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Catalytic Hydrogenation of Aromatic Hydrocarbons in a Trickle Bed Reactor

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Abstract: The hydrogenation of the main components of an anthracene oil has been investigated in a cocurrent downflow trickle bed reactor at 623 K and 9·8 MPa. The catalyst employed was sulfided Ni–Mo/γ-Al_2O_3. The product of the effectiveness factor and chemical rate constant was determined for the reactions involved in the hydrogenation of naphthalene, acenaphthene, phenanthrene, anthracene, fluoranthene and pyrene. Reaction rates were expressed as a weighted average of the rate on the liquid-covered surface and on the dry surface. The external surface of the catalyst was considered to consist of a dynamic and a low liquid renewal area. The latter, identified as the area wetted by stagnant liquid, was assumed to be not reactive. The product of the effectiveness factor and the intrinsic rate constant were determined for dry and wetted catalyst surfaces by employing an estimation of the unit fraction of inactive surface. An estimation of the effectiveness factors was performed by employing the kinetic constants previously determined by Rosal *et al.* (*Ind. Eng. Chem. Res.*, **31** (1992) 1007–12). The results showed that the effectiveness factor for the wetted surface followed a pattern in good agreement with theoretical predictions and was especially low for the hydrogenation of anthracene, a reaction whose rate was relatively high. © 1988 SCI

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Key words: trickle bed; catalytic hydrogenation; aromatic hydrocarbons; effectiveness factor

NOTATION

ACE	Acenaphthene
ANT	Anthracene
$C_{\mathrm{A,L}}$, $C_{\mathrm{HYD,L}}$	Liquid phase concentration of reactant A and hydrogen ($\mathrm{mol\ dm^{-3}}$)
$C_{\mathrm{A,G}}$, $C_{\mathrm{HYD,G}}$	Gas phase concentration of reactant A and hydrogen ($\mathrm{mol\ dm^{-3}}$)
d_r	Reactor diameter (m)
D_{A}	Effective diffusivity of A in the liquid filled pores of catalyst ($\mathrm{m^2\ s^{-1}}$)
DHA	9,10-Dihydroanthracene
DHP	9,10-Dihydrophenanthrene
DHPY	4,5-Dihydropyrene
f	Wetting efficiency (dimensionless)
f_{s}	Unit fraction of catalyst surface covered by stagnant liquid (dimensionless)
f_{td}	Wetting efficiency obtained form tracer data (dimensionless)
FLU	Fluoranthene
H_{A}	Henry's law constant (dimensionless)
k_{L}, k_{G}	Rate constant for a catalyst which external surface is covered by liquid and gas ($(\mathrm{dm^3})^2\ \mathrm{mol^{-1}\ s^{-1}}$ kg of catalyst^{-1} or $\mathrm{dm^3\ s^{-1}}$ kg of catalyst^{-1})

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L	Length of the packed bed (m)
n	Number of experiments
$N_{A,O}$, $N_{HYD,O}$	Inlet molar flow rate of reactant A and hydrogen (mol s^{-1})
NAP	Naphthalene
OHA	Octahydroanthracene
OHP	Octahydrophenanthrene
PHE	Phenanthrene
PYR	Pyrene
r	Reaction rate (mol s^{-1} kg of catalyst^{-1})
s	Number of different observed responses
TET	Tetralin
THAC	2*a*,3,4,5-Tetrahydroacenaphthene
THAN	1,2,3,4-Tetrahydroanthracene
THFL	1,2,3,10*b*-Tetrahydrofluoranthene
THP	1,2,3,4-Tetrahydrophenanthrene
v_G	Gas phase superficial velocity (m s^{-1})
v_L	Liquid phase superficial velocity (m s^{-1})
W	Weight of catalyst (kg)
x	Conversion (dimensionless)
y_{ki}	*i*th observed dependent variable for *k*th experiment
$y_{t,ki}$	*i*th calculated value for *k*th experiment
α_A	Liquid phase mole fraction of A Total mole fraction of A^{-1} (dimensionless)
ε	Porosity of the bed (m^3 of free space m^{-3} of reactor)
η_L, η_G	Effectiveness factor for the liquid and gas covered external surface of the catalyst
λ	Vapor to feed molar ratio (dimensionless)
Π_A, Π_{HYD}	Vapor–liquid equilibrium relationship for compound A or hydrogen, (Gas phase mole fraction) (Liquid phase mole fraction)$^{-1}$ (dimensionless)
ϕ	Thiele modulus (dimensionless)

Subscripts

A	Hydrocarbon reactant
G	Gas phase
HYD	Hydrogen
L	Liquid phase

1 INTRODUCTION

In recent years the catalytic hydroprocessing of organic fractions has received renewed interest. The tightening of environmental regulations concerning the emission of aromatic hydrocarbons forces further upgrading of fossil fuels with a particular interest in aromatic hydrogenation. The saturation of hydrocarbons takes place in multicomponent mixtures with simultaneous hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation and, depending on the acidic function of the catalyst, a certain extent of hydrocracking and ring opening reactions. At least the first stage of the operation must be carried out on catalysts that do not deactivate in contact with the sulfur-containing compounds present in industrial feedstocks. For this reason, almost all the available results concerning the hydrogenation of aromatic hydrocarbons have been obtained with sulfided hydroprocessing catalysts and especially Co–Mo/γ-Al_2O_3 and Ni–Mo/γ-Al_2O_3. Most of the research has been carried out on single compounds or binary mixtures with the aim of elucidating the complex reaction networks usually involved. Detailed reviews of this topic have been provided by Moreau and Geneste[1] and Girgis and Gates.[2]

The hydrogenation of naphthalene has been studied by Sapre and Gates[3] in a liquid phase batch reactor at 598 K and 7·5 MPa on a sulfided CoO–MoO_3/Al_2O_3 catalyst and by Huang and Kang[4,5] who employed Pt/Al_2O_3 in a trickle bed reactor at 513 K and 5·17 MPa. Both works were performed by employing a solution of naphthalene in *n*-hexadecane. A reaction pathway for the hydogenation of anthracene has been proposed by Wiser *et al.*[6] and Wiser[7] at 523 K and 17·1 MPa on a nickel–tungsten catalyst. The hydrogenation of phenanthrene was first studied by Shabtai *et al.*[8] at 473–653 K and 10 MPa and by Huang *et al.*[9] under similar conditions. Girgis[10] proposed a complete reaction pathway for the hydrogenation reaction of phenanthrene by conducting experiments carried out at 623 K and 17·1 MPa over a sulfided nickel–molybdenum on alumina catalyst. The hydrogenation of fluoranthene was studied by Lapinas *et al.*[11] in a batch reactor at 583–653 K and 15·3 MPa and by Girgis and Gates.[10] Pyrene reaction was studied by Shabtai *et al.*[8] at 614 K and 7·0–20·5 MPa and Stephens and Kottenstette[12] who also employed hexadecane as a solvent for reactions carried out at 621–673 K and 3·5–13·7 MPa on Ni–Mo/Al_2O_3. However, the data reported on the hydrogenation of complex mixtures of hydrocarbons are scarce. Girgis and Gates[10,13] determined quantitative reaction networks for the simultaneous hydroprocessing of several compounds that simulated a coal liquid fraction from the SRC-II process. The experiments were carried out at 623 K and 17·1 MPa over a sulfided Ni–Mo/Al_2O_3. Rosal *et al.*[14] determined first order specific reaction rates and activation energies for the first hydrogenation reaction of several two- to four fused-ring aromatic compounds. The work was performed at 564–621 K and 10·0–13·0 MPa employing a light fraction of anthracene oil with practically the same composition as that used in this work. Recently, Korre *et al.*[15] determined quantitative networks for the hydrogenation of a mixture of several aromatic hydrocarbons in cyclohexane at 623 K and a total pressure of 6·8 MPa.

