Diffusion and adsorption selectivities of hydrocarbons over FCC catalysts

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Abstract

The adsorption isotherms of hexane, toluene and decane on a commercial FCC catalyst were determined in experiments performed in a CREC Riser Simulator laboratory reactor injecting different volumes of the pure hydrocarbons at 250, 300 and 350 °C. The adsorption isotherms could be described by Langmuir expressions, and the parameters assessed from the information given by simple mass balances, showed to be in line with previous reports. The order of adsorption constants was decane > toluene > hexane. The heats of adsorption were assessed. The simulation of the evolution of the pressure in the system in short contact time experiments with an unsteady state diffusion–adsorption model that considered the influence of the concentration on diffusion, allowed to assess the diffusion parameters corresponding to diluted systems. It was observed that the mechanism for mass transfer of *n*-paraffins inside the Y zeolite pores above 250 °C is not purely configurational. Experiments with short contact times typical of the commercial FCC process showed that decane and toluene, but not hexane, were adsorbed close to equilibrium under these experimental conditions. Apparent and equilibrium adsorption, and diffusion selectivities were defined considering hexane as the reference hydrocarbon, and they clearly indicated that diffusion resistances mask the assessment of adsorption parameters. Apparent selectivities become closer to equilibrium selectivities at higher system pressures, due to increases in the effective diffusivities.
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1. Introduction

The pore systems of micro and mesoporous solid catalysts impose limitations to the mass transport processes that contact reactants and surface active sites, and affect the adsorption previous to reaction. In many of the commercial applications where the size of the reacting molecules is about the same magnitude of the pores, these restrictions on accessibility are severe and have negative consequences on the observed catalyst activity. This is specially true for the process of catalytic cracking of hydrocarbons (FCC), that is one of the key processes in refineries, aimed at the conversion of heavy feedstocks into lighter, more valuable products such as light olefins, liquefied petroleum gas (LPG), gasoline and diesel fuel.

The development of new catalyst formulations for the oil refining industry requires that the performance of commercial catalysts, that is usually determined with the help of pilot plant and/or laboratory facilities, be predicted safely, not only in terms of activity and product distributions, but also to estimate other system parameters, like adsorption constants. These parameters are useful for hardware design and process modeling and simulation. For example, it has been shown that adsorption phenomena in the FCC riser reactor strongly influence the overall hydrodynamics and reaction kinetics [1]. Besides the fact that reactant mixtures in FCC are extremely complex, an additional complexity factor is given by the competitive adsorption between hydrocarbons of various types and sulfur and nitrogen containing compounds. Moreover, in the stripping step of the process, steam is injected to desorb approximately 5–30% of the total amount of hydrocarbons that remain adsorbed after reaction, in order to avoid burning them in the regenerator [2]. However, the absence of reliable information about adsorption parameters is manifest.

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Nomenclature

b	Langmuir adsorption constant (psi^{-1})
C	local concentration in micropores ($mol\,cm^{-3}$)
C6	*n*-hexane
C10	*n*-decane
D_0	intracrystalline diffusivity at zero coverage ($cm^2\,s^{-1}$)
D_m	microporous diffusivity ($cm^2\,s^{-1}$)
D_p	matrix diffusivity ($cm^2\,s^{-1}$)
D^*	preexponential factor ($cm^2\,s^{-1}$)
E_d	activation energy of diffusion ($kJ\,mol^{-1}$)
F	dynamics effectivity factor
ΔH_{ads}	heat of adsorption ($kJ\,mol^{-1}$)
K	Henry constant ($mol\,kg^{-1}\,psi^{-1}$)
K'	dimensionless Henry constant
m	mass (g)
n	number of moles
p	pressure (atm)
q	local concentration of species adsorbed on the catalyst ($mol\,kg^{-1}$)
$\bar{q}$	volume average concentration of species adsorbed on the catalyst ($mol\,kg^{-1}$)
r	radial length dimension (cm)
r_c	zeolite particle radius (cm)
R	ideal gas constant ($atm\,L\,mol^{-1}\,K^{-1}$)
R_p	particle radius (cm)
S	adsorption selectivity
t	time (s)
T	temperature (K)
TOL	toluene
V	volume (L)
w	zeolite volume fraction

Greek letters

α	parameter defined by Eq. (24)
ε_m	zeolite void fraction
ε_p	matrix void fraction
θ	fractional coverage
τ_p	diffusion time constant in the matrix
τ_c	diffusion time constant in the zeolite

Subscripts

Cat	catalyst
gp	gas phase
i	component *i*
s	adsorption capacity at saturation
sol	solid
zeo	zeolite

Superscripts

app	apparent
dif	diffusion
eq	equilibrium
feed	feed to the reactor
0	initial

The FCC catalyst is a very complex composite, with the main component, the Y zeolite, deposited on a matrix, binders and various additives being also present [3].

