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Hydrotreating data interpretation by chemometrics

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ABSTRACT

Hydrotreating in the presence of dispersed catalysts has been considered a promising route to obtain valuable fuels from heavy hydrocarbon cuts. A laboratory-scale study on the effect of operating conditions on heavy feedstock hydrotreating performances is reported. In order to maximise the effectiveness of the research activity, chemometrics was exploited both for experimental design and data interpretation.

1. Introduction

The declining demand for residual fuel oil will force refiners to modify their present process configuration and convert this surplus of petroleum residues into maximum distillate transportation fuels. Among the various options available for upgrading bottom materials, slurry processes have an excellent potential. In fact, slurry processes offer an attractive option to deal with heavy feeds, because they combine the advantages of the carbon-rejection technologies in terms of flexibility with the high performances characteristic for hydrogen-addition processes [1,2].

Heavy feedstocks hydroconversion, employing dispersed catalysts, generally requires very high temperatures and pressures: catalysts and additives used in these processes have poor activity with respect to cracking reactions. As a consequence, conversion to lighter products is almost entirely a thermal process [1,3].

Under these reaction conditions, huge amounts of low molecular weight compounds, such as C_1–C_4 hydrocarbon gases, are formed. The production of these light ends is undesirable, because they are less valuable than liquids.

Furthermore, the high temperature favours condensation reactions between aromatic clusters which lead to the formation of mesophase and consequently, coke.

The catalyst contributes to restrain the above-mentioned undesirable reactions, favouring instead the hydrogenation reactions and interfering with the coalescence of the mesophase as well, thus allowing the reduction in the severity of the process and the improvement in the quality of the products. Typically, catalysts based on transition metal sulphides (TMS) are used for this purpose [4].

High levels of catalyst dispersion, that affect hydrogen uptake, can be obtained by *in-situ* thermal decomposition of small quantities of metal-organic precursors added to the feed [5].

Here we report the results from a laboratory-scale study on the effect of operating conditions on 500 °C+ feedstock hydrotreating performances in a slurry reactor, in the presence of a molybdenum-based dispersed catalyst. Specifically, correlations among operating variables, product yields and quality were quantified. In order to maximise the effectiveness of this research activity, a chemometric approach, based on statistical experimental design, was exploited.

Statistical experimental design is an effective tool to simultaneously evaluate the effect of several variables [6,7]. This consists of m variables (in a chemometric context, called *factors*) and n experiments set up to investigate a complex chemical system in a systematic way. An $n \times m$ matrix will then represent the variable space, $\mathbf{X}$. A response matrix, $\mathbf{Y}$, containing at least one *response* variable (*i.e.* a result) for each experiment, is necessary for data analysis, as well. The purpose of chemometric analysis is to perform a screening of the variables in order to find out the relation between $\mathbf{X}$ and $\mathbf{Y}$. In general, statistically designed experiments provide a fixed amount of information with less effort than the classical one-variable-at-a-time approach. An additional relevant benefit derives from the information about interactions among experimental factors in determining the responses.

Specifically, a factorial design was employed as the preferred strategy to organise the research here reported.

Factors explored by means of factorial designs are varied independently one to each other (factorial designs are *orthogonal*

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by definition). The absence of statistical correlations among factors guarantees independent estimations of the effect of each variable on the obtained response, apart from the chosen data analysis methodology.

In particular, when linear modelling is used to explore the resulting data-set, both independent and precise model parameter estimations came from factor orthogonally.

According to that, it is not surprising that several successful applications of this methodology in catalysis and material science (often coupled with high-throughput, HT, techniques) are reported both by industrial and academic research groups [8–12].

It is important to remarks that the statistical experimental design approach is intrinsically local. Differently to deterministic kinetic modelling, no assumption on the law-of-nature governing the studied phenomena is made a priori. As a consequence, the amount and the quality of the information available depend only on the specific data-set obtained from experimental runs. This makes the settlement of factor variations ranges (defining the *experimental domain* to be studied) a crucial step in order to obtain informative data and models. Typically, system response variations may be hardly distinguished from noise if a too narrow experimental domain is chosen. On the contrary, a too wide experimental domain may lead to an oversimplified description of the studied phenomena (sometimes merely an helicopter-view). According to that, in this study an experimental domain slightly narrower than the one considered in previous fundamental kinetic modelling activities [16] was selected.