The specific characteristic of trickle bed reactors is that part of the catalyst surface is covered by liquid and part by gas. In the common set up, the liquid phase flows downwards through the reactor cocurrently with a gas phase that partly consists of vaporized compounds. Except for relatively high liquid flow rates, the external surface of the catalyst is not completely wetted.[16] With regard to the internal surface, it has been stated that the volume inside the pores should be entirely filled with liquid due to capillarity.[17–19] However, in certain cases such as liquid maldistribution, a fractional pore fill-up might exist, as indicated by Dudukovic.[20] The limiting reactant may be nonvolatile at reaction conditions and therefore the reaction takes place only on the wetted part of the catalyst surface. On the dry zone, the depletion of the liquid reactant results in a decreased effectiveness factor relative to the wetted zone.[21] On the other hand, a significant volatility of the liquid reactant means that the reaction also takes place on the externally dry surface. In this case, due to the additional mass transfer resistance introduced by the liquid phase, it was observed that the reaction rate increased as wetting efficiency decreased. The derivation of the effectiveness factor for liquid and gas phase reaction was studied in detail by Sakornwimon and Sylvester[22] who also considered the possibility of incomplete internal wetting of the catalyst particle. Mills and Dudukovic[16] and El-Hisnawi *et al.*[23] determined wetting efficiencies for low pressure operation by assuming that they are directly measured by the square root of the ratio between the effective diffusivity of a tracer in two-phase flow and the same at liquid-full operation.[17,24] With regard to high pressure operation, the increase in gas–liquid interfacial drag causes an increase in the catalyst wetting efficiency.[25] Ring and Missen[26] and Al-Dahhan and Dudukovic,[25,27] also employing tracer techniques, developed a model-based correlation that relates wetting efficiency to liquid phase Reynolds and Galileo numbers and a dimensionless pressure gradient.

The objective of the present research was to study the competitive hydrogenation of the aromatic components of an anthracene oil fraction in a trickle bed reactor. The influence of the fraction of external catalyst area contacted by flowing liquid on the effectiveness factor has been estimated by employing first order kinetic constants previously determined under similar conditions by Rosal *et al.*[14] Wetting efficiencies were determined from the correlation of Al-Dahhan and Dudukovic.[27] In a previous work, it was considered that a certain fraction of the catalyst surface was wetted by stagnant liquid and therefore did not participate in the chemical reaction. This assumption reconciled the observed discrepancies between wetting efficiencies calculated by correlations developed from tracer data and those obtained by the chemical method. The latter were obtained from the hydrogenation of the anthracene contained in an anthracene oil fraction.[28] The data presented here were consistent with the unit fraction of inactive surface calculated in the aforementioned work. Reaction rates were calculated as a weighted average of the contributions of the externally wetted and dry surfaces of the catalyst and effectiveness factors were hence estimated for each zone. The results showed that the effectiveness factors for the liquid-covered surface followed a trend in good agreement with the theoretical predictions based on the estimated Thiele moduli. For increasing reactant molecular weight, an increase in the effectiveness factor was observed for the wetted surface that ranged from $\eta_L = 0{\cdot}40$ for naphthalene to $\eta_L = 0{\cdot}96$ for fluoranthene and probably unity for pyrene. For the gas-covered side, the effectiveness factors were high for the lighter compounds in the oil and decreased for low volatile reactants. For the hydrogenation of phenanthrene and the heavier compounds, the effectiveness factor for the gas-covered surface was lower than that for the wetted surface, an effect that was attributed to the difficulty in establishing complete vapor–liquid equilibrium for low volatile compounds.

2 EXPERIMENTAL

2.1 Materials and analyses

The liquid fed to the reactor consisted of 20 wt% of a light fraction of anthracene oil dissolved in toluene (purity >99·5%). Anthracene oil was supplied by NalonChem (Asturias, Spain), and Table 1 lists its main identified components. The catalyst employed was an NiO–MoO$_3$ on γ-Al$_2$O$_3$. The original form was 1/16 in. extrudates that were crushed and sieved to get 360–500 μm powder. The chemical and physical properties of the catalyst in oxidized form are given in Table 2. Textural properties were determined by nitrogen adsorption employing a Micromeritics ASAP 2000 apparatus and following standard procedures.

The analysis of feed and liquid product samples was performed by GC in a Hewlett-Packard 5890 chromatograph. A 30 m long, 0·25 mm i.d. fused silica column with a 0·5 μm film thickness non-polar stationary phase (SE-30) was employed. Peak assignment was performed by GC–MS in a Hewlett-Packard 5987A apparatus. Further details on the analytical method and the composition of raw and hydrogenated anthracene oil can be found in previous works.[29,30]

2.2 Experimental equipment and procedure

Experiments were carried out with a cocurrent downflow high-pressure trickle bed reactor. This consisted of

TABLE 1
Concentration of the Main Identified Compounds in the Anthracene Oil (wt%)

Indane	0·4	Methylfluorene	0·6
Naphthalene	2·8	Dibenzothiophene	1·2
2-Methylnaphthalene	0·9	Phenanthrene	15·2
1-Methylnaphthalene	0·4	Anthracene	5·2
Biphenyl	0·3	Carbazole	3·7
2-Ethylnaphthalene	0·2	Methylanthracene	0·9
1-Ethylnaphthalene	0·1	Methylphenanthrene	1·2
Dimethylnaphthalene	0·1	Cyclopenta[*def*]phenanthrene	1·5
Acenaphthene	4·1	2-Phenylnaphthalene	0·5
Dibenzofuran	2·4	Fluoranthene	8·6
Fluorene	4·0	Pyrene	4·9
Methylbiphenyl	0·5	Methylpyrene	1·4
Methyldibenzofuran	0·4	Benzofluorene	1·4
9,10-Dihydroanthracene	0·6	Chrysene	1·8

a stainless steel tube of 9 mm i.d. and 450 mm length that was placed inside an electrically heated furnace. The catalyst (2·4 g) was charged in the central zone of the reactor and was diluted with low area inert alumina of the same granulometry (Jansen). The reaction zone was 40 mm in length and both above and below it the reactor was also filled with alumina. The temperature of the bed was monitored by five thermocouples located at different reactor heights. The temperature of the catalyst bed, in the center of the reactor, was controlled by a PID Honeywell instrument. The flow rate of hydrogen fed to the system was regulated by a Brooks 5850TR/X-5879E mass flow meter and controller. The liquid feed containing the anthracene oil was pumped into the reactor by a Kontron LC T-414 pump. A Tescom back pressure regulator kept the pressure inside the line at the desired level. A 1000 cm^3 stainless steel cylinder served as a reactor effluent reservoir and a gas liquid separator. Samples were withdrawn from the reservoir by means of a two-valve system.