Most of the laboratory devices used for catalyst evaluation and the assessment of various parameters, such as fixed bed or fixed fluidized bed reactors, or even pilot units, do not allow to measure properly the extent of reactant adsorption. The problem is even more severe under the conditions of commercial operations, because data and conclusions are masked by the simultaneous existence of various transport and chemical processes in very complex systems. Microbalances are commonly used to assess adsorption constants in non-reacting environments. For example, Zhu et al. [4] worked with light alkanes over silicalite below 200 °C; Hershkowitz and Madiara [5] adsorbed decane over LaY zeolite below 300 °C; Lee et al. [6] contacted various paraffinic and aromatic hydrocarbons with commercial FCC catalysts under non-reacting conditions. Differently, a kinetic approach was applied to the conversion of vacuum gas oil (VGO) in a pulsed fixed-bed reactor, assessing adsorption and kinetics parameters simultaneously [7]. Other works (e.g. [8]) were aimed at the study of simultaneous adsorption and reaction phenomena of various hydrocarbons in a batch, fluidized bed laboratory reactor. These works either did not consider that adsorption and diffusion indeed interact, or assumed approximations such as particles operating under quasi-steady states or diffusion parameters independent of the concentration.

In this work, the adsorption isotherms of pure hydrocarbons, their apparent adsorption constants and various adsorption selectivities on equilibrium commercial FCC catalysts are assessed in a Chemical Reactor Engineering Centre (CREC) Riser Simulator reactor in equilibrium and short contact time experiments at temperatures of 250, 300 and 350 °C. It is also the objective of this paper to study the effect of concentration on diffusion and adsorption, a fact associated to the relation between reactant and catalyst (Catoil ratio), as well as to assess diffusion parameters.

2. Experimental

The laboratory CREC Riser Simulator reactor [9], that was designed specifically for studies of FCC issues, was used under its standard configuration. Its basic design concept considers that a small slice of an ideal riser reactor, comprising the mixture of catalyst particles and hydrocarbons that "see" each other while moving along the riser after being put into contact, can be located into a batch reactor with internal recirculation. In this way, residence time and position along the riser are equivalent to the reaction or contact time in the laboratory unit. An impeller rotating at very high speed over the chamber that keeps the catalyst between two metal porous plates induces the internal circulation of the gas phase in an upward direction through the chamber, thus fluidizing the catalyst. When the reactor is at the desired experimental conditions, the reactant is fed through an injection port, and immediately after the contact time is attained, products are evacuated instantly by contacting the reactor to a large, hot vacuum chamber. After that, a sampling valve can be actuated to get samples from the vacuum
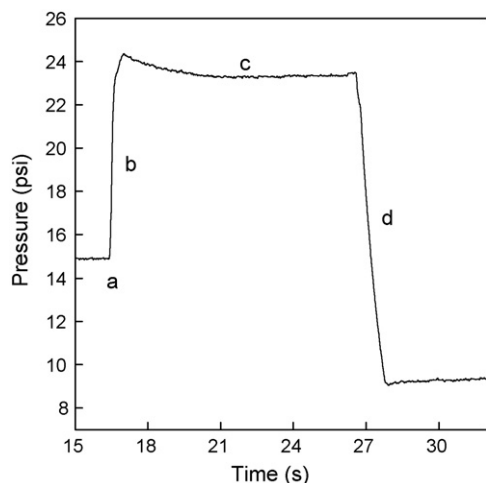
Fig. 1. Pressure profile in a short contact time experiment. C10; temperature, 250 °C, volume injected, 0.15 mL. Steps described in Section 3.

chamber that can be analyzed by gas chromatography. Before the injection of the hydrocarbons, the reactor is filled with inert nitrogen at atmospheric pressure. The standard configuration of the setup is shown in, for example, Tonetto et al. [10], and the modifications introduced to assess adsorption constants under reaction conditions were described in de la Puente et al. [11]. Pressure in the reactor and the vacuum chamber is recorded with digital sensors. A typical pressure profile is shown in Fig. 1.

