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Comparison of correlations to predict hydrotreating product properties during hydrotreating of heavy oils

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ABSTRACT

Eighteen correlations taken from the literature developed for predicting the properties and other process parameters during hydrotreating of petroleum fractions were tested with experimental information obtained at different conditions (type of feed, reactor and catalyst as well as reaction conditions) from which they were derived. Firstly, the original values of parameters of each correlation were used to reproduce the experimental data, finding that most of them failed to do so. Secondly, the values of all parameters were optimized and predictions notoriously improved, but some correlations still exhibited difficulties. Finally, an attempt to correlate parameters with feedstock properties was made. It was found that the polynomial type showed the best prediction accuracy in general. The exponential equation also showed good prediction capability and good correlation between its parameters and feedstock properties.

1. Introduction

In absence of suitable models based on theoretical fundamentals, the use of correlations is a choice to represent any type of phenomenon, assuming that correlations have theoretical or semi-theoretical underpinning that represents the underlying processes. Sufficient information must be provided to develop the best correlation, which is capable to reproduce with high precision the experimental data. Nonetheless, the equations and parameters are based on a very restricted set of data, thus their applicability is narrowed to the specific experimental conditions and setup, catalyst (if any) and properties of the feedstock from which they were derived, therefore the parameters would require some tuning if they are to represent new situations.

In the past, mainly due to computer capability restrictions, simple correlations were extensively employed for the design of complete industrial plants. Up until now, correlating commercial plant data with some operation parameters is still preferred by engineers, who need a quick tool to make predictions. The effect of reaction conditions on product yields and conversion, calculation of product properties, determination of some process parameters, are among others the most common uses of correlations.

In the case of hydrotreating of petroleum fractions, various attempts have been reported in the literature to correlate levels of impurities removal, e.g. hydrodesulfurization (HDS), with feed properties, process variables, etc. Tsamatsoulis et al. [1] published one of the first efforts to determine correlations between feed properties and hydrotreating process behavior. Their work consisted on developing equations to correlate HDS, hydrocracking, asphaltenic fraction desulfurization, non-asphaltenic fraction desulfurization, and hydrogen consumption with properties of an atmospheric residue of the Greek Thasos crude. The density and carbon residue were measured throughout the process and used to calculate API gravity and Conradson carbon residue (CCR), which in turn were correlated with desulfurization and asphaltene cracking. The authors derived polynomial equations with 4 fitting parameters to explain the relationship between all variables. They concluded that their study, although not generalized, indicated that an extensive desulfurization was followed by a drastic improvement of the feed properties.

Ng [2] provided an experimental database for assessing the applicability of solvent deasphalting (SDA) followed by catalytic cracking to nonconventional residuum upgrading from Athabasca crude oil. The phase behavior measurements were used to derive the equations, which explain the variations of total sulfur, CCR, metals, total nitrogen, and density of the deasphalted oils with asphalt content. In spite of being developed for a residue deasphalting process, the correlations proposed by Ng [2] may be useful for hydrocracking since the asphaltenes concentrate an important amount of heteroatoms such as oxygen, sulfur, nitrogen, vanadium and nickel; and the physical removal or catalytic conversion of asphaltenes results into an oil with less content of impurities than the original feedstock, what dictates a strong connection between the asphaltene content and the level of some

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Table 1
Operating conditions used to develop the correlations reported in the literature.

Reactor	Feedstock	Catalyst or solvent	T (°C)	P (MPa)	LHSV	H_2-to-oil ratio (std ft^3/bbl)	Ref.
TBR	AR 315 °C+ from Thasos crude oil	$CoMo/Al_2O_3$	350–465	5.0	0.16–1.46 (h^{-1})	1200–10500	[1]
CSTR[a]	VR 540 °C+ from Maya crude oil	$NiMo/\gamma$-Al_2O_3	375–415	10.0–15.0	1.4–7.1 (L/h g_{cat})	6000–10000	[3]
CSTR[a]	VR 540 °C+ from Maya crude oil	$NiMo/\gamma$-Al_2O_3	375–415	10.0–15.0	1.4–7.1 (L/h g_{cat})	6000–10000	[4]
TBR	HGO from Athabasca bitumen	$NiMoB/Al_2O_3$	340–420	6.1–10.2	0.5–2.0 (h^{-1})	3300	[7]
SDA and catalytic cracking (microreactivity test reactor) system	VR from Athabasca oils sands bitumen and Lloydminster heavy oil	Catalytic cracking over zeolite/Al_2O_3	510 °C	–	20 (g_{feed}/(h g_{cat}))	–	[2]
		Propane	75	3.21	–	–	
		n-Butane	120	2.86	–	–	
		n-Pentane	160	2.52	–	–	
		n-Heptane	75	0.45	–	–	

AR: atmospheric residue, VR: vacuum residue, HGO: heavy gas oil, TBR: trickle bed reactor, CSTR: continuous stirred tank reactor.
[a] Stirring rate: 2000–3500 rpm.

impurities in the oil. For all cases but density, the author found positive associations between variables showing concave increase at higher asphalt content, i.e. exponential equations. A positive linear relationship for density and asphalt content was also reported.