The hydrogenation reactions were carried out at 623 K and a total pressure of 9·8 MPa. A hydrogen flow of $4{\cdot}0 \times 10^{-3}$ dm^3 s^{-1} measured at standard temperature and pressure was employed for all runs. The liquid flow rate at room conditions varied between 5·0 and $33{\cdot}3 \times 10^{-6}$ dm^3 s^{-1}. The superficial velocities of liquid and gas at reaction pressure and temperature were calculated as indicated below. Prior to startup, the catalyst was presulfided *in situ* by passing a mixture of 10% of H_2S in H_2 over it at 673 K during 4 h at a flow rate of $5{\cdot}0 \times 10^{-4}$ dm^3 (NTP) s^{-1}. Additionally, 1·0 wt% CS_2 was added to the liquid to keep the catalyst in the sulfided form. A catalyst break-in period was observed which was always below 10 h. The results reported in this work corresponded to the period of steady activity that followed the break-in and preceded the beginning of deactivation. Finally, the interface temperature gradient was estimated following Herskowitz and Smith.[31] Even for the most unfavorable conditions, the calculated temperature difference was less than 1·5 K.

TABLE 2
Summary of the Main Catalyst Properties

Chemical composition (wt%):	
NiO	2·8
MoO_3	13·5
Na_2O	0·04
Physical characteristics:	
Surface area, BET (m^2 g^{-1})	171
Pore volume less than 1460 Å (cm^3 g^{-1})	0·48
Pore volume BJH ads. 17 to 3000 Å (cm^3 g^{-1})	0·49
Mean pore diameter (Å)	110

3 RESULTS AND DISCUSSION

The concentration of hydrogen can be expressed as a function of the inlet molar flow rate of hydrogen, $N_{\mathrm{HYD,O}}$, the vapor to feed molar ratio, λ, the vapor–liquid equilibrium relationship, Π_{HYD}, and the superficial liquid and gas velocities at reaction conditions. The calculation of these variables is described below and additional details may be found elsewhere.[28] The concentrations of hydrogen in the gas and liquid are given by the following expressions:

$$C_{\mathrm{HYD,G}} = \frac{4N_{\mathrm{HYD,O}}}{\pi v_{\mathrm{G}} d_{\mathrm{r}}^2 \varepsilon}\left[\frac{1+\lambda(\Pi_{\mathrm{HYD}}-1)}{\lambda\Pi_{\mathrm{HYD}}}\right] \qquad (1)$$

$$C_{\mathrm{HYD,L}} = \frac{4N_{\mathrm{HYD,O}}}{\pi v_{\mathrm{L}} d_{\mathrm{r}}^2 \varepsilon}\left[\frac{1+\lambda}{1+\lambda(\Pi_{\mathrm{HYD}}-1)}\right] \qquad (2)$$

It has been calculated that the concentration of hydrogen in the liquid phase remained essentially constant. Due to the large excess of hydrogen employed, the calculated concentration of hydrogen in the vapor phase was also almost constant for all the experimental range. Reaction rates were assumed to be first order with respect to the reactant hydrocarbons and zero order with respect to hydrogen. The derivation of second order kinetics, performed for example in the mentioned work of Llano *et al.*[28] and by Ruecker and Akgerman,[32] did not introduce any significant improvement due to the relatively narrow range of variation of vapor to liquid ratio at the reaction conditions employed in this work. The reaction rate in a trickle bed reactor may be written as a function of the rates on the liquid and vapor covered surface of the catalyst

$$r = fr_{\mathrm{L}} + (1 - f)r_{\mathrm{G}} \tag{3}$$

It was assumed that the external wetting efficiency, f, was essentially constant throughout the reactor. As the concentration of hydrogen remains constant, the rate expression becomes:

$$r = f\eta_{\mathrm{L}} k_{\mathrm{L}} C_{\mathrm{A,L}} + (1 - f)\eta_{\mathrm{G}} k_{\mathrm{G}} C_{\mathrm{A,G}} \tag{4}$$

The concentration of any hydrocarbon in gas and liquid phase may be expressed as a function of its inlet molar flow rate, $N_{\mathrm{A,O}}$ and the vapor–liquid equilibrium relationship, Π_{A}. The hydrocarbon was the limiting reactant and therefore N_{A} has been substituted by a function of its conversion $N_{\mathrm{A,O}}(1 - x_{\mathrm{A}})$:

$$C_{\mathrm{A,L}} = \frac{4(1 - \lambda)\alpha_{\mathrm{A}} N_{\mathrm{A,O}}(1 - x_{\mathrm{A}})}{\pi v_{\mathrm{L}} d_{\mathrm{r}}^{2} \varepsilon} \tag{5}$$

$$C_{\mathrm{A,G}} = \frac{4\lambda \Pi_{\mathrm{A}} \alpha_{\mathrm{A}} N_{\mathrm{A,O}}(1 - x_{\mathrm{A}})}{\pi v_{\mathrm{G}} d_{\mathrm{r}}^{2} \varepsilon} \tag{6}$$

where:

$$\alpha_{\mathrm{A}} = \frac{1}{1 - \lambda(1 - \Pi_{\mathrm{A}})} \tag{7}$$

The values of the liquid–vapor equilibrium relationship, Π_{A}, were determined by the method of Grayson and Streed[33] which is based on the correlation of Chao and Seader.[34] A mass balance allowed λ to be calculated from the inlet molar flow and the values of Π_{A} for hydrogen, hydrogen sulfide and all the hydrocarbons in the mixture. The viscosity of the liquid phase and the superficial liquid and gas velocities were calculated by means of the corresponding states principle employing methane as a reference. The gas–liquid surface tension was determined by the Macleod–Sugden expression as indicated by Reid *et al.*[35]

The determination of the external wetting efficiency for the same system at 573 K and 9·8 MPa has been described previously.[28] The values obtained in this work showed a systematic deviation from wetting efficiencies calculated from the available correlations that employ physical properties evaluated in reaction conditions.[26,27] Figure 1 plots the external wetting efficiencies obtained by Llano *et al.*[28] and those calculated from the correlation of Al-Dahhan and Dudukovic[27] for the same conditions. The correlation of Al-Dahhan and Dudukovic allowed the wetting efficiencies for the reaction conditions employed in this work to be calculated. The results, shown in Fig. 1; follow and partially overlap those obtained at 573 K when plotted as a function of superficial liquid mass flow rate. The discrepancy between wetting efficiencies obtained by the chemical reaction method and those derived from correlations based on pulse-tracer data might be explained if it is assumed that a certain fraction of the catalyst surface did not participate in the chemical reaction. This effect may be attributed to the existence of a stagnant liquid holdup that accumulated at the contact points between bed particles. The estimation of this holdup was carried out by means of the correlation proposed by Sáez *et al.*[36] for low Eötvös numbers. A quantitative insight into this phenomenon was first made by Sicardi *et al.*[24] who presented a geometrical model to calculate the fraction of surface wetted by static holdup, f_{s}. The packing was represented by a regular array of equal spheres with a number (n) of contact points where stagnant liquid accumulates. It was assumed that still liquid accumulated wherever two spheres are physically in contact and that stagnant zones do not overlap. Llano *et al.*[28] concluded that this model yields very high values for f_{s}. They proposed that the bed may be represented by a random packing of equal spheres in which a given particle is characterized by a given mean number of total contacts, some of which are close contacts, the rest being near contacts.[37] The consideration of this effect thus indicated lead to a reparameterization