Pure *n*-hexane (C6), *n*-decane (C10) and toluene (TOL), all of them with purity higher than 99%, were used without further treatments and injected at 250, 300 and 350 °C over an equilibrium commercial FCC catalyst (specific surface area, 125 m^2 g^{-1}; zeolite load, 19.6%; rare earth oxides, 2.94%; Ni + V, 10,900 ppm; MAT activity, 63%). Zeolite crystal sizes were confirmed by scanning electron microscopy to be in the 0.6–1.2 μm range. The volumes injected ranged from 0.03 to 0.40 mL. Experiments for the adsorption isotherms were done with contact times of 220 s. In order to reproduce conditions typical of the commercial FCC operation, other set of experiments was done with contact times of 10 s in all the cases. A sample of the gas phase was obtained at the final contact time and sent to analysis by standard capillary gas chromatography to assess its composition and confirm the absence of chemical reactions. Mass balances were performed after each experiment by comparing the mass injected with that recovered after the experiments, agreements being over ±1%. For all the calculations, the zeolite particle diameter was assumed to be 1 μm.

3. Results and discussion

3.1. Assessment of adsorption equilibrium parameters

Pressure data acquisition and recording is very important for the method used. Some of the characteristics of the pressure profiles during the experiments can be observed in the typical example shown in Fig. 1, that include: injection of hydrocarbons at point a, instantaneous vaporization (step b), adsorption during

contact time (step c), and very fast reactor evacuation (step d, used to get a gas phase sample to confirm the non-existence of chemical reactions).

The amounts of hydrocarbons adsorbed were assessed by means of

$$\bar{q}_i = \frac{n_i^{\text{feed}} - n_i^{\text{gp}}}{m_{\text{Cat}}} \tag{1}$$

where n_i^{feed}, the moles of hydrocarbon injected, are calculated with the known volume and the liquid hydrocarbon density, and n_i^{gp}, the moles of hydrocarbons in the gas phase at the final contact time, were estimated with the ideal gas law and experimental information. In this way, after numerous injections, adsorption isotherms were gathered for the different hydrocarbons. The adsorption processes were modelled with Langmuir type expressions, and the parameters were estimated by fitting the experimental data to the linear form of the adsorption isotherms

$$\frac{p_i}{q_i} = \frac{1}{b_i q_{i,s}} + \frac{p_i}{q_{i,s}} \tag{2}$$

This type of linear relationship is less sensitive to experimental deviations, since the observed pressure p_i is present in both variables [12].

The results observed at 250 °C are presented in Fig. 2 and Table 1, where it can be seen that the molar concentrations at the saturation follow the order TOL > C6 > C10. Moreover, as expected, the degree of non-linearity shown by the value of b_i is higher for decane.

The information about the adsorption parameters of hydrocarbons on FCC catalysts is scarce. However, if the results obtained in this work are compared against those extrapolated to 250 °C from Lee et al. [6], who used a TEOM microbalance to adsorb hexane, toluene and octane at 100–200 °C on a commercial FCC catalyst, similarities and discrepancies can be observed. In effect, even considering that the commercial FCC catalysts can be indeed different, the $q_{i,s}$ are close and the ranking among the various hydrocarbons is the same. Since at low pressures the assumption of linear adsorption can be accepted,
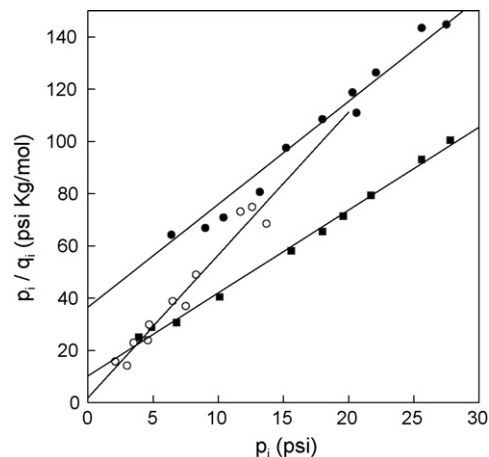

Fig. 2. Adsorption isotherms for C6, C10 and TOL. Temperature: 250 °C. Symbols: (●) C6; (○) C10; (■) TOL.

Table 1
Adsorption parameters for Langmuir and Henry isotherms at 250 °C

Hydrocarbon	$q_{i,s}$ (mol kg^{-1})			b_i (psi^{-1})		K_i (mol kg^{-1} psi^{-1}) [this work, zeolite]
	Lee et al. [6][a] (catalyst)	This work		Lee et al. [6][a] (catalyst)	This work (catalyst)	
		Catalyst	Zeolite			
C6	0.281	0.254	1.296	0.103	0.108	0.140
C10	0.196[b]	0.183	0.934	1.669[b]	3.018	2.821
TOL	0.400	0.315	1.607	0.075	0.310	0.498

[a] Data extrapolated to 250 °C.
[b] Corresponds to C8.

that is, the Henry's law is applicable, it can be stated that

$$q_{i,s}b_i = K_i \qquad (3)$$

The resulting K_i on the compound catalysts are similar to those from Lee et al. [6] (not shown) and give additional confidence to the values determined.