Trasobares et al. [3] analyzed the association of CCR conversion with feed properties such as asphaltenes content, hydrogen content, H/C atomic ratio, and residue content (350 °C+) in the catalytic hydroprocessing of a Maya residue. They found that CCR was linearly correlated with all the parameters. Gas yield was also found to be linearly dependent on CCR conversion.

Callejas and Martínez [4] analyzed the kinetics of sulfur, nitrogen, nickel and vanadium removal reactions of a residue from Maya crude, which was processed in a hydrotreating unit operated at high temperatures (375–415 °C) and hydrogen pressures (10–15 MPa). The experimental work allowed deriving linear relationships between the percentages of sulfur-removal and metal-removal in the hydrogenation process.

Ho [5] applied partial least squares method on a multivariate n X p matrix denoted by $X = \{x_{ij}\}$, where $n = 13$ was the number of feedstocks and $p = 24$ was the number of descriptors, i.e. physical and chemical properties such as sulfur content, nitrogen content, aromatics content, API gravity and dibenzothiophenes content. He arrived to an overall property–reactivity correlation, which allowed gaining quantitative understanding of feedstock effects on HDS of middle distillates.

Table 2
General form of the correlations reported in the literature.

Correlation ID	General form	Equation No.
SL	$y = a_0 + a_1 x$	(1)
P	$y = a_0 + a_1 x + a_2 x^2 + a_3 x^3$	(2)
MNL1	$y = (a_0 + a_1 T + a_2 x + a_3 P + a_4 x^2)^2 + a_5$	(3)
MNL2	$y = a_0 + a_1 T + a_2 x + a_3 x^2 + a_4 T x$	(4)
E1	$y = a_0 e^{(a_1 x)}$	(5)
E2	$y = a_0 x^{a_1}$	(6)

Ho and Markley [6], seeking for a compact and robust correlation (i.e. the fewest adjustable parameters) which relates the property–reactivity for HDS of pre-hydrotreated distillates, conducted a series of experiments using thirteen feedstocks of different sources and pre-processing histories, each feed was characterized by 10 properties. After sifting through all 10 feed properties and their combinations, they arrived to a linear function which satisfactory describes the reactivity data. Moreover, they concluded that nitrogen content was the most influential parameter.

Ferdous et al. [7] carried out a series of experimental and kinetics studies to optimize the process conditions and to evaluate kinetic parameters for hydrodenitrogenation (HDN) and HDS of heavy gas oil derived from Athabasca bitumen. The regression analysis of experimental data generated polynomial equations

Table 3
Parameter values of the correlations reported in the literature.

Correlation form	T (°C)	P (MPa)	y	a_0	a_1	a_2	a_3	a_4	a_5	x	Eq.
SL	375	10–15	HDNi[a]	5.46	1.35	–	–	–	–	HDS[a]	(7)
SL	400, 415	10–15	HDNi[a]	72.68	0.34	–	–	–	–	HDS[a]	(8)
SL	375	10–15	HDV[a]	14.04	1.64	–	–	–	–	HDS[a]	(9)
SL	400, 415	10–15	HDV[a]	54.8	0.60	–	–	–	–	HDS[a]	(10)
SL	375–415	10–12.5	Asph[b]	−0.393	0.657	–	–	–	–	CCR[b]	(11)
SL	75	3.45	$\rho_{15\,°C}$	0.9318	0.0021	–	–	–	–	Asph[b]	(12)
P	350–465	5–18	API	9.6	2.69e−1	−5.26e−3	4.58e−5	–	–	HDS[a]	(13)
P	350–465	5–18	API	9.6	5.31e−1	−9.33e−3	6.17e−5	–	–	HC[a]	(14)
P	350–465	5–15	CCR[a]	15.2	−1.76e−1	4.08e−3	−3.82e−5	–	–	HDS[a]	(15)
P	350–465	5–15	CCR[a]	15.2	−3.22e−1	5.33e−3	−3.69e−5	–	––	HC[a]	(16)
P	350–465	18.14	RCR[a]	14.1	−1.85e−1	3.97e−3	−3.61e−5	–	–	HDS[a]	(17)
P	350–465	18.14	RCR[a]	14.1	−3.26e−1	4.82e−3	−2.97e−5	–	–	HC[a]	(18)
MNL1	340–420	6.1–10.2	HDN[a]	−11.31069	0.054205	−6.38681	2.21e−3	1.700813	−0.07	LHSV	(19)
MNL2	340–420	6.1–10.2	HDS[a]	78.99496	0.086721	−121.97487	8.89582	0.23395	–	LHSV	(20)
E1	75	3.45	S[b]	3.107	0.0132	–	–	–	–	Asph[b]	(21)
E2	75	3.45	Met[c]	0.0032	2.905	–	–	–	–	Asph[b]	(22)
E2	75	3.45	CCR[b]	0.0815	1.3966	–	–	–	–	Asph[b]	(23)
E2	75	3.45	N[c]	116	0.9795	–	–	–	–	Asph[b]	(24)

Asph: Asphaltenes as insolubles in nC_7.
[a] Values in %.
[b] Values in wt%.
[c] Values in wppm.

Table 4
Properties of different feedstocks.