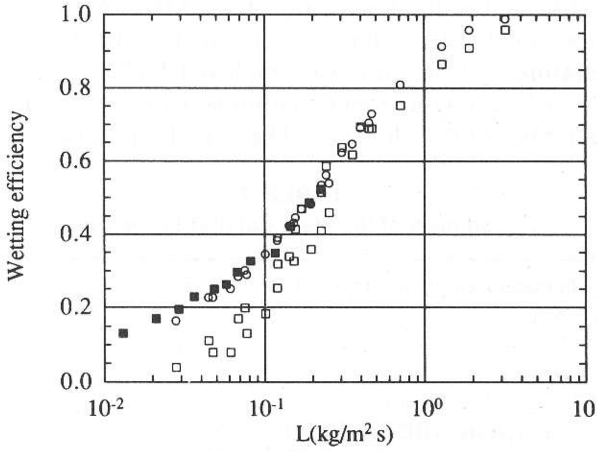

Fig. 1. External wetting efficiencies derived from the correlation of Al-Dahhan and Dudukovic[27] for this work (■) and for the data taken at 573 K by Llano *et al.*[28] (○) and experimental wetting efficiencies obtained at 573 K by Llano *et al.* (□).

in the weighted average expression of the reaction rate that excludes the chemically inactive surface:

$$f = \frac{f_{\mathrm{td}} - f_{\mathrm{s}}}{1 - f_{\mathrm{s}}} \tag{8}$$

From the data shown in Fig. 1, Llano *et al.* calculated a value of $f_s = 0{\cdot}16$ for the unit fraction of inactive surface.[28] As the wetting efficiencies calculated for the reaction conditions employed in this work follow the same trend as those obtained previously, it was considered that the stagnant liquid covers the same fraction of surface. Assuming plug flow, the reaction rate may be expressed as a function of the hydrocarbon conversion:

$$r = N_{\mathrm{A,\,O}} \frac{\mathrm{d}x_{\mathrm{A}}}{\mathrm{d}W} \tag{9}$$

The estimation of model parameters, $\eta_{\mathrm{L}} k_{\mathrm{L}}$ and $\eta_{\mathrm{G}} k_{\mathrm{G}}$, was based on the minimization of the following determinant:[38]

$$\begin{aligned}\det(B) &= \det(b_{ij}) \\ &= \det\left[\sum_{k=1}^{n} (y_{ki} - y_{\mathrm{t},\,ki})(y_{kj} - y_{\mathrm{t},\,kj})\right]\end{aligned} \tag{10}$$

where i and j extend to the number of dependent variables, i.e. the number of observed concentrations in the proposed model. Differential equations were integrated by means of a fourth order Runge–Kutta algorithm and minimization of the determinant B was performed using a Simplex optimization routine. Confidence intervals were obtained from the α-probability level confidence surface given by:

$$\det(b_{ij}) = \det(b_{ij})_{\min}[\exp \chi^2(s - 1, 1 - \alpha)/n] \tag{11}$$

where s is the number of different observed responses and $\det(b_{ij})_{\min}$ the minimum value of the objective determinant.[39]

Under the experimental reaction conditions employed in this work, the components of the anthracene oil that hydrogenated to a certain measurable degree were naphthalene (NAP), acenaphthene (ACE), anthracene (ANT), phenanthrene (PHE), fluoranthene (FLU) and pyrene (PYR). Some other compounds, such as cyclopenta[def]phenanthrene, methylanthracene or methylphenanthrene, also hydrogenated. However, their low concentration and consequently the difficulty in obtaining reliable chromatographic data impeded any quantitative analysis. The hydrogenation products that were quantified were tetralin (TET) and *cis*- and *trans*-decalin from naphthalene; 2*a*,3,4,5-tetrahydroacenaphthene (THAC) from acenaphthene; 9,10-dihydrophenanthrene (DHP), 1,2,3,4-tetrahydrophenanthrene (THP) and *sym*- and *asym*-octahydrophenanthrene (OHP) from phenanthrene; 9,10-dihydroanthracene (DHA), 1,2,3,4-tetrahydroanthracene (THAN) and *sym*- and *asym*-octahydroanthracene (OHA) from anthracene; 1,2,3,10*b*-tetrahydrofluoranthene (THFL) from fluoranthene and 4,5-dihydropyrene (DHPY) from pyrene. For the hydrogenation of phenanthrene, anthracene, fluoranthene and pyrene, the material balance indicated the amount of hydrogenated compounds other than those mentioned above that had been produced. In what follows, the hydrogenated compounds or ring opening products whose concentration was not measured will be denoted as 'other.' In the case of naphthalene, tetralin and the two isomers of decalin accounted for all the material balance closure. The best fit of the data was obtained considering a reversible reaction between naphthalene and tetralin. The hydrogenation of tetralin to decalin was not considered in the model because the kinetic parameters obtained were not significantly different from zero. This was due to the low amount of decalin produced, as shown in Fig. 2. Acenaphthene and THAC attained a good material balance closure indicating that THAC did not react to any appreciable extent. With regards to phenanthrene, the concentrations of DHP, THP and the isomers of OHP were lumped together into a single compound whose concentration was considered to decay following a first order irreversible reaction to yield other hydrogenated compounds. The reason for this was the complex network required for a complete description of the interconversion reactions and the elevated number of parameters involved that impeded the obtention of statistically significant kinetic constants. The same procedure was employed for anthracene by lumping together DHA, THAN and OHA in a single intermediate. The only hydrogenated compound identified from fluoranthene was THFL, but the material balance did not close only with FLU and THFL, but required a reaction that

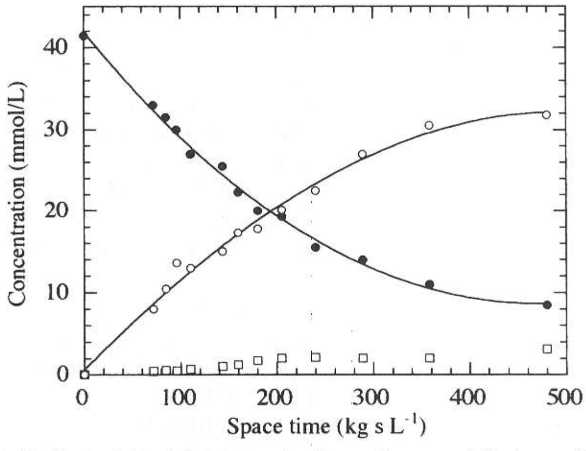

Fig. 2. Experimental concentrations for naphthalene (●), tetralin (○) and decalin (□) as a function of space time and calculated profiles for naphthalene and tetralin.

yielded other reaction products. The case of pyrene was similar except for the fact that a consecutive reaction network did not adequately represent the obtained concentration data of PYR and DHPY. A model considering two hydrogenation reactions of pyrene in parallel was found to closely fit the experimental data. The unidentified compounds represented by 'other' were probably *sym*- and *asym*-hexahydropyrene as indicated by Girgis and Gates[13] and Korre *et al.*[15] who also proposed a parallel reaction scheme.

