

INTERCRITERIA AND REGRESSION ANALYSES TO
INVESTIGATE THE DEPENDENCE OF CATALYTIC
CRACKING FEED CONVERSION AND PRODUCT
SELECTIVITY ON FEED CHARACTERIZATION

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Abstract

The feed quality is the single factor that most affects the performance of fluid catalytic cracking (FCC) unit. It can be characterized by mass spectrometry, saturates, aromatics, polars (resins) (SAP analysis), and empirical methods on the basis of measurement of physical and chemical properties of FCC feed. This research explores the capability of intercriteria and regression analyses to investigate the relations between the conversion level and product selectivity obtained in a laboratory microactivity (MAT) unit during catalytic cracking of feeds whose conversion varies between 50 and 85 wt.% with the feed parameters determined by the mass spectrometry, SAP analysis, and the empirical methods. The strongest relations are identified and discussed.

Key words: catalytic cracking, mass spectrometry, empirical parameters, ICrA, regression, empirical modelling

Introduction. The fluid catalytic cracking (FCC) contributes to about 50% of the produced automotive gasoline that is used to drive the internal combustion engines of gasoline vehicles. About 600 FCC units worldwide process approximately 14 million barrels per day of blends of atmospheric and vacuum gas oils as the major components, atmospheric residues, coker and visbreaking gas oils, hydrocracking residues, hydrotreated gas oils and residues, furfural extracts,

demetalised oil (DMO), whose conversion, at which the gasoline yield is maximal, can vary between 50 and 85% [1]. Several studies have identified that the quality of FCC feed is the single factor that most influences the FCC unit performance [1–4]. While the activity of catalyst can bring about 10% conversion increase in a laboratory FCC unit at the same operating conditions [5, 6], the reaction temperature can provide also about 10% conversion increment [7], and the feedstock quality itself can ensure 35% conversion enhancement [1]. This can explain why so many studies have been devoted to investigate the effect of feedstock quality on the FCC unit performance [1–4, 7–10]. Different analytical techniques such as mass spectrometry [2], saturates, aromatics, resins (polars) (SAR(P)) analysis [4], and empirical methods like n-d-M (ASTM D3238), paraffinic (P), naphthenic (N) and aromatic (A) Portions (API Procedure 2B4.1 and 3) [11], aromatic carbon and hydrogen contents (Total, and Conoco Philips correlations) [12, 13], Kw-characterizing factor [14], and others have been correlated to the catalytic cracking conversion and product yields. However, to the best of the author's knowledge no comparative investigation between the capability of different methods for FCC feed characterization to predict the conversion at which the gasoline yield is maximal, and product selectivities has been made so far. That was the reason for the author of this research to perform this study using intercriteria and regression analysis availing the mass spectrometric data of very different nine gas oils, SAP analysis of the nine gas oils, their bulk properties employed to calculate the empirical feed parameters by the n-d-M method, PNA method [11], and the contents of aromatic carbon (C_A) and hydrogen (H) by the Total method [12], and utilizing the FCC experimental data reported by FISHER [2].

The aim of this examination is to identify which feed parameters determined by the methods described above best correlates with the conversion at which the gasoline yield is maximal, and product selectivities at this point.

Materials and methods. The n-d-M method is a correlation that calculates the distribution of carbon in paraffins (C_P), naphthenes (C_N) and aromatics (C_A) of VGOs by using the following equations:

$$\begin{aligned} (1) \quad C_A &= av + \frac{3660}{MW} \\ (2) \quad C_N &= C_R - C_A \\ (3) \quad C_N + C_P + C_A &= 100. \end{aligned}$$