Properties	Feedstocks					
	A	B	C	D	E	F
Specific gravity 60 °F/60 °F	1.0336	1.0504	1.0053	1.0464	1.0609	0.9284
API gravity	5.40	3.21	9.25	3.73	1.88	20.91
Total sulfur, wt%	5.74	6.21	3.74	4.51	5.08	3.44
Asphaltenes[a], wt%	21.77	25.1	10.18	17.75	25.46	12.4
Nitrogen, wt%	NA[b]	NA[b]	4400	6100	6200	3700
Metals, wppm						
Ni	102.00	119.00	56.20	84.30	130.00	54.70
V	620.00	637.00	297.30	418.30	647.90	298.80
Ni + V	722.00	756.00	353.50	502.60	777.90	353.50
Conradson carbon, wt%	20.80	20.34	14.30	22.59	22.83	11.73
Ramsbottom carbon, wt%	22.18	21.48	13.39	24.98	25.41	10.50

[a] Asphaltenes as insoluble in nC_7.
[b] NA: not available.

with 6 fitting parameters describing the association of total nitrogen and sulfur conversion with temperature, pressure and liquid hourly space velocity (LHSV).

If the correlations described in the literature were used to predict hydrotreating process experimental data from conditions other than those they were derived, they surely would fail to do so, and parameters would need to be re-calculated for broadening their applicability. Thus, the main objective of the present work was to compare the prediction capability of the reported correlations with our experimental data. The values of correlation parameters were optimized to improve predictions.

2. Description of correlations

Eighteen correlations found in the literature were used in the present work for comparison purposes. Table 1 reports the operating conditions, type of feedstock, catalyst and reactor employed to develop such correlations. The general forms of all correlations are shown in Table 2, and the values of their corresponding parameters are presented in Table 3.

The correlations were classified as straight-line, polynomial, multiple non-linear, and exponential. In the following part a brief description of them is mentioned taking as reference the equations given in Tables 2 and 3.

- *Straight-line correlations (SL).* The straight-line correlations reported in the literature have the general form of Eq. (1). Callejas and Martínez [4] developed SL equations that associate the percentage of sulfur-removal with the metal-removal (particularly Ni and V). The dependence with HDS of Ni-removal (HDNi, Eqs. (7) and (8)) and V-removal (HDV, Eqs. (9) and (10)) was found to be linear with correlation coefficients (r) between 0.88 and 0.99. Trasobares et al. [3] developed a linear relationship between asphaltenes content (insolubles in nC_7) and CCR given by Eq. (11) with $r \approx 0.93$. Ng [2] found a linear dependence between density and asphalt content with correlation coefficient of 0.9129 (Eq. (12)).
- *Polynomial correlations (P).* All the polynomials correlating product properties were found to be of degree 3, which have the general form of the Eq. (2). Tsamatsoulis et al. [1] developed polynomial correlations for predicting properties of products such as API gravity, CCR and Ramsbottom carbon residue (RCR) as function of levels of HDS and hydrocracking (HC) in catalytic hydrotreating. These correlations (Eqs. (13)–(18)) are valid for HDS and HC values less than 97–98%.
- *Multiple non-linear correlations (MNL).* The general form of these correlations is given by Eqs. (3) and (4). Ferdous et al. [7] reported two multiple non-linear correlations to predict hydrodenitrogenation (HDN) and HDS from operating conditions such as temperature, pressure and LHSV. The MNL1 for calculating HDN (Eq. (19)) and MNL2 for calculating HDS (Eq. (20)), were reported to have r^2 of 0.97 and 0.93, respectively.
- *Exponential correlations (E).* These correlations have the general form of Eqs. (5) and (6). Ng [2] established various exponential correlations to predict variations of total sulfur, metals (Ni + V), CCR and nitrogen contents in deasphalted oils (DAO) as function of the asphalt content (defined by the author as the sum of resins and asphaltenes). The correlation for sulfur (Eq. (21)) shows a moderate r^2 value (0.6328); while the Eqs. (22)–(24) for metals, CCR and nitrogen have r^2 between 0.8819 and 0.9389.

3. Results and discussion

3.1. Experimental data

The experimental data used in this work were obtained from the hydrotreating of six different feedstocks, which were named as follows: A (atmospheric residue 343 °C+ from 13°API crude oil), B (atmospheric residue 390 °C+ from 13°API crude oil), C (atmospheric residue 326 °C+ from a blend of various crude oils), D (vacuum residue from a blend of various crude oils), E (vacuum residue 538 °C+ from Maya crude oil), and F (Maya crude oil). The properties of such feedstocks are given in Table 4. These properties cover a wide range of API gravity (from 3.2 to 21), total sulfur (from 3.4 to 6.2 wt%), and Ni + V (from 353 to 778 wppm). All the feeds were hydrotreated using the catalysts shown in Table 5. Table 6 summarizes the operating conditions, catalytic system, and reactors configuration at which each feedstock was hydrotreated.

3.2. Predictions using literature values of parameters

The correlations given by Eqs. (7)–(24) were used to predict hydrotreating product properties such as API gravity, CCR, RCR, asphaltenes, metals and sulfur contents. They have as independent

Table 5
Catalysts used in hydrotreating experiments.

Catalyst ID	Type
I	$NiMo/Al_2O_3$ for HDM
II	$NiMo/Al_2O_3$ for HDM/HDS
III	$NiMo/Al_2O_3$ for HDS
IV	Equilibrium H-Oil
V	Fresh H-Oil
VI	Activated carbon–Fe
VII	$NiMo/\gamma\text{-}Al_2O_3$
VIII	$NiMo/\gamma\text{-}Al_2O_3$–$TiO_2$ for HDM
IX	$CoMo/\gamma\text{-}Al_2O_3$–$TiO_2$ for HDS

Table 6
Operation conditions, feedstocks and type of catalytic system of this work.