2. Procedure

The study was organised according with the following tasks:

- experimental design definition;
- factors and responses selection;
- factor variation ranges settlement;
- experimental design implementation;
- experimental result statistical evaluation;
- model interpretation.

Eight different hydrotreating batch runs, organised as a 2^3 factorial design, were performed by using a 500 °C+ charge (whose main properties are reported in Table 1) in order to study the effect of three factors (reaction temperature, *T*, contact time, *t*, amount of added molybdenum-based catalyst, *Q*) on hydrotreating performances. Factors variation ranges were defined taking into account previous experience [16,17] and reported in Table 2.

Two replicate experiments, performed in the middle of the chosen domain, were added to the factorial design in order to check the experimental result reproducibility.

Experiments were carried out randomly to minimise the effect of systematic errors.

For each experimental run, eight different responses were considered (codes utilised in this paper are reported between brackets):

- light hydrocarbon (C_1–C_4 paraffins) yield (HGAS);
- solid yield (SOLS);
- naphtha (C_5 – 170 °C cut) yield (NAPH);
- atmospheric gasoil (170–350 °C cut) yield (GOIL);
- vacuum gasoil (350–500 °C cut) yield (VOIL);
- heavy residue yield (500 °C+ cut) yield (RESI);
- liquid fraction Conradson residue (CCRL);
- hydrodesulphurisation performance (HDSL).

Table 2
Experimental factors level and values

Factors	Units	Factors levels and values		
		−1 lowest	0 mean	+1 highest
T	(°C)	400	410	420
t	(h)	1	2	3
Q	(ppm wt)	1000	2000	3000

T: reaction temperature, *t*: contact time, *Q*: amount of molybdenum-based catalyst added to the feed.

The obtained data-set was explored by using correlation matrix analysis. Then, quantitative relations among factors and responses were computed by multivariate linear modelling (ordinary least squares, OLS, method).

Correlation matrix contains the linear correlation coefficients $r_{u,w}$ computed for each couple (*u*, *w*) of the studied variables.

Linear correlation coefficients can be considered as a measure of the linear association between the variable *u* and variable *w*. Their values are always comprised between −1 (maximum *inverse correlation*, *i.e. u* and *w* values lie on a straight line with negative slope in the (*u*, *w*) plane) and +1 (maximum direct correlation, *i.e. u* and *w* values lie on a straight line with positive slope in the (*u*, *w*) plane).

A model including linear terms (resuming factors *effects* on the response, in the explored experimental domain) and crossproducts terms (representative of *interactions* between the factors in determining the response) was computed for responses highly correlated with factors (Eq. (1)):

$$y = b_o + b_T T + b_t t + b_Q Q + b_{T,t} Tt + b_{T,Q} TQ + b_{t,Q} tQ. \tag{1}$$

Before computing, factor actual values were converted into scaled values (comprised between −1 and +1) by using the *range-scaling* transformation (Eq. (2)) in order to obtain effect estimations independent from the used units.

$$x = \frac{(x_{\text{act}} - \bar{x}_{\text{act}})}{\delta x_{\text{act}}}, \tag{2}$$

where:

- x is the factor value after range-scaling ($-1 \le x \le +1$);
- x_{act} is the actual value of the factor;
- $\bar{x}_{\text{act}} = \frac{x_{\text{act}}^{\text{high}} + x_{\text{act}}^{\text{low}}}{2}$;
- $\delta x_{\text{act}} = x_{\text{act}}^{\text{high}} - \bar{x}_{\text{act}}$.

Significance of each model coefficient, *b*, was evaluated performing a *t*-test based on model residual sum of squares, RSS (at 95% confidence level).

Data processing was operated by using the statistical package StatSoft Statistica for Windows (version 5.1 G, 1997).

Batch experiments were carried out by using a 30 ml stainless-steel autoclave, equipped with a swinging capillary stirring device. The autoclave was loaded with 10 g of feedstock + a variable

Table 1
Main characteristics of the 500 °C+ feedstock utilised

Density (g/cm^3)	N content (wt%)	S content (wt%)	CCR (wt%)	Metal content (ppm wt)
0.9760	0.43	2.33	9.78	95

amount of oil-soluble molybdenum catalyst precursor (consistent with the chosen factorial design strategy adopted). Then, the system was pressurised with hydrogen (Sapio, 4.5 grade) and heated up to the desired reaction temperature. Hydrogen pressure was kept constant at $P = 16.0$ MPa throughout the experiment by means of an automatic gas-dosing device.