The results can be expressed on the basis that the adsorption of hydrocarbons is performed only on the zeolite component, considering that adsorption in the matrix component of typical FCC catalysts is negligible in comparison to that in the zeolite [6]. The corresponding zeolite Henry's constants are included in Table 1. Again the information about the adsorption of hydrocarbons on Y zeolite at moderate temperatures is limited, and a wide variation of K_i values is observed in the literature. For example, for the case of hexane at 250 °C (extrapolated values, in mol (kg psi)$^{-1}$) Denayer et al. [13] reported 0.317 on Na-Y and 0.073 on Na-USY, and Lee et al. [6] reported 0.065 on RE-USY, while our observation was 0.140 for this RE-Y. Although these catalysts are different, the wide range of constants does not allow to state conclusions.

The experiments performed at 300 and 350 °C showed consistent results that are presented in Fig. 3 for the example of toluene, together with the isotherm at 250 °C, but the same behavior was observed for the other two hydrocarbons. It can be observed that the isotherm lines are essentially parallel, obeying the hypothesis that the saturation coverage $q_{i,s}$, given by the reciprocal of the slope of the line, is constant [12]. The
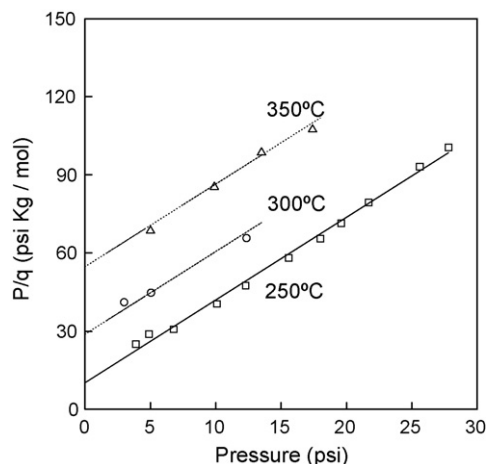

Fig. 3. Adsorption isotherms for TOL. Symbols: (□) 250 °C; (○) 300 °C; (△) 350 °C.

adsorption parameters obtained from the linear regression at the various temperatures and the corresponding heats of adsorption, as regressed from the Van't Hoff's law, are shown in Table 2. It can be seen that, as expected, b_i decreases as a function of temperature.

The heats of adsorption order according to the b_i parameters, that is, increasing with the molecular weight of the hydrocarbons, and they compare well to some values published in the literature. For the adsorption of hexane over different faujasite type materials or FCC catalysts, an average heat of adsorption of -44 ± 8.2 kJ mol^{-1} can be observed [14,13,6]. For the case of decane the average is -94.6 ± 12.7 kJ mol^{-1} [15–17]). Lee et al. [6] reported -55.0 kJ mol^{-1} for toluene over a FCC catalyst.

3.2. Assessment of diffusion parameters

The simultaneous, unsteady-state isothermal diffusion and adsorption in spherical particles with uniform size can be described following the generalized Maxwell–Stefan non-linear model applicable to a zeolite solid catalyst [18] to express the flux of a given hydrocarbon species, subjected to these most important assumptions [19,20]:

- Reactor design and operation ensure complete mixing in the gas phase and no concentration and temperature gradients are observed outside the catalyst particles.
- Restrictions to mass transfer and adsorption in the matrix component of this typical FCC catalyst are considered negligible in comparison to those in the zeolite component [6,20].
- Local adsorption equilibrium is attained at the surface of the zeolite particles, following a Langmuir type isotherm.

The assumption of mass transfer resistances located only in the zeolite component of the catalysts can be justified by comparing the diffusion time constants in the matrix (τ_p) and the zeolite (τ_c), respectively, even though it is not easy to find reliable infor-

Table 2
Heats of adsorption and adsorption parameters at various temperatures

Hydrocarbon	b_i (psi^{-1})			ΔH_{ads} (kJ mol^{-1})
	250 °C	300 °C	350 °C	
C6	0.108	0.055	0.029	−35.8
C10	3.018	0.230	0.062	−107.4
TOL	0.310	0.110	0.058	−46.0

mation. The matrix includes all the other catalyst components. For the case of hexane, and according to Bidabehere and Aldao [21]:

