

Acknowledgements

The General Secretariat of Research and Technology Hellas is gratefully acknowledged for providing financial support. The Greek refineries HAR and MOH are also acknowledged for the supply of feedstocks.

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