Feedstock ID	Reactors[a] R_1/R_2	Catalysts loaded to reactors (R_1/R_2)[b]	T (°C)	P, MPa	Overall (LHSV h^{-1})	H_2/oil scf/bbl
A	TBR/TBR	(I–II/II–III)	350–380	9.8	0.25	5000
B	EBR/EBR TBR/EBR EBR/TBR	(IV–V/IV–V)	380	9.8	0.25	5000
C	EBR/EBR	(IV–V/IV–V)	400	6.9–14.7	0.10–0.20	3000
D	TBR/TBR	(VI/VI)	400–415	18.1	0.15	7500
E	CSTR/–	(VII)/– (VI)/–	400–435 400–421	9.8	0.12	15000
F	TBR/TBR	(VIII/IX)	360–400	5.3–6.9	0.25–1.25	5000

[a] R_1 and R_2 denote reactors 1 and 2, respectively.
[b] The roman numbers between parenthesis refer to ID of catalyst reported in Table 5.

variables some product properties as well as some operating conditions. Most of the equations are relatively simple such as linear, polynomials and exponential functions that rely on one property. The more complex correlations are multiple non-linear equations that rely on two or more operating conditions.

Each correlation was initially tested with experimental hydrotreating results and properties of each feedstock and then with data of all feeds using the parameter values reported in the literature. This analysis gave a total of 89 different plots corresponding to the Eqs. (25)–(113) summarized in Table 7. As

Table 7
Correlations obtained with the feedstocks available.

Equation number	Feedstock	r^2	Equation number	Feedstock	r^2	Equation number	Feedstock	r^2
(25)[a]	A	0.5566	(55)[b]	E	0.8984	(85)[c]	B	0.3394
(26)[a]	B	0.365	(56)[b]	F	0.8287	(86)[c]	C	0.0456
(27)[a]	F	0.8409	(57)[b]	(A–F)	0.4313	(87)[c]	D	0.8729
(28)[a]	(A,B,F)	0.4154	(58)[d]	A	0.9380	(88)[c]	E	0.4689
(29)[a]	C	0.8798	(59)[d]	B	0.4608	(89)[c]	F	0.9101
(30)[a]	D	0.2563	(60)[d]	C	0.2147	(90)[c]	(A–F)	0.4337
(31)[a]	E	0.8254	(61)[d]	D	0.8072	(91)[e]	B	0.755
(32)[a]	(C,D,E)	0.2776	(62)[d]	(A–D)	0.1368	(92)[e]	C	0.6648
(33)[f]	A	0.6685	(63)[g]	C	0.6373	(93)[e]	D	0.2437
(34)[f]	B	0.2329	(64)[g]	D	0.6938	(94)[e]	E	0.6125
(35)[f]	F	0.7975	(65)[g]	E	0.9078	(95)[e]	F	0.7467
(36)[f]	(A,B,F)	0.1422	(66)[g]	F	0.8209	(96)[e]	(A–F)	0.2477
(37)[f]	C	0.8802	(67)[g]	(C–F)	0.6881	(97)[h]	A	0.7449
(38)[f]	D	0.903	(68)[i]	C	0.1839	(98)[h]	B	0.8703
(39)[f]	E	0.7322	(69)[i]	D	0.7352	(99)[h]	C	0.7064
(40)[f]	(C,D,E)	0.1459	(70)[i]	(C,D)	0.3853	(100)[h]	D	0.315
(41)[j]	C	0.3252	(71)[k]	C	0.6251	(101)[h]	E	0.9351
(42)[j]	D	0.2139	(72)[k]	D	0.6124	(102)[h]	F	0.8718
(43)[j]	E	0.0018	(73)[k]	E	0.9168	(103)[h]	(A–F)	0.8228
(44)[j]	(C,D,E)	0.0002	(74)[k]	F	0.824	(104)[l]	C	0.8809
(45)[m]	B	0.8505	(75)[k]	(C,E,F)	0.8843	(105)[l]	D	0.2209
(46)[m]	C	0.6626	(76)[n]	C	0.1887	(106)[l]	E	0.8968
(47)[m]	D	0.2765	(77)[n]	D	0.732	(107)[l]	F	0.8661
(48)[m]	E	0.8596	(78)[n]	(C,D)	0.3656	(108)[l]	(C–F)	0.8092
(49)[m]	F	0.7988	(79)[o]	C	0.8755	(109)[p]	C	0.7494
(50)[m]	(B–F)	0.5056	(80)[o]	D	0.0442	(110)[p]	D	0.0381
(51)[b]	A	0.9228	(81)[o]	E	0.5268	(111)[p]	E	0.8457
(52)[b]	B	0.7323	(82)[o]	F	0.8896	(112)[p]	F	0.8416
(53)[b]	C	0.9171	(83)[o]	(C–F)	0.3300	(113)[p]	(C–F)	0.3973
(54)[b]	D	0.8657	(84)[c]	A	0.9787			