$$\tau_p = \frac{R_p^2 (1 - \varepsilon_p) w K'}{15 D_p \varepsilon_p} \tag{4}$$

$$\tau_c = \frac{r_c^2}{15 D_0} \tag{5}$$

where R_p and r_c are the radii of the matrix and zeolite particles, respectively, D_p and D_0 the diffusion coefficients in the matrix and zeolite, respectively, w the zeolite volume fraction, K' the Henry dimensionless constant and ε_p is the matrix porosity. The corresponding values used were $D_p = 3.3\,\mathrm{e}{-}3\,\mathrm{cm^2\,s^{-1}}$, that was obtained according to the equations of a transition regime, taking into account the contribution of molecular [22] and Knudsen diffusions [23], $D_0 = 1\,\mathrm{e}{-}11\,\mathrm{cm^2\,s^{-1}}$ [24], $R_p = 75\,\mu\mathrm{m}$, $r_c = 0.5\,\mu\mathrm{m}$, $w = 0.28$, $\varepsilon_p = 0.3$ and $K' = 71.6$. The calculations showed that $\tau_p = 0.063\,\mathrm{s}$ and $\tau_c = 16.7\,\mathrm{s}$; thus their relationship τ_p/τ_c is 0.0038, and the assumption is justified.

Then, the mass balance for a given hydrocarbon inside the zeolite particles can be written as

$$\frac{\partial \theta_i}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 D_{0,i} \frac{1}{1 - \theta_i} \frac{\partial \theta_i}{\partial r} \right] \tag{6}$$

linked to that in the gas phase:

$$\frac{V_{gp}}{RT} \frac{dp_i}{dt} = -m_{zeo} \frac{d\bar{q}_i}{dt} \tag{7}$$

where

$$\theta_i = \frac{q_i}{q_{i,s}} \tag{8}$$

and

$$\bar{q}_i = \frac{3}{r_c^3} \int_0^{r_c} q_i r^2 \, dr \tag{9}$$

subjected to the following initial and boundary conditions:

$$t = 0, \quad p_i = p_i^0, \quad \theta_i = 0, \quad 0 < r < r_c \tag{10}$$

$$r = r_c \quad \theta_i = \frac{b_i p_i}{1 + b_i p_i}, \quad r = 0 \quad \frac{\partial \theta_i}{\partial r} = 0 \tag{11}$$

The numerical solution of the partial differential equations was done according to the method of lines (MOL) that converts partial differential equations into a system of ordinary differential equations [25]. The estimation of parameters was performed with a conventional non-linear least squares method. At low pressure, the solutions of this model (evolution of the pressure in the gas phase) are coincident with those from a model where adsorption is considered linear (the adsorption isotherms follow the Henry's law) and the diffusivity does not depend on concentration, as shown in Fig. 4 for various catalyst masses at 250 °C.

The only unknown parameter in the descriptive model given by Eqs. (6)–(11), $D_{0,i}$, can be assessed by fitting the model to the observed evolution of the pressure in the reactor in the
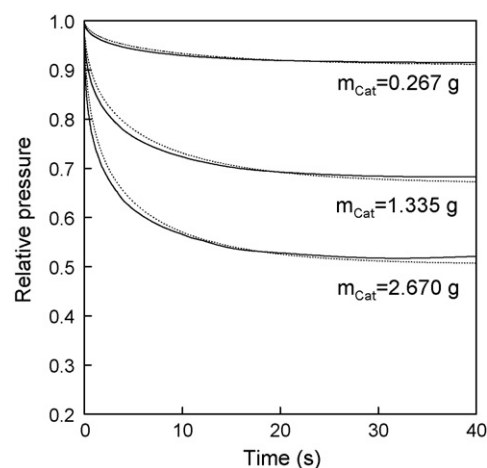

Fig. 4. Simulation of the pressure profiles in the injection of C6 for various catalyst masses. Comparison between linear (dotted lines) and non-linear (full lines) models at low pressures. Temperature, 250 °C; volume injected, 0.05 mL.

short contact time experiments. To observe changes more pronounced as a function of contact time, the pressure profiles used are those corresponding to the common smallest injection volume (0.05 mL). Optimum $D_{0,i}$ values are compared with those reported in Masuda et al. [24] in Table 3, where it can be seen that there is good agreement in the magnitude and the ranking of the values for the various hydrocarbons.

It is to be noted that the variations in $D_{0,i}$ due to changes in the concentration are much smaller than those of the correcting factor $1/(1 - \theta_i)$. For example, in the case of hexane, the maximum change in $D_{0,i}$ when pressure changes from 5.3 to 19.0 psi is 5.9%, while the correcting factor changes 30.5%. Similar behaviors were observed for toluene and decane.