The simplified reaction scheme proposed in this work is shown below, where the compounds indicated in bold represent those whose concentrations were experimentally determined. Table 1 lists all parameter estimates with their corresponding 95% confidence intervals.

NAP ⇄ **TET**

ACE → **THAC**

PHE → [**DHP** + **THP** + **OHP**] → OTHER

ANT → [**DHA** + **THAN** + **OHA**] → OTHER

FLU → **THFL** → OTHER

PYR ↗**DHPY**
↘OTHER

The concentration profiles of naphthalene, tetralin and decalin are shown in Fig. 2 as a function of the inverse space velocity expressed in kg of catalyst s dm^3 of liquid feed^{-1}. From the data obtained in this work it was not possible to determine intrinsic rate constants or efficiency factors unless an estimation of either of them is provided. Rosal *et al.*[14] hydrogenated a light fraction of anthracene oil employing a similar catalyst and obtained kinetic constants and activation energies for the hydrogenation of naphthalene, acenaphthene, phenanthrene, anthracene, fluoranthene and pyrene. Their experiments were performed over an experimental range of temperature and pressure that included the conditions employed in this work. The reaction rate obtained by these authors for the hydrogenation of naphthalene at 623 K and 9·8 MPa was $k_L = 2{\cdot}1 \times 10^{-3}$ dm^3 s^{-1} kg^{-1}. The effectiveness factor would be then $\eta_L = 0{\cdot}4$ for the liquid-covered surface of the catalyst. For the gas-covered surface, an estimation of the effectiveness factor requires rewriting the reaction rate as a function of Henry's law constant that leads to: $k_L = k_G H_A$. The values of Henry's law constant changed somewhat throughout the experimental range due to the variation in λ. For this reason, only a range of variation could be estimated for η_G. The effectiveness factor for the gas-covered surface was calculated by means of eqns (3) and (4), which yielded H_A, and the mentioned value of k_L from the work of Rosal *et al.*[14] For naphthalene hydrogenation $\eta_G > 0{\cdot}9$, indicating that the reaction took place preferably on the gas-covered surface. This revealed that the gas-covered portion of the catalyst was more efficient so that a decrease in wetting efficiency led to an increase in the overall efficiency factor: $\eta_{TB} = f\eta_L + (1-f)\,\eta_G$. Rosal *et al.*[14] fitted the data of naphthalene hydrogenation to a first order irreversible reaction. This was possible because their experiments were performed at relatively low conversion in comparison with those presented in this work and therefore no information could be obtained on effectiveness factors for the reverse reaction of tetralin dehydrogenation.

TABLE 3
Parameter Estimates for the Proposed Models (k_i in dm^3 s^{-1} kg of catalyst^{-1})

NAP → TET (NAP ⇄ TET)	TET → NAP (NAP ⇄ TET)
$\eta_L k_L = 8{\cdot}45 \times 10^{-4} \pm 4{\cdot}9 \times 10^{-5}$	$\eta_L k_L = 1{\cdot}93 \times 10^{-2} \pm 6{\cdot}9 \times 10^{-3}$
$\eta_G k_G = 3{\cdot}57 \times 10^{-2} \pm 8{\cdot}4 \times 10^{-3}$	$\eta_G k_G = 8{\cdot}4 \times 10^{-1} \pm 2{\cdot}6 \times 10^{-1}$
ACE → THAC	
$\eta_L k_L = 1{\cdot}32 \times 10^{-3} \pm 7{\cdot}6 \times 10^{-4}$	
$\eta_G k_G = 7{\cdot}31 \times 10^{-2} \pm 4{\cdot}7 \times 10^{-3}$	
PHE → DHP + THP + OHP	DHP + THP + OHP → OTHER
$\eta_L k_L = 1{\cdot}52 \times 10^{-3} \pm 3{\cdot}5 \times 10^{-4}$	$\eta_L k_L = 8{\cdot}53 \times 10^{-4} \pm 3{\cdot}05 \times 10^{-4}$
$\eta_G k_G = 9{\cdot}37 \times 10^{-2} \pm 4{\cdot}5 \times 10^{-3}$	$\eta_G k_G = 1{\cdot}34 \times 10^{-2} \pm 3{\cdot}6 \times 10^{-3}$
ANT → DHA + THAN + OHA	DHA + THAN + OHA → OTHER
$\eta_L k_L = 1{\cdot}74 \times 10^{-2} \pm 1.6 \times 10^{-3}$	$\eta_L k_L$ n.d.[a]
$\eta_G k_G = 1{\cdot}38 \times 10^{-1} \pm 1{\cdot}7 \times 10^{-2}$	$\eta_G k_G = 3{\cdot}98 \times 10^{-2} \pm 3{\cdot}1 \times 10^{-3}$
FLU → THFL	THFL → OTHER
$\eta_L k_L = 5{\cdot}99 \times 10^{-3} \pm 4{\cdot}6 \times 10^{-4}$	$\eta_L k_L = 1{\cdot}23 \times 10^{-2} \pm 1{\cdot}7 \times 10^{-3}$
$\eta_G k_G = 1{\cdot}82 \times 10^{-1} \pm 1{\cdot}8 \times 10^{-2}$	$\eta_G k_G = 2{\cdot}49 \times 10^{-1} \pm 3{\cdot}5 \times 10^{-2}$
PYR → DHPY	PYR → OTHER
$\eta_L k_L = 1{\cdot}01 \times 10^{-3} \pm 0{\cdot}3 \times 10^{-4}$	$\eta_L k_L = 1{\cdot}22 \times 10^{-3} \pm 2{\cdot}2 \times 10^{-4}$
$\eta_G k_G = 1{\cdot}52 \times 10^{-2} \pm 7{\cdot}7 \times 10^{-4}$	$\eta_G k_G = 2{\cdot}54 \times 10^{-2} \pm 6{\cdot}3 \times 10^{-3}$

[a] Not determined: this parameter was not significantly different from zero.

Korre *et al.*[15] determined the reaction network for pure naphthalene hydrogenation as well as in a mixture with several hydrocarbons in cyclohexane at 623 K. They found that the rate constant for the dehydrogenation of tetralin was two orders of magnitude higher than that for the hydrogenation of naphthalene ($k_{\mathrm{NAP \to TET}} = 0{\cdot}358\ \mathrm{dm^3\ s^{-1}\ kg^{-1}}$, $k_{\mathrm{TET \to NAP}} = 38{\cdot}2\ \mathrm{dm^3\ s^{-1}\ kg^{-1}}$). These relatively high values refer to the hydrogenation of ~ 5 wt% in cyclohexane and considerable inhibition was observed in mixtures with other hydrocarbons, especially with the presence of three- and four-ring compounds. In this work, the relationship between $\eta_L k_{\mathrm{L(TET \to NAP)}}$ and $\eta_L k_{\mathrm{L(NAP \to TET)}}$ was about 20, lower than that obtained by Korre *et al.*[15] This probably revealed a low efficiency factor for the dehydrogenation of tetralin ($\eta_L < 0{\cdot}1$).