Equations (1)–(3) include parameters a , v , w , and C_R , which are estimated by equations (4)–(7). Equations (4)–(7) are summarized below:

$$\begin{aligned} (4) \quad v &= 2.51 (RI - 1.475) - (d - 0.851) \\ a &= 430 \quad \text{if } v > 0 \\ a &= 670 \quad \text{if } v < 0 \end{aligned}$$

$$(5) \quad w = (d - 0.851) - 1.11(RI - 1.475) \\ \text{if } w > 0$$

$$(6) \quad C_R = 820w - 3S + \frac{10000}{MW} \\ \text{if } w < 0$$

$$(7) \quad C_R = 1440w - 3s + \frac{10600}{MW}.$$

The API Procedure for predicting the composition of heavy petroleum fractions with $MW > 200$ g/mol presented in Equations (8)–(10) was used in this study:

$$(8) \quad P = 193.82 + 0.74855m - 19.966CH$$

$$(9) \quad N = -42.260 - 0.777m + 10.7625CH$$

$$(10) \quad A = 100 - P - N.$$

Parameters m and CH of the investigated VGOs were calculated using the following formulas:

$$(11) \quad m = MW(RI - 1.4750)$$

$$(12) \quad CH = \frac{C}{H}.$$

The Total method uses the values of specific gravity, molecular weight, sulphur content, viscosity at 98.9°C , ASTM D1160 distillation data, and equations (13)–(16) for estimation of the characteristic parameters of the vacuum gas oils (VGOs) under study.

$$(13) \quad C_A = -814.136 + 635.192RI - 129.266SG + 0.013MW \\ - 0.340S - 6.872 \ln(VIS)$$

$$(14) \quad H = 52.825 - 14.260RI - 21.329SG - 0.0024MW \\ - 0.052S + 0.757 \ln(VIS)$$

$$(15) \quad RI = 1 + 0.8447SG^{1.2056}(T + 273.16)^{-0.0557}MW^{-0.0044}$$

$$(16) \quad T = \frac{(T_{10} + T_{30} + T_{50} + T_{70} + T_{90})}{5}.$$

K_w -characterizing factor of studied VGOs is calculated by using equation (17).

$$(17) \quad K_w = \frac{\sqrt[3]{1.8 \times (T_{50}(^\circ\text{C}) + 273.15)}}{\text{specific gravity}}.$$

The assessment of relationships between the FCC feed characteristics and the conversion and product selectivities at the point of maximum gasoline yield

was performed by using intercriteria analysis (ICrA) [16]. Details of the theory and application of ICrA are presented in [17]. The ICrA approach calculates two intuitionistic fuzzy functions: μ and ν whose values define the degree of the relationship between the criteria. For $\mu = 0.75 \div 1.00$ and $\nu = 0 \div 0.25$, a region of statistically meaningful positive consonance is determined, while at $\mu = 0 \div 0.25$ and $\nu = 0.75 \div 1.00$, an area of statistically meaningful negative consonance is derived. All other cases are considered to be dissonance. Before ICrA evaluation, all variables are normalized using the normalization formula (Equation (18)).

$$(18) \quad X_{\text{new}} = \frac{X - X_{\min}}{X_{\max} - X_{\min}}.$$

The data of cracking experiments along with mass spectrometric data, and bulk properties of the nine vacuum gas oils under study are detailed in [2]. The FCC conversion is defined as sum of yields of products: dry gas (C_2 fraction), LPG (C_3C_4 fraction), cracked naphtha (CN, fraction $C_5 - 215^\circ C$) and coke. The bottoms cracking is defined as $\frac{\text{Yield of fr.215-343}^\circ C}{(\text{Yield of fr.215-343}^\circ C + \text{yield of fr. } > 343^\circ C)} \times 100$.

Gasoline precursors (Gasoline prec.) are defined as the sum of normal and iso-paraffins, cycloparaffins, and mononuclear aromatic hydrocarbons. They have been determined by mass spectroscopy.

The methodology applied in this study is summarized in Fig. 1.