3.3. Effect of temperature on diffusion

Configurational diffusion inside zeolite channels is generally described as an activated process [26], following Eyring's equation as a function of temperature:

$$D_{0,i} = D_i^* \exp\left(\frac{-E_{d,i}}{RT}\right) \tag{12}$$

The changes in the diffusion parameters for the various hydrocarbons as a function of temperature are shown in Fig. 5. It can be observed that the highest energy of activation belongs to decane ($-100.1\,\mathrm{kJ\,mol^{-1}}$), followed by hexane ($-47.2\,\mathrm{kJ\,mol^{-1}}$) and toluene ($-24.9\,\mathrm{kJ\,mol^{-1}}$). The analysis of these observations is usually controversial. For example, the high energies of activation for decane and hexane might suggest a macropore diffusion

Table 3
Intracrystalline diffusivities at zero coverage ($D_{0,i} \times 10^{11}$, $\mathrm{cm^2\,s^{-1}}$) values at 250 °C

Hydrocarbon	Optimum, this work	Masuda et al. [24][a]
C6	1.70	3.90
C10	0.28	0.20
TOL	0.79	1.30

[a] Constant volume method, C10: assumed from C8 value.
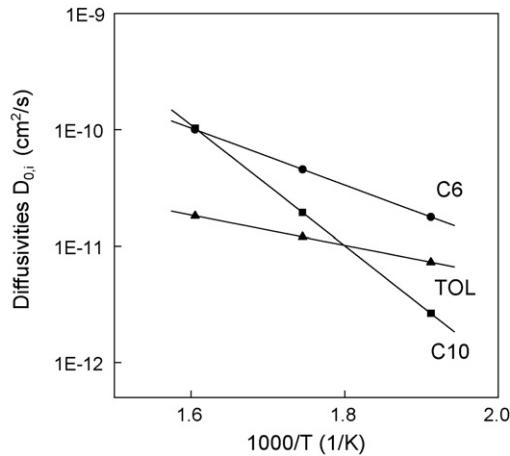
Fig. 5. Intracrystalline diffusivities at zero coverage. Temperature: 250, 300 and 350 °C. Symbols: (●) C6; (■) C10; (▲) TOL.

Fig. 6. Microporous diffusivities as a function of temperature. Temperature: 250, 300 and 350 °C. Symbols: (●) C6; (■) C10.

control regime, with a temperature dependence close to the heat of adsorption [27]. After comparison of the diffusion time constants in the matrix (meso and macropores) and the zeolite (micropores) components, in this case this possibility can be excluded, as shown with the analysis of Eqs. (4) and (5) above. Other authors consider that, besides configurational diffusion, an activated Knudsen type flow also exists [26,28]. Bidabehere and Sedran [20] found for hexadecane that at higher temperatures in the range from 440 to 550 °C, the energy of activation of diffusion was essentially equal to the heat of adsorption, and showed that it was consistent with a diffusion model controlled by mass transfer in the zeolite micropores. In that case, for linear adsorption processes, the mass balance can be described by means of

$$\frac{\partial C_i}{\partial t} = \frac{\varepsilon_m}{\varepsilon_m + K_i'} D_{m,i} \nabla^2 C_i \qquad (13)$$

If it is compared with a configurational diffusion process under dilute conditions:

$$\frac{\partial q_i}{\partial t} = D_{0,i} \nabla^2 q_i \qquad (14)$$

and it is possible to state that the relation between microporous diffusivity D_m and intracrystalline diffusivity at zero coverage D_0 is

$$D_{0,i} = \frac{\varepsilon_m}{\varepsilon_m + K_i'} D_{m,i} \qquad (15)$$

Moreover, considering that $K_i' \gg 1$ and that for Y zeolite ε_m is about 0.5 [29], then

$$D_{0,i} = \frac{\varepsilon_m}{K_i'} D_{m,i} \qquad (16)$$

The values of $D_{m,i}$ for hexane and decane calculated with Eq. (16) and the values of K_i and $D_{0,i}$ obtained previously, are shown in Fig. 6, where it can be seen that they are essentially constant in that temperature range. Note that for hexane and decane the energy of activation of diffusion were close to the heats of adsorption (refer to Table 2). Since the functionality of $D_{m,i}$ with temperature is much less sensitive than that of K_i', the energy of
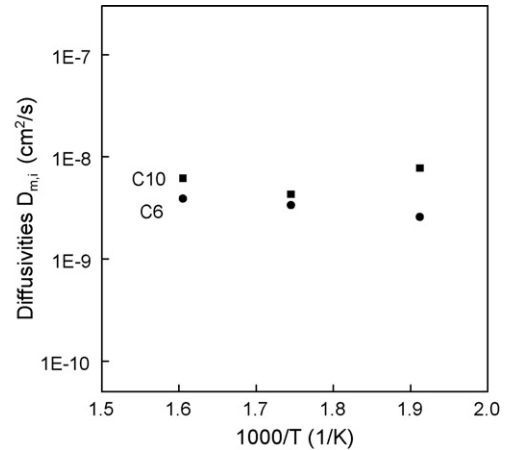
activation of $D_{0,i}$ would be indeed that of the adsorption constant. This would be suggesting that a mechanism different from purely configurational applies to the diffusion of n-paraffins at temperatures above 250 °C, and that a higher contribution from gaseous phase flow would be observed. Micropore diffusion control could be considered in this case. This possibility has been examined extensively in the literature, as indicated by, for example, the works of García and Weisz [30], Chen et al. [31], Weisz [32] or Reyes et al. [33]. However, this is not the case for toluene, that showed an energy of activation for diffusion that increased over that from a configurational mechanism (e.g. Masuda et al. [24]), but it kept lower than the heat of adsorption.