[a] General form of Eq. (1) in Table 2: $HDN_i = f(HDS)$.
[b] General form of Eq. (2) in Table 2: $API = f(HDS)$.
[c] General form of Eq. (4) in Table 2: $HDS = f(T,LHSV)$.
[d] General form of Eq. (2) in Table 2: $API = f(HC)$.
[e] General form of Eq. (5) in Table 2: $S = f(Asph)$.
[f] General form of Eq. (1) in Table 2: $HDV = f(HDS)$.
[g] General form of Eq. (2) in Table 2: $CCR = f(HDS)$.
[h] General form of Eq. (6) in Table 2: $Met = f(Asph)$.
[i] General form of Eq. (2) in Table 2: $CCR = f(HC)$.
[j] General form of Eq. (1) in Table 2: $Asph = f(CCR)$.
[k] General form of Eq. (2) in Table 2: $RCR = f(HDS)$.
[l] General form of Eq. (6) in Table 2: $CCR = f(Asph)$.
[m] General form of Eq. (1) in Table 2: $\rho_{15\,°C} = f(Asph)$.
[n] General form of Eq. (2) in Table 2: $RCR = f(HC)$.
[o] General form of Eq. (3) in Table 2: $HDN = f(T,LHSV,P)$.
[p] General form of Eq. (6) in Table 2: $N = f(Asph)$.

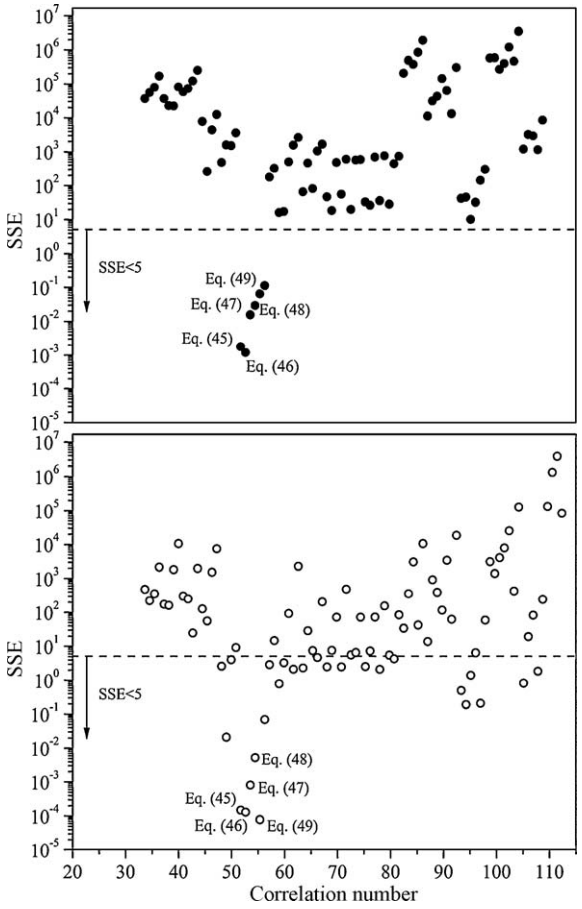

Fig. 1. SSE calculated with each correlation: (●) using values of parameters reported in literature and (○) using values of optimized parameters.

mentioned before, the reported parameters values are valid only for the feedstocks and conditions from which they were derived (Table 3); that is why for most of the cases the values of r^2 are low when using our hydrotreating experimental data. Some of the correlations require certain information that is not available for all the feedstocks, so that not all of them were used to evaluate all the feedstocks. In the particular case of exponential function the asphaltenes content as insolubles in nC_7 was used as the independent variable instead of the asphalt content.

To measure the accuracy of the predictions the Sum of Square Errors (SSE) between experimental and calculated values was used. The SSE values obtained for all correlations are shown in Fig. 1. Most of the correlations exhibited values of SSE higher than 10.

Parity plots of experimental versus calculated product properties were also obtained. It was found that other five correlations (Eqs. (38), (51), (58), (84), and (104)), of different type, adequately reproduce the results of some feedstocks.

It was also observed that some correlations gave acceptable predictions for some feedstocks, while for others the predictions were poor. For instance Eq. (14) produced a more acceptable prediction of API gravity of hydrotreated products obtained with feedstock A than for products obtained when hydrotreating feedstock C, as can be clearly observed in Fig. 2.

The best distribution of the data around the parity line when all the feedstocks were used to test the accuracy of correlations was Eq. (103). The plot of this correlation is shown in Fig. 3, which showed acceptable results for literature values of parameters applied to another set of experimental data, indicating a strong relation between metals and asphaltene content.

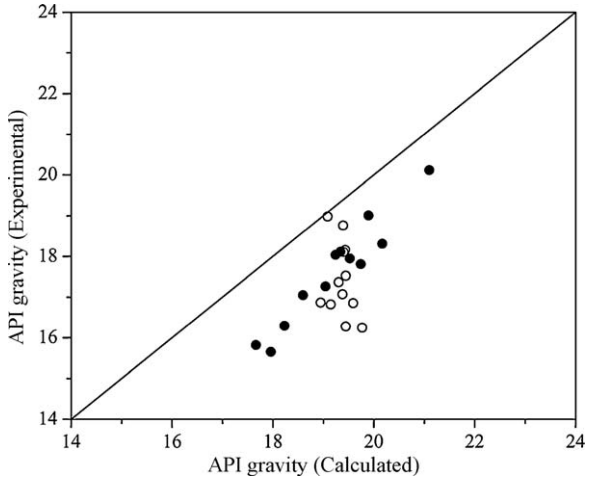

Fig. 2. API gravity of hydrotreated products with reported values of parameters: (●) Eq. (58) (feed A) and (○) Eq. (60) (feed C).