At the end of each run, after cooling till room temperature, reaction products were recovered, quantified and characterised off-line (balance closures around 99 wt.% were obtained).

- Gases were analysed by gas-chromatography (HP 5890 gas-chromatograph equipped with a separation system based on the combination of molecular sieve 13X and Porapak N packed columns).
- Solids (typically coke, molybdenum sulphide catalyst generated *in situ* during reaction, and other sulphides coming from metals contained in the feedstock) were sampled from the hydrotreated charge by filtration and studied by X-ray diffraction (XRD). Structural analysis was carried out using a vertical Philips X' PERT diffractometer equipped with a Cu Kα ($\lambda = 0.154178$ nm) radiation source, a scintillation counter and a secondary curved graphite crystal monochromator. Data were collected in the spectral interval $7^\circ \le 2\theta \le 70^\circ$ with steps of 0.03° in 2θ and accumulation times of 12 s/step. Phase identification was made by search-match procedures comparing the positions and the relative intensity of the diffraction lines with the data contained in the JCPDS data-bank.
- Liquids (containing suspended solids) were reclaimed from the autoclave without the help of any auxiliary solvent. In order to determine cut yields, 0.5 g samples of hydrotreated liquids (as discharged from the autoclave) were dissolved in the minimum amount of carbon disulphide (T.J. Baker, UV-spectrophotometric grade), filtered (Millipore, Millex FH 0.45 μm syringe filters) and then characterised by SIM-DIST (Thermo Finnigan Trace GC equipped with a Restek MXT-1HT column). The main part of the obtained liquids was dissolved in tetrahydrofuran (Merck, LiChrosolv grade) and filtered (Millipore, Fluoropore FHUP 0.45 μm filters) to recover the suspended solids. After tetrahydrofuran removal on Buchi 011 Rotavapor, Conradson residue (Normalab NMC 210 micro RCC, ASTM D4530 method) and sulphur content (Leco SC432 elemental analyser, ASTM 1552 method) were measured.

3. Results and discussion

The obtained data-set is resumed in Table 3.

From correlation matrix analysis (Table 4) emerges that reaction temperature, T and contact time, t are highly correlated with the considered responses. In other words, T and t are by far the most important factors influencing hydrotreating performances. This finding agrees with the fact that dispersed catalysts do not contain acidic functions, so that the feedstock conversion is thermally controlled [3].

Table 4
Linear correlations among factors and responses

$r_{x,y}$	T	t	Q
T	1	0	0
t	0	1	0
Q	0	0	1
HGAS	0.73	0.61	0.10
SOLS	0.71	0.05	0.29
NAPH	0.46	−0.14	0.26
GOIL	0.76	0.58	−0.01
VOIL	0.76	0.62	0.10
RESI	−0.78	−0.59	−0.06
CCRL	−0.50	−0.72	−0.36
HDSL	0.50	0.75	0.40

Notice the absence of correlations among the experimental factors (T, t, and Q) due to the factorial approach adopted to plan experiments.

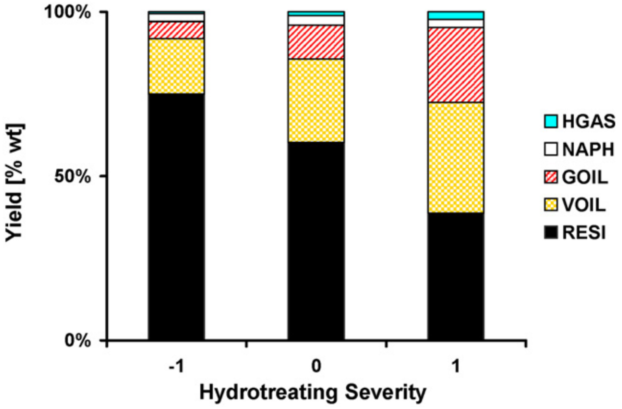

Fig. 1. Effect of hydrotreating severity on product yields (−1 and +1 correspond, respectively, to the least and the most severe conditions in the studied experimental domain: −1 = [$T = 400\,^\circ$C, $t = 1$ h, $Q = 1000$ ppm wt], 0 = [$T = 410\,^\circ$C, $t = 2$ h, $Q = 2000$ ppm wt]; +1 = [$T = 420\,^\circ$C, $t = 3$ h, $Q = 3000$ ppm wt]).