With regards to the hydrogenation of acenaphthene, phenanthrene, anthracene and fluoranthene, a similar approach has been carried out to that based upon the intrinsic kinetic data previously obtained by Rosal *et al.*[14] Figures 3–8 show the experimental concentrations of the aromatic reactants and the determined reaction products whenever the profile was calculated. The kinetic constants reported by the mentioned authors were: $k_{\mathrm{L(ACE \to THAC)}} = 1{\cdot}98 \times 10^{-3}$, $k_{\mathrm{L(PHE \to DHP+THP+OHP)}} = 2{\cdot}02 \times 10^{-3}$, $k_{\mathrm{L(ANT \to DHA+THAN+OHA)}} = 7{\cdot}47 \times 10^{-2}$, $k_{\mathrm{L(FLU \to THFL)}} = 6{\cdot}21 \times 10^{-3}$, all of these expressed in $\mathrm{dm^3\ s^{-1}\ kg\ of\ catalyst^{-1}}$. Combining these results

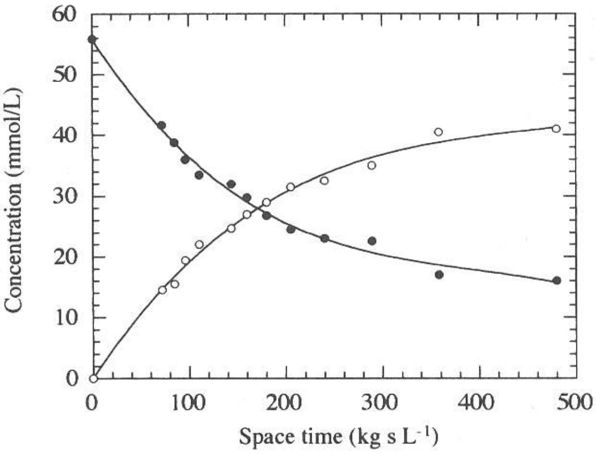

Fig. 3. Concentration profiles for acenaphthene (●) and THAC (○).

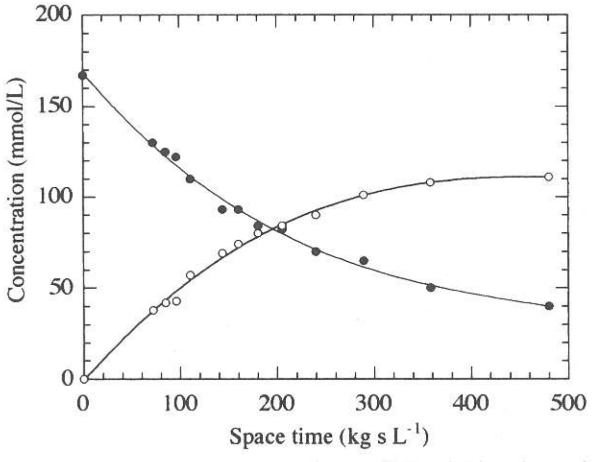

Fig. 4. Experimental concentrations and calculated profiles for phenanthrene (●) and DHP + THP + OHP (○).

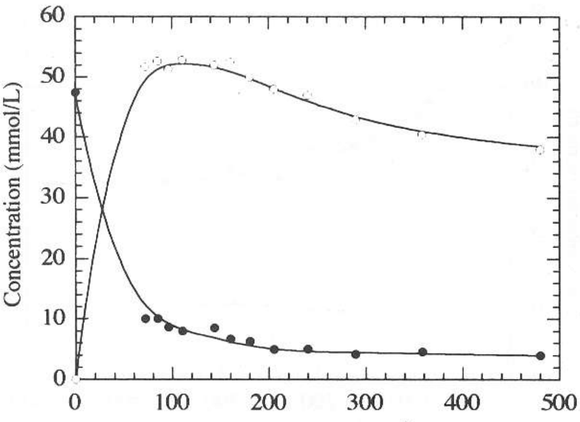

Fig. 5. Experimental concentrations and calculated profiles for anthracene (●) and DHA + THAN + OHA (○).

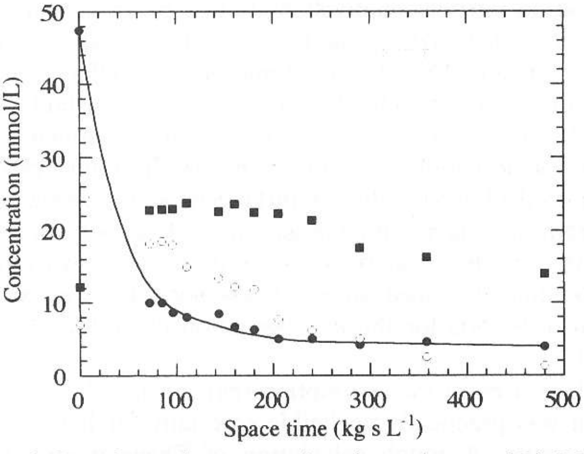

Fig. 6. Experimental concentrations for anthracene (●), DHA (○), and THAN (■) as a function of space time and calculated profile for anthracene.

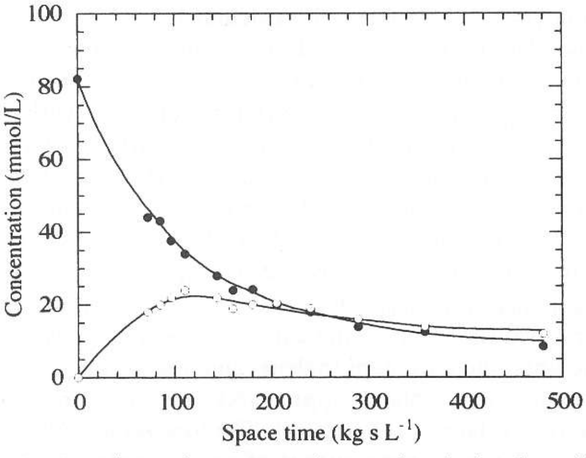

Fig. 7. Experimental concentrations and calculated profiles for fluoranthene (●) and THFL (○).