3.3. Prediction using optimized values of parameters

Although for some cases an acceptable trend in the hydrotreated product properties was obtained, most of the predictions using values of parameters reported in literature were completely unsatisfactory. This obviously indicated that parameter values can be optimized for each correlation in order to determine which one can predict our experimental data with suitable accuracy.

Parameter optimization was performed by means of linear and non-linear regression analysis using Polymath 5.0, STATISTICA 5.1, and the Excel solver function; which use the Levenberg-Marquardt, Quasi-Newton, and Newton algorithms, respectively.

With the optimized values of parameters 26 correlations showed SSE values lower than 5 (Fig. 1), most of them corresponded to polynomials. The lowest SSE was obtained using Eqs. (45)–(49), which are linear correlations derived from the deasphalting process. In all cases lower SSE value, higher values of r^2, and better distribution of the data around the parity line were obtained (Fig. 4), compared with predictions obtained using the values of parameters reported in literature. These correlations seem to be appropriate to predict the density as function of the asphaltenes content, however the low values of SSE obtained are due to the small values of density compared with the other predicted properties and not to the good fit of the correlation (r^2 from 0.2 to 0.86).

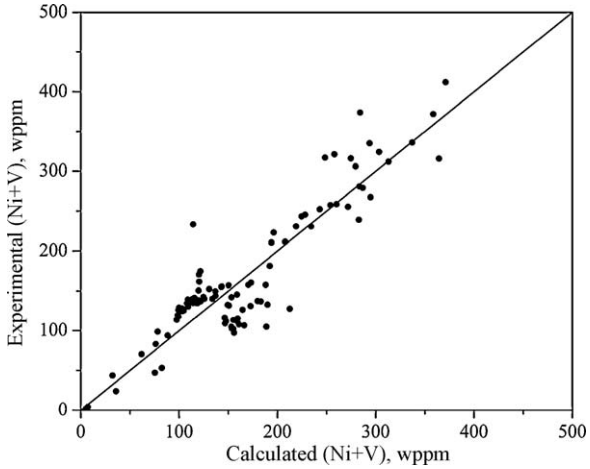

Fig. 3. Total metal content for all the feedstocks with Eq. (103) using the reported values of parameters.

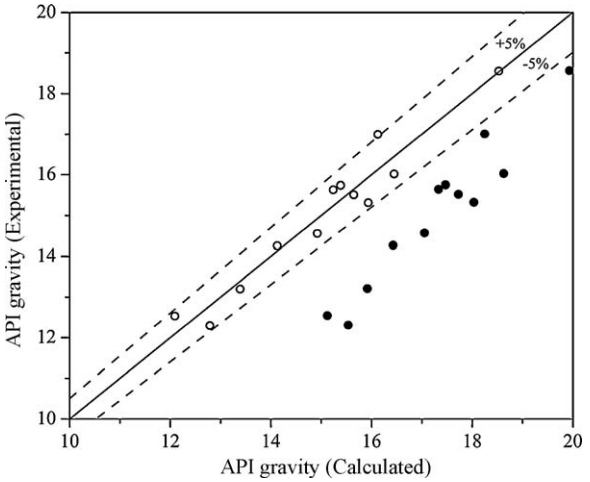

Fig. 4. API gravity predicted with Eq. (58): (●) using values of parameters reported in literature and (○) using values of optimized parameters.

The best correlation to calculate API gravity as function of HDS was a polynomial, Eqs. (51)–(56), with correlation coefficients in the range of 0.73–0.92 for the six feedstocks. The best correlation for the prediction of sulfur content as function of insolubles in nC_7 was an exponential function (Eqs. (91), (92), (94) and (95)), which correlates data of all the feedstocks tested but for feedstock D, with r^2 values in the range of 0.6–0.97 (Table 7).

The worst predictions were obtained with straight-line correlations and an exponential correlation used to predict the nitrogen content; since most of the reported values of r^2 were between 0.0018 and 0.8. Multiple non-linear correlations showed values of r^2 in the range of 0.87–0.97. MNL correlations use pressure, temperature and LHSV as independent variables to predict HDN and HDS. From our experimental data set, this information is only available for feedstock F (three temperatures, two pressures and four LHSV) and for feedstock C at constant temperature, four pressures and two LHSV. Experimental data of the other feedstocks (A, B, D and E) were obtained at constant pressure and LHSV, varying only temperature. Taking into account these remarks, it can be stated that Eq. (89) is useful to predict the level of sulfur-removal in hydrotreated products; however, a more complete data set is necessary to verify its accuracy. Although having values of r^2 close to 0.98 and SSE of 1.29, Eq. (84) cannot be ranked as one of the best correlations since parameter optimization was done at constant LHSV, which makes this correlation dependent only on temperature.