Naphtha yield (NAPH) is virtually uncorrelated with factors in the studied experimental domain. According to that, Fig. 1 shows that conversion of 500 °C+ into gasoil increase with hydrotreating condition severity while naphtha yield is almost invariant. At the same time, C_1–C_4 hydrocarbon yield (HGAS) increases slightly with hydrotreating severity. This behaviour can be interpreted assuming that, in the studied experimental domain, naphtha acts as an

Table 3
Data-set obtained from hydrotreating experiments

ID	Order	T (°C)	t (h)	Q (ppm wt)	HGAS (wt%)	SOLS (wt%)	NAPH (wt%)	GOIL (wt%)	VOIL (wt%)	RESI (wt%)	CCRL (wt%)	HDSL (%)
O1	1	410	2	2000	1.15	1.27	2.83	10.08	24.86	59.02	5.05	53.04
O2	2	410	2	2000	1.28	1.39	2.21	10.71	24.81	58.88	5.52	51.95
A	3	400	1	1000	0.49	0.53	2.38	5.14	16.76	74.42	7.90	28.05
B	7	420	1	1000	1.00	1.16	2.74	11.61	23.80	59.02	6.02	42.28
C	8	400	3	1000	0.92	0.37	1.91	8.70	22.09	65.20	5.45	47.98
D	5	420	3	1000	2.06	1.27	2.26	22.20	32.20	39.15	4.70	61.16
E	6	400	1	3000	0.59	1.02	1.81	4.45	18.19	73.44	7.55	41.86
F	10	420	1	3000	1.19	1.00	3.07	11.15	24.82	58.08	4.78	50.48
G	9	400	3	3000	0.99	0.75	2.84	9.33	23.43	61.94	4.03	57.01
H	4	420	3	3000	2.19	1.48	2.50	22.21	32.94	37.87	3.31	67.82

ID: experiment identification, order: test sequence, T: reaction temperature, t: contact time, Q: amount of molybdenum-based catalyst added to the feed, HGAS: light hydrocarbon yield, SOLS: solid yield, NAPH: naphtha yield, GOIL: atmospheric gasoil yield, VOIL: vacuum gasoil yield, RESI: heavy residue yield, CCRL: liquid fraction Conradson residue, HDSL: hydrodesulphurisation performance.

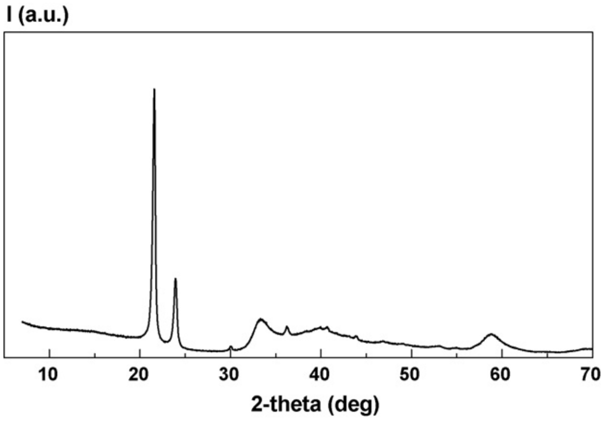

Fig. 2. XRD pattern representative of all the examined samples. Sharp diffraction lines are due to wax and the broad halos to MoS_2 (a.u.: arbitrary units).

intermediate product in the cracking of heavier fractions into C_1–C_4 hydrocarbons.

XRD patterns of the solids recovered at the end of each trial appeared to be invariant and thus not related to the severity of the treatment. A typical one is reported in Fig. 2.

Two crystalline phases are clearly identifiable: well crystalline wax and poorly crystalline MoS_2. No graphitic coke is detectable. The XRD pattern of the molybdenite clearly shows a typical bi-dimensional micro-crystalline organisation due to dispersed MoS_2 sheets with an almost negligible *c* stacking.

This can be explained considering that the formation of the highly dispersed MoS_2 catalyst from the oil-soluble precursor is almost instantaneous within the explored experimental domain and favoured by the surrounding organic environment [5,13,14].

Due to the considerable noise introduced by solid recovery operations (because of the presence of crystalline paraffins in the hydrotreated products) no linear correlations between solid yield (SOLS) and molybdenum catalyst concentration (*Q*) are evident. Thus, differently from results previously published, concerning different feedstocks [16,17], in this case no relevant model was obtained among solid yield (SOLS) and factors.

