

Selective hydrogenation in trickle-bed reactor: experimental and modelling including partial wetting

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Abstract

A steady state model of a trickle-bed reactor is developed for the consecutive hydrogenation of 1,5,9-cyclododecatriene on a $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst. Various experiments have shown that the selectivity of this reaction towards the product of interest is much lower in co-current down-flow (trickle-bed) than in up-flow. This is due to uneven liquid distribution and to partial wetting of the catalyst surface at low liquid flow rates.

The non-isothermal heterogeneous model proposed here takes into account the partial wetting of the catalyst, as well as the resistances to heat and mass transfer at the gas–liquid, liquid–solid and solid–gas interfaces. It assumes that the catalyst particles can be divided into two distinct concentration zones corresponding to the wetted and dry catalyst surfaces; mass transfer between these two zones is described by a simplified diffusion mechanism.

Compared to previous models assuming a uniform concentration of liquid-phase components inside the catalyst particles, this model improves the prediction of the outlet concentrations of hydrogenation products.

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1. Introduction

Fixed-bed reactors with down-flow of gas and liquid (trickle-bed reactors) have been extensively studied and widely used in industrial practice for many years. In recent works, the performance of such reactors was studied for various operating conditions and several models were proposed for the studied reactions.

Three phase catalytic reactions are most often carried out in trickle-bed reactors despite poor thermal control, uneven liquid distribution and, at low liquid flow rate, partial wetting of the catalyst. This phenomenon of partial wetting may have positive effects on the reaction rate when gas–liquid mass transfer is the major rate limitation. Nevertheless it reduces selectivity as far as consecutive reactions are concerned.

Models accounting for partial wetting are generally oversimplified due to two major problems. The first one arises through the poor knowledge of wetting, only quantified by an overall external wetting efficiency of the catalytic bed, whose determination is highly questionable and which does not describe local features at the particle level: are all the pellets equally partially wetted or on the contrary does this wetting efficiency corresponds to the number fraction of pellets completely wetted, the remaining pellets being completely dry? The second point concerns the coupling of reaction and mass transfer inside the catalyst pores where complete internal wetting by capillarity is generally assumed. In the case of partially wetted pellets, the unsymmetrical conditions at the catalyst surface should lead to multidimensional diffusion equations which are rarely taken into account in the modelling. Simplified expressions of the effectiveness factor are

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Nomenclature

a_c	catalyst external area per reactor volume unit (m^{-1})
A_1	inner wall reactor surface (m^2)
C	concentration (mol/m^3)
$C_{\text{L},\text{H}_2}^*$	hydrogen solubility concentration (mol/m^3)
D_{Li}	liquid diffusion coefficient of compound i (m^2/s)
f_w	external wetting efficiency
F	molar flow per surface unit ($\text{mol}/(\text{s m}^2)$)
F_h	enthalpy flux per surface unit (W/m^2)
h_{FS}	fluid to solid heat transfer coefficient ($\text{W}/(\text{m}^2 \text{K})$)
h_w	bed to wall heat transfer coefficient ($\text{W}/(\text{m}^2 \text{K})$)
ΔH_{R}	heat of reaction (J/mol)
k_{GS}	gas–solid mass transfer coefficient (m/s)
k_{LA}	gas–liquid volumetric mass transfer coefficient (s^{-1})
k_{LS}	liquid–solid mass transfer coefficient (m/s)
L_{cd}	diffusional characteristic length (m)
r'_i	apparent reaction rate per catalyst weight ($\text{mol}/(\text{s kg})$)
S	selectivity
T	temperature (K)
V_{R}	reactor volume (m^3)
X	molar fraction (based on the sum of the four hydrocarbons: CDT, CDD, CDE, CDA)
z	reactor length (m)

Greek letters

ν	stoichiometric coefficient
ρ_{B}	density of catalyst bed (kg/m^3)
Ω_{H_2}	overall hydrogenation advancement

Subscripts

C	calculated
d	dry
E	experimental
F	fluid
G	gas
L	liquid

M	Marlotherm
S	solid
W	wetted
W1	inner reactor wall

usually used, accounting only for concentration gradients of the limiting reactant. Tan and Smith [12] compared those approximate solutions (weighting factor models, as reported in [8]) to rigorous results for slab geometry with two faces of equal areas covered at different reactant concentrations (wetting factor = 0.5) and cubic particle with one or more faces covered by liquid. They concluded that those simplified expressions give reasonably good results for a simple first-order (gas-limited) reaction.