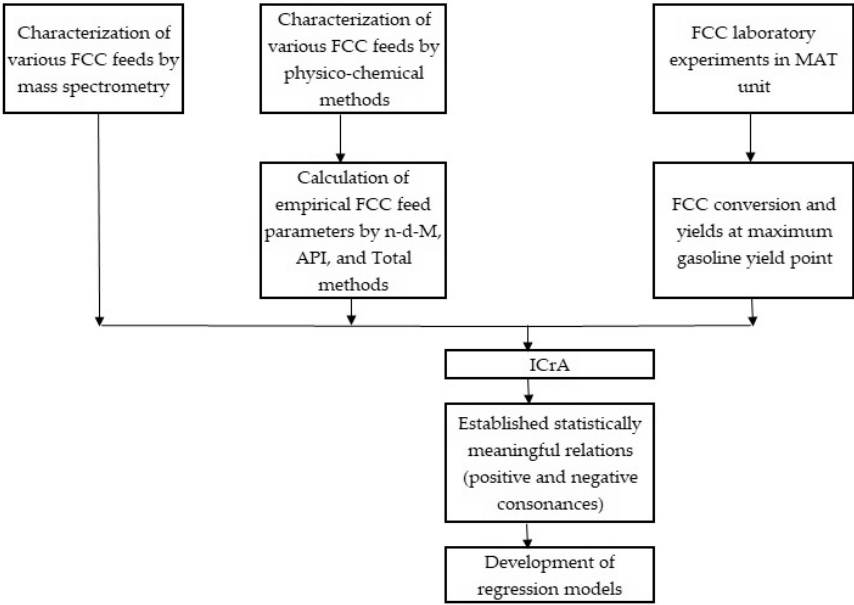


Fig. 1. Methodology of the investigation

T a b l e 1

Results from characterization of the nine studied gas oils by mass spectrometry, SAP analysis, and empirical methods together with FCC experimental data

Type of analysis	Number of tested gas oils	1	2	3	4	5	6	7	8	9
Mass spectrometry	Gasoline precursors, wt. %	85	82.5	77	75.8	65.8	65.4	61.9	49.9	42.4
Mass spectrometry	Diaromatics, wt. %	7.1	8.4	10.6	10.2	14	14.6	16	16.6	19.6
Mass spectrometry	Triaromatics, wt. %	2.8	3.5	4.5	4.6	5.9	6.1	5.3	15.1	10
Mass spectrometry	Tetra-aromatics, wt. %	2.2	2.2	2.7	4.5	4.3	5	3	8.2	9.2
Mass spectrometry	Aromatic sulphur, wt. %	1.7	1.1	1.4	1.9	7.1	6.7	7.6	7.3	9.5
SAP analysis	Saturates, wt. %	73.7	71.7	61.9	62.9	48.2	50	47.4	40.3	25.3
SAP analysis	Aromatics, wt. %	25.1	26	34.3	34.1	48.9	47.8	46.4	56.8	65.4
SAP analysis	Polars, wt. %	1.2	2.2	3.9	3	3	2.2	6.2	2.9	9.3
Empirical methods	K_w	12.53	12.09	12.06	11.95	11.55	11.56	11.11	10.93	10.72
n-d-M	C_P , %	66.6	60.9	62.2	63.9	56.9	54.2	32.5	46.7	
n-d-M	C_N , %	23	26.8	21.3	17.3	21.4	23.9	15.4	7.4	
n-d-M	C_A , %	11.4	12.3	16.5	18.8	21.7	21.9	52.1	45.9	
PNA	P , %		63	59.6	64.1	47.1	47.1	36	24.5	17.2
PNA	N , %		26.7	27.6	24.6	34.1	34.1	38.2	39.4	36.2
PNA	A , %		10.3	12.8	11.3	18.8	18.8	25.8	36.1	46.6
Total	C_A , wt. %	11	13.3	17.3	15.6	20.8	21.1	29.6	45.6	38.8
Total	H , wt. %	13.2	13.2	12.3	12.7	11.5	11.6	10.9	10.1	9.6
FCC experimental data	Conversion, wt. %	85	82.2	78	76	69	72	63	50	50
FCC experimental data	Δ Coke, %	0.84	1.06	1.21	1.13	1.3	1.24	1.63	1.63	2.64
FCC experimental data	C_2 selectivity, %	1.76	1.70	2.44	2.24	3.33	3.61	3.65	4.00	7.60
FCC experimental data	C_3C_4 selectivity, %	22.71	19.46	21.28	19.74	21.16	21.11	19.21	21.20	19.00
FCC experimental data	Gasoline selectivity, %	71.76	73.36	70.13	72.37	69.86	69.44	60.32	62.00	56.00
FCC experimental data	Bottoms cracking, %	84.0	75.8	75.0	75.0	67.7	74.3	70.3	56.0	60.0
FCC experimental data	Coke selectivity, %	2.82	5.23	7.05	7.89	14.49	10.00	17.46	44.00	40.00