Table 5
Effect estimation by linear modelling: significant coefficients *b* and R^2 values are reported for each model (*n.s.*: not significant)

	b_0	*T*	*t*	*Q*	*Tt*
HGAS					
b	1.19	0.43	0.36	n.s.	0.15
(±)	0.066	0.074	0.074	n.s.	0.074
R^2	0.984				
GOIL					
b	11.56	4.94	3.76	n.s.	1.65
(±)	0.64	0.72	0.72	n.s.	0.72
R^2	0.988				
VOIL					
b	24.39	4.16	3.39	0.57	0.74
(±)	0.29	0.32	0.32	0.32	0.32
R^2	0.997				
RESI					
b	58.70	−10.11	−7.60	−0.81	−2.42
(±)	0.51	0.57	0.57	0.57	0.57
R^2	0.999				
CCRL					
b	5.43	−0.77	−1.10	−0.55	0.40
(±)	0.27	0.30	0.30	0.30	0.30
R^2	0.970				
HDSL					
b	50.16	5.85	8.91	4.71	n.s.
(±)	1.69	1.89	1.89	1.89	n.s.
R^2	0.974				

For each coefficient 95% confidence limits (±) are reported, as well.

Interpretable linear models were computed respectively for GOIL, VOIL, RESI, CCRL and HDSL responses (Table 5, Figs. 3 and 4).

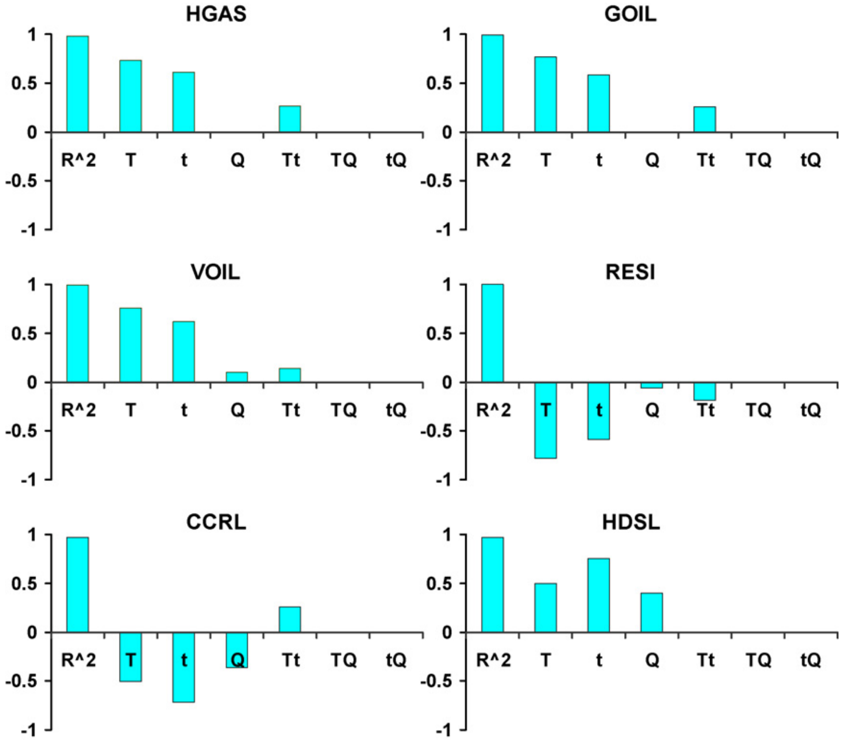

Fig. 3. Effect estimation by linear modelling: significant standardised coefficients *β* and R^2 values are reported for each model.