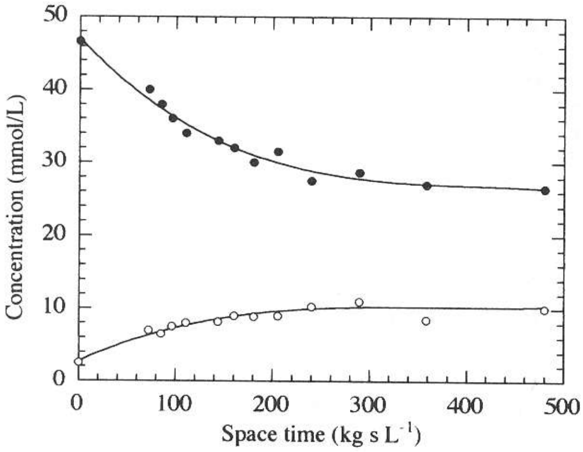

Fig. 8. Experimental concentrations and calculated profiles for pyrene (●) and DHPY (○).

with the values of $\eta_L k_L$ obtained in this work, the following estimations of the effectiveness factors for the wetted surface have been made: $\eta_{L(ACE \rightarrow THAC)} = 0{\cdot}67$, $\eta_{L(PHE \rightarrow DHP+THP+OHP)} = 0{\cdot}75$, $\eta_{L(ANT \rightarrow DHA+THAN+OHA)} = 0{\cdot}23$, $\eta_{L(FLU \rightarrow THFL)} = 0{\cdot}96$. The effectiveness factor η_L showed low values for anthracene, whose hydrogenation rate was relatively high. In a previous work, it was reported that for the hydrogenation of anthracene at 573 K and 9·8 MPa an estimation of the effectiveness factor was $\eta_L = 0{\cdot}40$ for a rate constant of $2{\cdot}83 \times 10^{-2}$ dm^3 s^{-1} kg^{-1}. At 573 K it was shown that the reaction took place preferably in the liquid phase due to the low volatility of anthracene which yielded an effectiveness factor for the gas-covered surface approximately in the range $0{\cdot}05 < \eta_G < 0{\cdot}22$.[28] Following the procedure described above, it was possible to estimate that $\eta_G \sim 0{\cdot}05$ for the hydrogenation of anthracene at 623 K.

This stressed the assumption that the gas phase reaction was practically negligible especially for high reaction rates. A rough calculation of Thiele moduli for both temperatures with the assumption that D_A varied from 10^{-5} to 10^{-6} [40] indicated that ϕ doubled from 573 K to 623 K with $1{\cdot}5 < \phi < 4{\cdot}0$ for 573 K. By employing these values, the calculated trickle bed efficiency factors were in good agreement with the experimental values presented in this work. The efficiency factors η_L increased for similar reaction rates with the molecular weight of the aromatic hydrocarbon, which is the expected behavior considering that D_A is greater for heavier compounds. With regards to the efficiency factors for the gas-covered surface, the following estimations were carried out: $\eta_{G(ACE \rightarrow THAC)} > 0{\cdot}8$, $\eta_{G(PHE \rightarrow DHP+THP+OHP)} > 0{\cdot}5$, $0{\cdot}1 < \eta_{G(FLU \rightarrow THFL)} < 0{\cdot}4$. These values seem to indicate that for relatively light reactants such as naphthalene and acenaphthene, the reaction takes place appreciably through the gas-covered surface of the catalyst. The low values obtained for η_G may be a consequence of an incomplete internal wetting of the part of the catalyst that is covered by vapor as shown by Dudukovic[20] or may reflect the fact that vapor–liquid equilibrium was not completely established all over the reactor.

The work of Rosal *et al.*[14] showed that good mass balance closure was attained by considering that DHPY was the only reaction product. Due to the different reaction path employed with regard to that of Rosal *et al.*,[14] only a guess of the effectiveness factors may be formulated. As in the mentioned work $k_{L(PYR \rightarrow DHPY)} = 5{\cdot}62 \times 10^{-4}$ dm^3 s^{-1} kg^{-1}, the effectiveness factor for the wetted surface of the catalyst was probably near unity, whereas for the gas-covered part it was similar to that of fluoranthene. Figure 7 shows the experimental concentrations of pyrene and DHPY and their calculated profiles as a function of the space time.

4 CONCLUSIONS

The hydrogenation of the main components of an anthracene oil was carried out in a trickle bed reactor with the purpose of obtaining information on the effectiveness factors both for the externally wetted and dry zones of the catalyst. The conversion data allowed us to calculate the product of the intrinsic kinetic constant and the effectiveness factor for the reactions included in the network. The reaction pathways were designed with the aim of comparing the fitting constants with rate constants previously determined by Rosal *et al.*[14] for the first hydrogenation step of the same compounds in similar conditions. The wetting efficiency was calculated by employing the correlation developed for high pressure trickle bed reactors by Al-Dahhan and Dudukovic.[27] It was assumed that the reaction rate can be expressed as a weighted average of the rates on the external liquid- and gas-covered catalyst surfaces with external wetting efficiencies as weighting factors.

The results reported here in combination with the intrinsic reaction constants obtained from the work of Rosal *et al.*[14] permitted the evaluation of effectiveness factors for the liquid- and gas-covered surface of the catalyst. The results showed that, for the hydrogenation of anthracene, for which the Thiele modulus was especially high, the effectiveness factor for the wetted surface was $\eta_L = 0{\cdot}23$, whereas for the rest of the hydrogenation reactions $\eta_L > 0{\cdot}4$. The effectiveness factor for the liquid-covered surface increased as expected with increasing reactant molecular weight. For the gas-covered surface, an estimation of the effectiveness factors allowed us to conclude that the lighter compounds reacted preferentially on the externally dry surface for which a lower mass transfer limitation existed. For heavier compounds, the observed decrease in the effectiveness factor was probably due to the fact that vapor–liquid equilibria were not established at the dry zone gas–liquid interface. In the case of anthracene, whose reaction rate was relatively high, the system approached a liquid phase depletion of a nonvolatile reactant. However, the reaction rate on the gas-covered surface of the catalyst could not be ignored in any case.