3.4. Adsorption selectivities

The amounts of hydrocarbons adsorbed in the experiments at short contact times are compared against the adsorption isotherms in Fig. 7. It is interesting to observe that in the cases of TOL and C10 most of the experiments, except at low pressures, show amounts of adsorbed hydrocarbons that are close
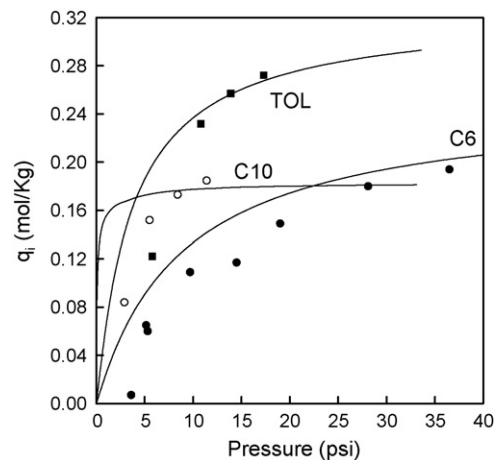

Fig. 7. Comparison between short contact time experiments (symbols) and adsorption isotherms (lines). Temperature: 250 °C. Symbols: (●) C6; (○) C10; (■) TOL.

to those of the corresponding adsorption isotherm. For example, at about 10 psi for decane and about 15 psi for toluene, the equilibrium seems to be attained. Moreover, note that according to the adsorption parameters assessed, q_{C10}^{eq} should be about 98% of $q_{C10,s}$ at 26 psi). In the case of C6, however, the adsorption is essentially smaller than that at equilibrium in the range of pressures used. This suggests that under FCC process conditions, specially in units operating at very low contact times, these effects could be more significant, and the different adsorption of the various hydrocarbons should be considered carefully. This issue is particularly important in the design of stripping units.

The equilibrium adsorption selectivity in separation processes can be defined as follows [12,27]:

$$S_{i,j}^{eq} = \frac{q_i^{eq}/p_i}{q_j^{eq}/p_j} \tag{17}$$

where q_i^{eq} is the adsorption concentration at the equilibrium. Note that in this work these selectivities were assessed with the information from the adsorption of pure hydrocarbons. In a linear system, the equilibrium adsorption selectivity would be given by the relationship between the corresponding Henry's constants:

$$S_{i,j}^{eq} = \frac{K_i}{K_j} \tag{18}$$

According to these experiments with particular hydrocarbons, deviation from linearity is significant. This suggests that the equilibrium adsorption selectivity will change with process conditions, and results and conclusions from usual dilute systems and linear adsorption models could be not applicable to commercial processes. For example, if linear adsorptions are considered, $S_{C10,C6}^{eq}$ would be larger than $S_{TOL,C6}^{eq}$. However, in the range of pressures used for this study the contrary is noticed.

In the case that the adsorption equilibria can be represented by Langmuir isotherms, as proposed here, the equilibrium adsorption selectivity will be a function of pressure:

$$S_{i,j}^{eq} = \frac{q_{i,s}b_i}{q_{j,s}b_j}\left(\frac{1+b_jp_j}{1+b_ip_i}\right) \tag{19}$$

The observed adsorption processes lead to the definition of the apparent adsorption selectivities according to

$$S_{i,j}^{app} = \frac{\bar{q}_i/p_i}{\bar{q}_j/p_j} \tag{20}$$

If the impact of diffusion on adsorption, and consequently on apparent adsorption selectivities, is considered, the differences between the apparent and equilibrium selectivities can be accounted for by kinetics factors included in the diffusion selectivity:

$$S_{i,j}^{dif} = \frac{F_i}{F_j} \tag{21}$$

where

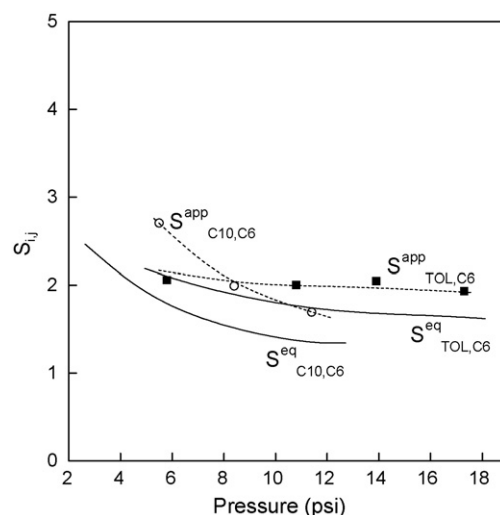$$F_i = \frac{\bar{q}_i}{q_{i,R_p}} \tag{22}$$