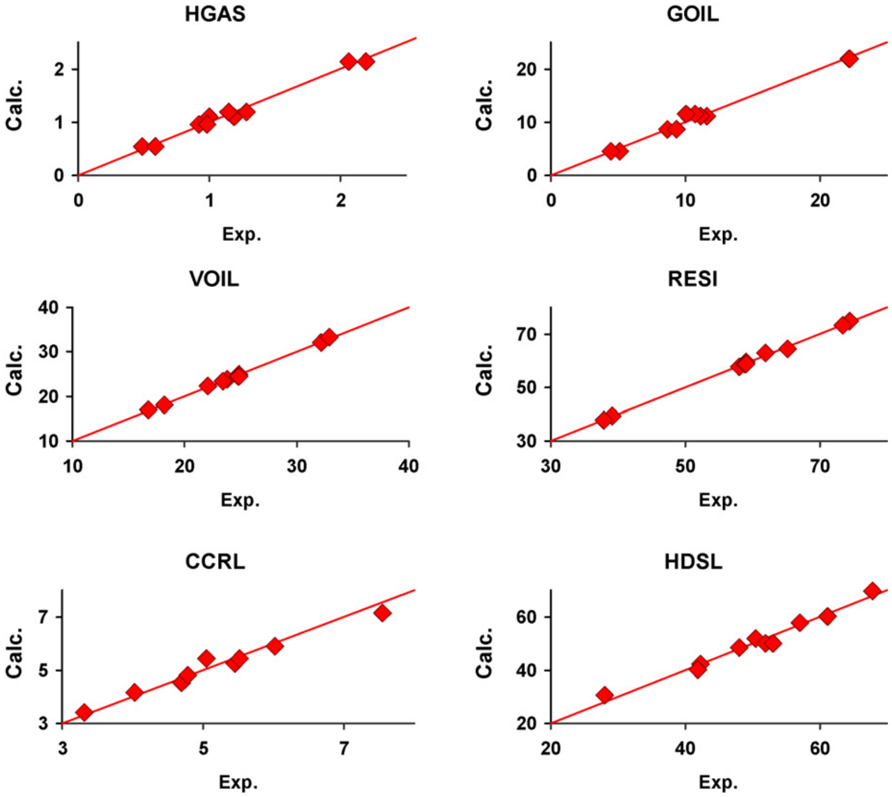

Fig. 4. Model parity plots: agreement between calculated and experimental responses is evident.

Notice that standardised coefficient values, β, (always comprised among -1 and +1) are reported in Fig. 3 in order to make easier the comparison among the magnitude of effects and interactions from models regarding different responses.

Effect estimation by linear modelling confirms that distillate production is strongly influenced by reaction severity ($T + t$ combination).

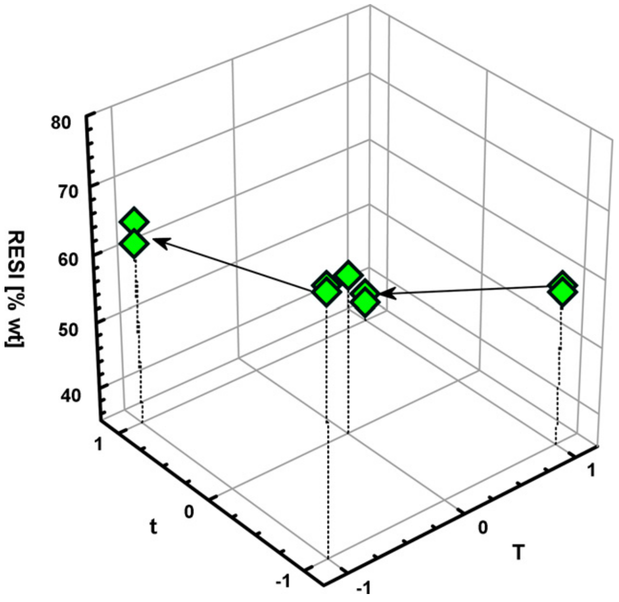

Fig. 5. Influence of temperature, T and contact time, t on the 500 °C+ cut yield (RESI). ***T*** and ***t*** are reported as range-scaled values.

An additional catalytic contribution, represented by *Q* coefficient, is requested for heavy residue (500 °C+ cut) conversion into lighter products (RESI model). This is probably due to the relevant content of stable aromatic compounds typical of heavy cuts (*e.g.* polynuclear aromatic compounds, nitrogen-containing and/or sulphur-containing etherocycles): both catalytic hydrogenation and thermal cracking are necessary to convert these undesired species into lighter and more valuable ones [15].

In agreement with this hypothesis, a catalytic contribution is needed also to promote vacuum gasoil (350–500 °C cut) yield (VOIL model).

On the other hand, product quality (hydrodesulphurisation, HDSL and product Conradson carbon residue, CCRL) are affected both by reaction severity and catalyst concentration, as well. High reaction temperature, contact time and catalyst concentration favour hydrogenation reactions, promoting the upgrading of the feedstock.

These results are consistent with the evidences referred in [16,17].

HGAS, GOIL, VOIL, CCRL models contain positive *Tt* interaction terms. This is consistent with a relevant synergy existing between reaction temperature and contact time in determining response values.