3.4. An attempt to correlate values of parameters with feed properties

Once the set of optimized parameters for all correlations was determined, an attempt was made to correlate those parameters with properties of the feedstock such as API gravity, sulfur, metals, nitrogen, asphaltenes, Conradson and Ramsbottom carbon contents. The calculations were performed with the DataFit version 7.1.44 software. Only correlations with acceptable values of r^2 (>0.8), determined previously, for at least three different feedstocks were selected, which were:

- Polynomial correlation for API gravity, Eqs. (51), and (53) to (56) ($r^2 > 0.82$).
- Multiple non-linear correlation for sulfur-removal, Eqs. (84), (87), and (89) ($r^2 > 0.87$).
- Exponential correlation for metal content, Eqs. (98), (101) and (102) ($r^2 > 0.87$).
- Exponential correlation for Conradson carbon content, Eqs. (104), (106) and (107) ($r^2 > 0.86$).

As mentioned previously, the exponential equations were derived from a process different to hydrotreating/hydrocracking, however, it is not surprising that metals and Conradson carbon content be well predicted when they are related to asphaltene concentration since it is well known that metals concentrate in the asphaltene fraction and that asphaltenes are directly associated to coke formation [8].

The form of correlations obtained with DataFit varied from simple equations with one parameter to more complex ones with four or more parameters. Firstly, individual properties of the feedstock were correlated with each optimized parameter, and then correlations with the combination of two properties were also developed. Trying to correlate more than two properties with parameters was not considered to avoid complexity of equations. Neither trigonometric functions nor more than two parameters were chosen to maintain the correlation as simply as possible. The highest value of r^2 was found for the first case, i.e. correlation with one feedstock property. In the second case (correlation with two feedstock properties), three parameters were allowed to improve accuracy.

For P and MNL correlations it was not possible to reproduce all their parameter values as function of feedstock properties with high precision since these correlations, having four and six parameters, respectively, are very sensitive to slight variations in the parameter values; thus over-prediction and under-prediction of the hydrotreated product properties for some feedstocks was obtained, as shown in Fig. 5 for the polynomial correlation. The exponential correlations with only two parameters given by Eqs. (104), (106) and (107), although better than P and MNL correlations, also over- and under-predicted the hydrotreated product properties as illustrated in Fig. 6.

Only correlations (98), (101) and (102) showed good prediction of parameters as function of feedstock properties. The approach mentioned above to correlate parameters and feedstock properties tends sometimes to be problematic since the new parameters get errors generated during the estimation of the original parameters. Therefore, for a better parameter estimation the correlations obtained (a_0 and a_1 in Table 8) were plugged into the original exponential equation (Eq. (22)) to replace the original parameters, then the SSE was minimized and a new set of parameters was determined. With the new parameters a better fitting was

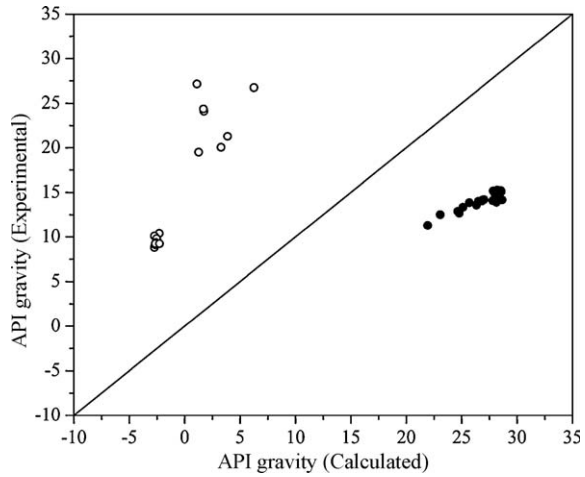

Fig. 5. Over- and under-predicted API gravity using Eq. (13) and parameters values correlated with feedstock properties: (●) feedstock D and (○) feedstock E.

Table 8
Optimized and correlated parameters for Eq. (22).

Correlations for predicting parameters	b_0	b_1	Feedstock	Parameter values			
				Original		Predicted	
				A_0	a_1	a_0	a_1
$a_0 = \frac{b_0 b_1 S_F}{1+b_1 S_F}$	15.4810	−0.4810	B	21.6820	1.0225	22.8744	0.9984
$a_1 = b_0 API_F + b_1 As ph_F$	0.0137	0.0380	E	24.8503	1.0050	25.5933	0.9940
			F	45.3056	0.6437	37.1681	0.7571

S_F, $Asph_F$: total sulfur and asphaltenes contents in the feedstock, wt%.
API_F: API gravity of the feedstock.

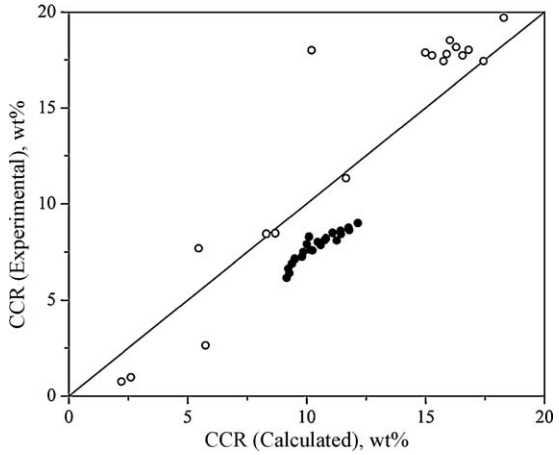

Fig. 6. Over- and under-predicted Conradson carbon content using Eq. (23) and parameters values correlated with feedstock properties: (●) feedstock F and (○) feedstock E.