Fig. 8. Apparent (dotted lines) and equilibrium (full lines) selectivities as a function of pressure. Symbols: (○) C10; (■) TOL.

is a dynamics effectivity factor. It results that:

$$S_{i,j}^{app} = S_{i,j}^{eq}S_{i,j}^{dif} \tag{23}$$

In dilute systems, and when the adsorption capacity is low, factors F_i depend only on diffusion [34]. The condition for low adsorption capacity in the system can be expressed by means of values much smaller than 1 of the parameter:

$$\alpha = \frac{V_{sol}}{V_{gp}}K' \tag{24}$$

a fact that can be easily achieved in the experimental setup used. The impact of the system parameter α is addressed in a paper by Bidabehere and Sedran [35].

When the equilibrium is reached, at sufficiently long times, both F_i and F_j become the unit value, and

$$S_{i,j}^{app} = S_{i,j}^{eq} \tag{25}$$

The changes in the selectivities as a function of pressure, considering C6 as the reference compound, are shown in Fig. 8 and Table 4. It is clear that the adsorptions of C10 and TOL are larger than that of C6 in the range of pressures used. The equilibrium selectivities, as predicted by Eq. (19) according to the particular Langmuir parameters, tend to constant values as the

Table 4
Diffusion selectivities

Hydrocarbon i	p (psi)	$S_{i,j}^{dif}$
C6[a]	–	1.0
TOL	5.8	1.0
	10.8	1.2
	13.9	1.2
	17.3	1.2
C10	5.5	1.5
	8.2	1.5
	11.3	1.3

Temperature 250 °C.
[a] Used as reference hydrocarbon j.

pressure increases. More pronounced, similar trends are shown by the apparent selectivities. Usually diffusion effects are not considered in the evaluation of adsorption parameters in the laboratory; for example, the assessment of Henry constants under reaction conditions was performed with data gathered at very short contact times, assuming that equilibrium is reached and that it is not affected by diffusion [36]. Also, the effect of concentration, that is, the Catoil ratio, on diffusion and adsorption in FCC catalysts has not been investigated. At higher pressures the values of $S_{i,j}^{app}$ must tend to those of equilibrium, due to the increase in the effective diffusivity as a consequence of the increase in coverage, that are larger for C10 and TOL than for C6. In other words, the increase in the effective diffusion coefficient for decane due to coverage as a function of pressure (the correction factor in Darken's equation for Langmuir adsorption is $1/(1 - \theta_i)$ [12] (see Eq. (6)) is larger than those in toluene and hexane, respectively. Moreover, it can be accepted that these diffusion effects are only due to the mass transfer process in the pore system of the solid catalyst, that is accounted for by the dynamics effectivity factor F_i, because the mixing characteristics of the reactor assure the absence of mass transfer resistances external to the catalyst particles [37].

4. Conclusions

The CREC riser simulator reactor allows to determine the adsorption isotherms of hydrocarbons on commercial FCC catalysts at moderate to high temperatures and to study the effect of concentration (Catoil ratios) on the adsorption selectivities. A non-linear diffusion–adsorption model was used to analyze the system's dynamics responses according to Langmuir isotherms, its solutions matching those of the linear adsorption models at low pressures. The diffusion parameters for various hydrocarbons, obtained from fitting the model to short contact time experiments, were in line with published parameters, and indicated that a non-fully configurational diffusion mechanism applies to the mass transfer of *n*-paraffins inside the Y zeolite pores. It was observed that, due to the non-linearity of the isotherms and diffusion restrictions, changes in the system's pressure induce changes in the apparent adsorption selectivity. For a given mass of catalyst, changes in the Catoil ratio, and pressure, modify both equilibrium and diffusion factors, leading apparent selectivities to have a ranking in the order inverse to that expected for dilute systems. These results grant a basis for the assessment of adsorption and diffusion parameters of pure hydrocarbons at special conditions (moderate to high temperatures, changing Catoil ratios, short contact times, commercial catalysts), and open opportunities for the study of mixtures. These factors have an important impact on FCC issues related to the operation of stripper and riser reactor sections.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2007.01.020.

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