It is interesting to point out that the negative *Tt* interaction, significant in the 500 °C+ cut yield (RESI) model, represents the different behaviour of the system at low and high temperature, varying the contact time (Fig. 5). Specifically, at low temperature, RESI is almost invariant with contact time. Conversely, at high temperature, RESI decreases by increasing contact time (*i.e.* 500 °C+ cut conversion is favoured).

Furthermore, the value of RESI continuously decreases when starting from the mildest hydrotreating conditions (corresponding to the lowest temperature and contact time) and going to the most severe (corresponding to the highest temperature and contact time).

4. Conclusions

Evidences from slurry hydrotreating experiments, in presence of a molybdenum-based catalyst, report an effective ugrading of the 500 °C+ cut utilised as fed.

Specifically, multivariate linear models, computed from the data-set generated accordingly with a factorial experimental design, confirm that temperature and contact time are by far the most important factors in determining distillate yields while an additional catalytic contribution is requested to improve product quality (sulphur content and Conradson residue): dispersed MoS_2 catalyst promotes hydrogenation reactions enhancing feedstock upgrading.

It is also evident that the production of light hydrocarbons (that are less valuable than liquids, thus undesired) was well controlled even at the maximum hydrotreating severity (in the explored experimental domain) where the upgrading of the charge is maximised. Furthermore, no coke formation was detected by XRD in the solids recovered at the end of the reaction. Conversely, crystalline paraffins were evidenced.

In spite of their simplicity, multivariate models reported in this work provide a local description of the studied complex chemical system consistent with previous fundamental studies. Thus, the chemometric approach, based on statistical experimental design, can be considered both alternative and complementary to deterministic kinetic modelling.

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References

[1] A. Del Bianco, N. Panariti, M. Marchionna, Chem. Tech. 25 (11) (1995) 35.
[2] M.S. Rana, V. Sámano, J. Ancheyta, J.A.I. Diaz, Fuel 86 (2007) 1216.
[3] E.C. Sanford, Ind. Eng. Chem. Res. 33 (1994) 109.
[4] R.R. Chianelli, M.H. Siadati, M. Perez De la Rosa, G. Berhault, J.P. Wilcoxon, R. Bearden Jr., B.L. Abrams, Catal. Rev. 48 (2006) 1.
[5] N. Panariti, A. Del Bianco, G. Del Piero, M. Marchionna, Appl. Catal. A Gen. 204 (2000) 203.
[6] R. Carlson, Design and Optimisation in Organic Synthesis, Elsevier, Amsterdam, 1992.
[7] J.P. Box, W.G. Hunter, J.S. Hunter, Statistics for Experimenters, Wiley, New York, 1987.
[8] G. Øye, O. Siöblom, M. Stöcker, M. Micropor, Mesopor. Mater. 34 (2000) 291.
[9] A. Cichocki, P. Kościelniak, Micropor. Mesopor. Mater. 41 (2000) 241.
[10] R.J. Hendershot, W.B. Rogers, C.M. Snively, B.A. Ogunnaike, J. Lauterbach, Catal. Today 98 (2004) 375.
[11] K.M. Hardiman, C.G. Cooper, A.A. Adesina, Ind. Eng. Chem. Res. 43 (2004) 6006.
[12] M. Moliner, J.M. Serra, A. Corma, E. Argente, S. Valero, S. Valente, Micropor. Mesopor. Mater. 78 (2005) 73.
[13] G. Berhault, A. Mehta, A.C. Pavel, J. Yang, L. Rendon, M.J. Jácaman, L.C. Araiza, A.D. Moller, R.R. Chianelli, J. Catal. 198 (2001) 9.
[14] C. Glasson, C. Geantet, M. Lacroix, F. Labruyere, P. Dufresne, J. Catal. 212 (2002) 76.
[15] R. Prins, M. Egorova, A. Rötlisberger, Y. Zhao, N. Sivasankar, P. Kukula, Catal. Today 111 (2006) 84.
[16] N. Panariti, F. Bazzano, A. Del Bianco, M. Marchionna, R. Montanari, S. Rosi, ACS Div. Petroleum Chem. Preprints 46 (1) (2001) 78.
[17] N. Panariti, A. Del Bianco, G. Del Piero, M. Marchionna, P. Carniti, Appl. Catal. A Gen. 204 (2000) 215.