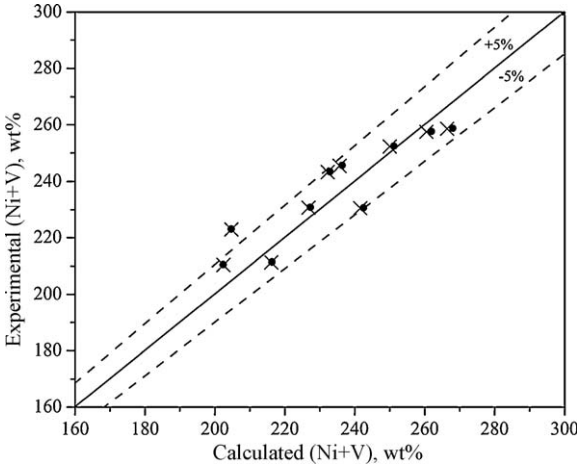

Fig. 8. Comparison between experimental and predicted total metals content for feedstock B. (●) with original values of parameters and (×) with predicted values of parameters.

obtained, since the residual values are lower than those obtained with the previous approach (Fig. 7). The results are shown in Table 8. A comparison between experimental data and calculated product properties is presented in Fig. 8. It can be clearly observed that predictions with parameters correlated with feed properties and original values of parameters are quite similar. These results indicate that for a reduced number of parameters, a good correlation between feedstock properties and such parameters can be obtained; nevertheless, it is imperative to analyze a larger number of feedstocks to ensure the accuracy of this type of correlations.

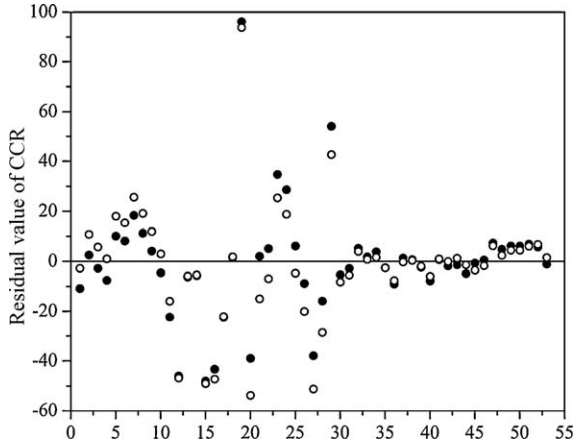

Fig. 7. Residual values of CCR content obtained with the exponential correlation (Eq. (23)) for feedstocks B, E and F. (●) replacing the parameters of derived correlations into the original exponential equation and (○) with parameters values as function of feedstock properties (Table 8).

3.5. Conclusions

Good prediction was obtained with the multiple non-linear correlations but only for some feedstocks; on the contrary, poor prediction was observed with straight-line equations. The polynomial correlation to calculate API gravity as function of HDS and the exponential correlation to predict the total metals content as function of insolubles in nC_7 resulted with the highest values of r^2 (0.7–0.93) for most of the feedstocks. Other correlations neither reproduced our experimental data nor even the tendencies, what indicated that they cannot be extended to different feedstock from which they were derived.

The use of correlations with parameters as function of feedstock properties resulted either in over-prediction or under-prediction of product properties with the polynomial and multiple no-linear correlations. This behavior is attributed to the number of parameters, since a slight change in one of them considerably affected predictions.

An exponential function with two parameters used to predict the total metal content as function of insolubles in nC_7, resulted to be the best approach, indicating that it is possible to correlate feedstock properties with parameter values.

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References

[1] D. Tsamatsoulis, E. Koutoulas, N. Papayannakos, Improvement of characteristic reactions and properties of a heavy residue by catalytic hydrotreatment, Fuel 70 (1991) 741–746.
[2] S.H. Ng, Nonconventional residuum upgrading by solvent deasphalting and fluid catalytic cracking, Energy Fuels 11 (1997) 1127–1136.

[3] S. Trasobares, M.A. Callejas, A.M. Benito, M.T. Martínez, D. Severin, L. Brouwer, Kinetics of Conradson carbon residue conversion in the catalytic hydroprocessing of a Maya residue, Ind. Eng. Chem. Res. 37 (1998) 11–17.
[4] M.A. Callejas, M.T. Martínez, Hydroprocessing of a Maya residue. Intrinsic kinetics of sulfur-, nitrogen-nickel-, and vanadium-removal reactions, Energy Fuels 13 (1999) 629–636.
[5] T.C. Ho, Property–reactivity correlation for HDS of middle distillates, Appl. Catal. A: Gen. 244 (2003) 115–128.
[6] T.C. Ho, G.E. Markley, Property–reactivity correlation for hydrodesulfurization of prehydrotreated distillates, Appl. Catal. A: Gen. 267 (2004) 245–250.
[7] D. Ferdous, A.K. Dalai, J. Adjaye, Hydrodenitrogenation and hydrodesulfurization of heavy gas oil using $NiMo/Al_2O_3$ catalyst containing boron: experimental and kinetic studies, Ind. Eng. Chem. Res. 45 (2006) 544–552.
[8] J. Ancheyta, J.G. Speight, Hydroprocessing of Heavy Oils and Residua, CRC Press, Taylor & Francis Group, 2007.