However concerning complex reactions and selectivity analysis only few works have been dedicated to the effects of partial wetting, although in any reactor modelling selectivity provides a very sensitive tool, with which no fitting parameter can be adjusted and may lead to possible misunderstanding of actual features.

For wetting efficiency determinations a pseudo-effective 1D diffusivity has sometimes been identified from tracer analysis or effective reaction rates but most often reactor models keep diffusion unchanged. In other words no comprehensive statement of the liquid reagent behaviour under the dry surface of the catalyst has been addressed up to now.

Vergel Hernandez [14] studied the selective hydrogenation of butadiene in trickle-bed and flooded-bed reactors. He noticed that the selectivity remains stable in up-flow in a wide range of fluid velocities, but decreases in the trickle-bed at low velocities. The author proposed that the flow conditions inside the down-flow reactor can be represented by two parallel plug flow reactors of equal volume, receiving different fractions of the liquid and gas flow rates but completely wetted.

Rajashekharam et al. [7] investigated the hydrogenation of 2,4-dinitrotoluene in a trickle-bed reactor. They combined the contributions of stagnant liquid covered as well as unwetted zones on the catalyst surface, but neglected liquid–solid and intraparticle mass transfer resistances for the liquid-phase components.

In this work the selective hydrogenation of 1,5,9-cyclododecatriene (CDT) to cyclododecene on

a shell-type Pd/Al₂O₃ catalyst was investigated for being a complex and highly exothermic reaction of industrial interest. The consecutive hydrogenation steps result in the formation of the following products: cyclododecadiene (CDD), cyclododecene (CDE), and cyclododecane (CDA). Julcour et al. [6] worked on the same reaction and same reactor as in the present study (diluted bed). The authors observed a poor heat transfer and a low selectivity in the down-flow mode. A classical model assuming a uniform catalyst wetting but including direct gas–solid mass transfer to the dry catalyst fraction was proposed. The concentration gradients of the liquid-phase components inside the catalyst were also neglected. This model could fit the overall conversion, but not the selectivity due to heterogeneities of liquid flow and partial wetting.

Chaudhari et al. [1] investigated the same reaction in a smaller bench-scale reactor. In their short and non-diluted trickle-bed, channelling of liquid flow being not significant, the model of Rajashekharam et al. [7] satisfactorily described the behaviour of the reactor.

2. Experimental set-up

The experimental set-up that was used is presented elsewhere [5,6]. The reactor consists of a jacketed packed-bed column with an inner diameter of 0.026 m and a bed height of 1.2 m. The tube is filled with a mixture of 1/6 of catalyst pellets (0.5% Pd on alumina from Degussa) and 5/6 of inert alumina pellets of the same shape. The liquid reactant is also diluted, as previous experiments have shown that hot spots could not be avoided otherwise [5]: a 15 wt.% solution of CDT in isododecane is used as feedstock.

Before entering the reactor gas and liquid-phases are mixed in an inert fixed-bed in order to homogenize the temperature and to achieve gas–liquid equilibrium.

Five automatic valves commanded simultaneously by a switch are placed along the gas and liquid circuits in order to manage the fluid circulation mode (up- and down-flow). Seven temperature probes and six liquid sampling valves are located along the reactor in order to measure axial temperature and concentration profiles. The control of the reactor temperature is achieved by a fast flowing of thermal oil (Marlotherm) in the jacket at a nearly constant temperature (the main operating conditions are listed in Table 1).

3. Modelling

3.1. Model (I): uniform catalyst wetting, and uniform concentrations in liquid-phase components inside the catalyst (classical model)

First of all, the model used by Julcour et al. [6] was applied. This model assumes that the surface of the catalyst pellet can be divided into two zones (Fig. 1). A dry zone where the gaseous reactant is in direct contact with the catalyst, and a wetted zone where hydrogen is transferred through the liquid-phase. The organic compounds are supplied to the catalyst through the wetted zone only.

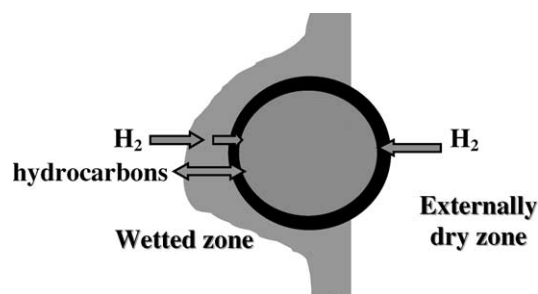


Fig. 1. Classical model of a partially wetted particle.