Results and discussion. Data of feed characterization by mass spectroscopy, SAP analysis, and the empirical methods explained before along with FCC experimental data are summarized in Table 1. It is evident from this data that the conversion varies between 50 and 85 wt.%, that is it embraces the whole range of FCC conversions that can be obtained from any FCC feed [1]. One can see from the data in Table 1 that the API method cannot be applied to characterize VGO 1, while the n-d-M method cannot be availed to characterize VGO 9.

Table 2 summarizes the results from ICrA evaluation of the FCC feed characterization data and conversion and product selectivities at maximum gasoline yield in terms of calculated μ -, and ν -values. The data in Table 2 indicates that the strongest consonances with conversion exhibit the feed parameters Gasoline prec., Saturates, K_w -characterizing factor, and A (Aromatic portions (API method) ($\mu = 0.96$, $\nu = 0.04$). Δ Coke has the strongest consonances with H ($\mu = 0.00$, $\nu = 0.93$), K_w and P ($\mu = 0.04$, $\nu = 0.89$), followed by Diaro (diaromatic hydrocarbons) ($\mu = 0.93$, $\nu = 0.04$). The selectivity towards production of dry gas (C_2 sel.) has the strongest positive consonances with the feed parameters Diaro, A , and C_A^{Total} ($\mu = 0.96$, $\nu = 0.04$), and the strongest negative consonance with H ($\mu = 0.04$, $\nu = 0.93$). Interestingly the selectivity of propane-propylene-butane-butylene (C_3C_4) fraction has dissonance with all studied feed parameters. The gasoline selectivity (CN sel.) demonstrates the strongest negative consonance with the feed characterizing parameter A ($\mu = 0.04$, $\nu = 0.93$). The bottoms cracking displays equally negative consonances with Diaro, Triaro (triaromatic hydrocarbons), A , and C_A^{Total} ($\mu = 0.07$, $\nu = 0.89$). The coke selectivity (Coke sel.) has the strongest negative consonances with the gasoline precursors and Saturates ($\mu = 0.04$, $\nu = 0.96$), and K_w ($\mu = 0.00$, $\nu = 0.96$).

This comparative investigation shows that all relations between FCC conversion and product selectivity, and feed characterizing parameters obtained by using the sophisticated mass spectroscopy can be derived by employment of easy accessible and less expensive routine laboratory analysis with the help of the empirical methods (Equations (1)–(17)).

Having in mind that the conversion at maximum gasoline yield is the best descriptor of quality of a FCC feed the gasoline precursors (mass spectrometry), (saturates, aromatics, polars) SAP analysis, K_w -characterizing parameter, and the Total empirical parameters C_A and H were regressed against the conversion. The worst model was obtained when SAP analysis data were used ($R = 0.955$, st. error = 4.8 %). The other regression models are given in Equations (19)–(21) presented below.

$$(19) \quad \text{FCC conv. (wt.\%)} = 10.533 + 0.8757 \times \text{Gasoline prec.}$$

$$R = 0.982, \quad \text{st. error} = 2.56\%$$

$$(20) \quad \text{FCC conv. (wt.\%)} = -170.938 + 20.7045 \times K_w$$

$$R = 0.969, \quad \text{st. error} = 3.37\%$$

T a b l e 2

μ - and ν -values from ICrA evaluation of the FCC feed characterization data and conversion and product selectivities at maximum gasoline yield