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REFERENCES

1. Moreau, C. & Geneste, P., Factors affecting the reactivity of organic model compounds. In *Hydrotreating Reactions, Theoretical Aspects of Heterogeneous Catalysts*, ed J. Moffat. van Nostrand Reinhold, New York, 1990, pp. 256–306.
2. Girgis, M. J. & Gates, B. C., Reactivities, reaction networks, and kinetics in high pressure catalytic hydroprocessing. *Ind. Eng. Chem. Res.*, **30** (1991) 2021–58.
3. Sapre, A. V. & Gates, B. C., Hydrogenation of aromatic hydrocarbons catalyzed by sulfided $CoO–MoO_3/Al_2O_3$. Reactivities and reaction networks. *Ind. Eng. Chem. Process Des. Dev.*, **20** (1981) 68–73.
4. Huang, T. C. & Kang, B. C., Naphthalene hydrogenation over Pt/Al_2O_3 catalyst in a trickle bed reactor. *Ind. Eng. Chem. Res.*, **34** (1995) 2349–57.
5. Huang, T. C. & Kang, B. C., The hydrogenation of naphthalene with platinum/alumina–aluminum phosphate catalysts. *Ind. Eng. Chem. Res.*, **34** (1995) 2955–63.
6. Wiser, W. H., Singh, S., Qader, S. A. & Hill, G. R., Catalytic hydrogenation of multiring aromatic coal tar constituents. *Ind. Eng. Chem. Prod. Res. Dev.*, **9** (1972) 350–6.
7. Wiser, W. H., *Chemistry and Catalysis of Coal Liquefaction: Catalytic and Thermal Upgrading of Coal Liquid and Hydrogenation of CO to Produce Fuels.* DOE Report DOE/ET/14700-9, Department of Energy, Washington DC, 1982, pp. 39–41.
8. Shabtai, J., Velusmany, L. & Oblad, A. G., Steric effects in phenanthrene and pyrene hydrogenation catalyzed sulfided $Ni–W/Al_2O_3$. *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, **23** (1978) 107–13.
9. Huang, C. S., Wang, K. C. & Haynes, H. W., Hydrogenation of phenanthrene over a commercial cobalt molybdenum sulfide catalyst under severe reaction conditions. In *Liquid Fuels from Coal*, ed. R. T. Ellington. Academic Press, New York, 1977, pp. 63–78.
10. Girgis, M. J. & Gates, B. C., Catalytic hydroprocessing of simulated heavy coal liquids. 1. Reactivities of aromatic hydrocarbons and sulfur and oxygen heterocyclic compounds. *Ind. Eng. Chem. Res.*, **33** (1994) 1098–106.
11. Lapinas, A. T., Kelin, M. T., Gates, B. C., Macris, A. & Lyons, J. E., Catalytic hydrogenation and hydrocracking of fluoranthene: reaction pathways and kinetics. *Ind. Eng. Chem. Res.*, **26** (1987) 1026–33.
12. Stephens, H. P. & Kottenstette, R. J., The kinetics of catalytic hydrogenation of pyrene: implications for direct coal liquefaction processing. *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, **28** (1983) 161–70.
13. Girgis, M. & Gates, B. C., Catalytic hydroprocessing of simulated heavy coal liquids. 2. Reaction networks of aromatic hydrocarbons and sulfur and oxygen heterocyclic compounds. *Ind. Eng. Chem. Res.*, **33** (1994) 2301–13.
14. Rosal, R., Díez, F. V. & Sastre, H., Catalytic hydrogenation of multiring aromatic hydrocarbons in a coal tar fraction. *Ind. Eng. Chem. Res.*, **31** (1992) 1007–12.
15. Korre, S. C., Klein, M. T. & Quann, R. J., Polynuclear aromatic hydrocarbons hydrogenation. 1. Experimental reaction pathways and kinetics. *Ind. Eng. Chem. Res.*, **34** (1995) 101–17.
16. Mills, P. L. & Dudukovic, M. P., Evaluation of liquid–solid contacting in trickle-bed reactors by tracer methods. *AIChE J.*, **27** (1981) 893–904 and Erratum, **28** (1982) 526.
17. Colombo, A. J., Baldi, G. & Sicardi, S., Solid–liquid contacting effectiveness in trickle-bed reactors. *Chem. Eng. Sci.*, **31** (1976) 1101–8.
18. Herskowitz, M., Carbonell, R. G. & Smith, J. M., Effectiveness factors and mass transfer in trickle-bed reactors. *AIChE J.*, **25** (1979) 272–83.
19. Tan, C. S. & Smith, J. M., Catalyst particle effectiveness with unsymmetrical boundary conditions. *Chem. Eng. Sci.*, **35** (1980) 1601–9.
20. Dudukovic, M. P., Catalyst effectiveness factor and contacting efficiency in trickle-bed reactors. *AIChE J.*, **23** (1977) 940–4.
21. Harold, M. P. & Ng, K. N., Effectiveness enhancement and reactant depletion in a partially wetted catalyst. *AIChE J.*, **33** (1987) 1448–65.
22. Sakornwimon, W. & Sylvester, N. D., Effectiveness factors for partially wetted catalysts in trickle-bed reactors. *Ind. Eng. Chem. Process Des. Dev.*, **21** (1982) 16–25.
23. El-Hisnawi, A. A., Dudukovic, M. P. & Mills, P. L., Trickle-bed reactors: dynamic tracer tests, reaction studies and modeling of reactor performance. *ACS Symp. Ser.* No. 196, 1982, pp. 421–40.
24. Sicardi, S., Baldi, G., Gianetto, A. & Specchia, V., Catalyst areas wetted by flowing and semistagnant liquid in trickle-bed reactors. *Chem. Eng. Sci.*, **35** (1980) 67–73.
25. Al-Dahhan, M. & Dudukovic, M. P., Pressure drop and liquid holdup in high pressure trickle-bed reactors, *Chem. Eng. Sci.*, **49** (1994) 5681–98.
26. Ring, Z. E. & Missen, R. W., Trickle-bed reactors: tracer study of liquid holdup and wetting efficiency at high temperature and pressure. *Can. J. Chem. Eng.*, **69** (1991) 1016–20.
27. Al-Dahhan, M. & Dudukovic, M. P., Catalyst wetting efficiency in trickle-bed reactors at high pressure. *Chem Eng. Sci.*, **50** (1995) 2377–89.
28. Llano, J. J., Rosal, R., Sastre, H. & Díez, F. V., Determination of wetting efficiency for the hydrogenation of anthracene in a trickle bed reactor. *Ind. Eng. Chem. Res.*, **36** (1997) 2616–25.
29. Rosal, R., Díez, F. V. & Sastre, H., Estimation of the concentration of hydroaromatic compounds in a hydrogenated anthracene oil. *Fuel*, **71** (1992) 761–5.
30. Llano, J. J., Rosal, R., Sastre, H. & Díez, F. V., Catalytic hydrogenation of anthracene oil with red mud. *Fuel*, **73** (1994) 688–94.
31. Herskowitz, M. & Smith, J. M., Trickle-bed reactors: a review. *AIChE J.*, **29** (1983) 1–18.
32. Ruecker, C. M. & Akgerman, A., Determination of wetting efficiencies for a trickle-bed reactor at high temperatures and pressures. *Ind. Eng. Chem. Res.*, **26** (1987) 164–6.
33. Grayson, H. G. & Streed, C. W., Vapor–liquid equilibria for high temperature, high pressure hydrogen–hydrocarbon systems. *Proceedings of the Sixth World Petroleum Congress*, Section VII, 1963, pp. 233–45.
34. Chao, K. C. & Seader, J. D., A general correlation of vapor–liquid equilibria in hydrocarbon mixtures. *AIChE J.*, **7** (1961) 598–605.

35. Reid, R. C., Prausnitz, J. M. & Poling, B. E., *The Properties of Gases and Liquids.* McGraw-Hill, New York, 1988, p. 642.
36. Sáez, A. E., Yépez, M. M., Cabrera, C. & Soria, E. M., Static liquid holdup in packed beds of spherical particles. *AIChE J.*, **37** (1991) 1733–6.
37. Bernal, J. D. & Mason, J., Coordination of randomly packed spheres. *Nature*, **188** (1960) 910–5.
38. Hunter, W. G., Estimation of unknown constants from multiresponse data. *Ind. Eng. Chem. Fundam.*, **6** (1967) 461–3.
39. Froment, G. F. & Hosten, L. H., Catalytic kinetics: modelling. In *Catalysis, Science and Technology*, Vol. 2, eds. J. R. Anderson & M. Boudart. Springer-Verlag, New York, 1981, pp. 97–170.
40. Carberry, J. J., *Chemical and Catalytic Reaction Engineering.* McGraw-Hill, New York, 1976, p. 493.