m	Gasoline prec.	Diaro	Triaro	Tetra-aro	Aromatic sulphur	Saturates	Aromatics	Polars	K_w	C_P	C_N	C_A^{ndM}	P	N	A	C_A^{Total}	H
Conversion	0.96	0.07	0.11	0.18	0.11	0.96	0.11	0.29	0.96	0.82	0.79	0.07	0.86	0.11	0.04	0.07	0.93
Δ Coke	0.07	0.93	0.82	0.71	0.86	0.00	0.89	0.68	0.04	0.11	0.21	0.89	0.04	0.82	0.93	0.89	0.00
C_2 sel.	0.07	0.96	0.86	0.79	0.86	0.07	0.86	0.61	0.07	0.14	0.21	0.89	0.04	0.86	0.96	0.96	0.04
C_3C_4 sel.	0.61	0.43	0.46	0.46	0.46	0.54	0.54	0.36	0.57	0.68	0.50	0.36	0.57	0.46	0.43	0.46	0.54
CN sel.	0.86	0.11	0.21	0.25	0.14	0.86	0.21	0.32	0.82	0.86	0.68	0.11	0.89	0.14	0.04	0.07	0.93
Bottoms cracking	0.89	0.07	0.07	0.14	0.14	0.93	0.04	0.29	0.89	0.79	0.71	0.11	0.82	0.11	0.07	0.07	0.89
Coke sel.	0.04	0.93	0.89	0.79	0.89	0.04	0.89	0.64	0.00	0.18	0.18	0.93	0.11	0.86	0.89	0.93	0.07
n	Gasoline prec.	Diaro	Triaro	Tetra-aro	Aromatic sulphur	Saturates	Aromatics	Polars	K_w	C_P	C_N	C_A^{ndM}	P	N	A	C_A^{Total}	H
Conversion	0.04	0.93	0.89	0.79	0.89	0.04	0.89	0.64	0.00	0.18	0.18	0.93	0.07	0.82	0.89	0.93	0.04
Δ Coke	0.89	0.04	0.14	0.21	0.11	0.96	0.07	0.21	0.89	0.86	0.71	0.07	0.89	0.11	0.00	0.04	0.93
C_2 sel.	0.93	0.04	0.14	0.18	0.14	0.93	0.14	0.32	0.89	0.86	0.75	0.11	0.93	0.11	0.00	0.04	0.93
C_3C_4 sel.	0.39	0.57	0.54	0.50	0.54	0.46	0.46	0.57	0.39	0.32	0.46	0.64	0.39	0.50	0.54	0.57	0.46
CN sel.	0.14	0.89	0.79	0.71	0.86	0.14	0.79	0.61	0.14	0.14	0.29	0.89	0.07	0.82	0.93	0.89	0.11
Bottoms cracking	0.07	0.89	0.89	0.79	0.82	0.04	0.93	0.61	0.04	0.18	0.21	0.86	0.11	0.82	0.86	0.89	0.04
Coke sel.	0.96	0.07	0.11	0.18	0.11	0.96	0.11	0.29	0.96	0.82	0.79	0.07	0.86	0.11	0.07	0.07	0.93

$$(21) \quad \text{FCC conv. (wt.\%)} = -0.36441 \times C_A + 6.6859 \times H$$

$$R = 0.993, \quad \text{st. error} = 1.80$$

The performed regression analysis indicates that the FCC conversion is best modelled when the empirical parameters aromatic carbon (C_A) and hydrogen (H) contents are employed. They can be easily obtained from the routine laboratory analyses which are daily performed in any petroleum refinery.

Conclusions. The combination of intercriteria and regression analyses enables the identification of feedstock parameters that control the conversion and product selectivity in the catalytic cracking process. It was found that by using ICra the same relations between feed characteristics determined by availing costly mass spectrometry and those derived by empirical parameters calculated on the basis of cheap routine laboratory analyses of the FCC feed and conversion, and product selectivity are established. The most accurate regression model to predict the FCC conversion is obtained when the empirical parameters aromatic carbon (C_A) and hydrogen (H) contents are utilized.

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