Table 1
Operating conditions

Experiment no.	Liquid velocity (m/s)	Gas velocity (m/s)	Marlotherm temperature (°C)	Hydrogen pressure (bar)
1	0.00068	0.015	120	4
2	0.00068	0.080	120	4
3	0.00068	0.035	120	4
4	0.00098	0.035	120	4

The assumptions of the model are the following ones:

- gas and liquid are in plug flow;
- gas and liquid are considered as a pseudo-homogeneous fluid for the energy balance;
- the liquid-phase reactant is non-volatile;
- internal diffusion limitations (intraparticle resistance for H_2) are taken into account through an apparent kinetics;
- complete internal wetting is achieved due to capillary forces;
- the catalyst temperature is uniform;
- the contribution of stagnant liquid covered zones is negligible;
- the liquid-phase reactant is in large excess with respect to the gaseous reactant so that concentration gradients of the liquid-phase components inside the catalyst may be ignored;
- severe intraparticle gradients are expected for H_2 which is consumed within a very thin zone close to the catalyst surface;
- the catalyst wetted fraction is the same for all pellets (f_w).

The equations of the model are:

1. Mass balances

- *Liquid-phase* (plug flow)
 - Hydrocarbons (k)

$$0 = -\frac{\partial F_{L,k}}{\partial z} - f_w a_c (k_{LS})_k (C_{L,k} - C_{S,k}) \quad (1)$$

where $k = \text{CDT, CDD, CDE, CDA}$.

- H_2

$$0 = -\frac{\partial F_{L,H_2}}{\partial z} - f_w a_c (k_{LS})_{H_2} \times (C_{L,H_2} - C_{Sw,H_2}) + k_L a (C_{L,H_2}^* - C_{L,H_2}) \quad (2)$$

- *Catalytic phase*
 - Hydrocarbons (k)

$$0 = f_w a_c (k_{LS})_k (C_{L,k} - C_{S,k}) + \rho_B \sum_i v_{ik} (f_w r'_{i,w} (C_{S,m}, C_{Sw,H_2}, T_S) + (1 - f_w) r'_{i,d} (C_{S,m}, C_{Sd,H_2}, T_S)) \quad (3)$$

where $k = \text{CDT, CDD, CDE, CDA}$; $m = \{\text{CDT, CDD, CDE}\}$.

- H_2

wetted part

$$0 = f_w a_c (k_{LS})_{H_2} (C_{L,H_2} - C_{Sw,H_2}) + \rho_B \sum_i v_{iH_2} (f_w r'_{i,w}) \quad (4)$$

dry part

$$0 = (1 - f_w) a_c (k_{GS})_{H_2} (C_{L,H_2}^* - C_{Sd,H_2}) + \rho_B \sum_i v_{iH_2} ((1 - f_w) r'_{i,d}) \quad (5)$$

2. Energy balances

- *Fluid phase* (gas + liquid)

$$0 = -\frac{\partial ((Fh)_F)}{\partial z} + a_c h_{FS} (T_S - T_F) - \frac{h_w A_1}{V_R} (T_F - T_{W1}) \quad (6)$$

- *Catalyst phase*

$$0 = -a_c h_{FS} (T_S - T_F) - \rho_B \sum_i \Delta H_{Ri} (f_w r'_{i,w} + (1 - f_w) r'_{i,d}) \quad (7)$$

- *Cooling oil* (Marlotherm)

$$0 = -\frac{\partial ((Fh)_M)}{\partial z} + \frac{h_2 A_1}{V_{an}} (T_{W1} - T_M), \quad 0 = h_w A_1 (T_F - T_{W1}) - h_2 A_1 (T_{W1} - T_M) \quad (8)$$

3.1.1. Model parameters

Model (I) involves around 20 parameters representing complex kinetics, heat and mass transfer. The parameters of the apparent kinetics were identified from batch experiments carried out with the 3.1 mm diameter pellets.

A Eley–Rideal model was selected:

$$r'_i = \frac{k_i K_j C_j C_{H_2}^{\alpha_i}}{1 + \sum_{j=1}^3 K_j C_j} \quad (9)$$

Parameters can be found in [5]. Here i is the reaction number, and j the component number ($j = 1, \text{CDT}$; 2, CDD; 3, CDE).

This model has been first assessed for up-flow mode, using a wetting efficiency equal to unity and

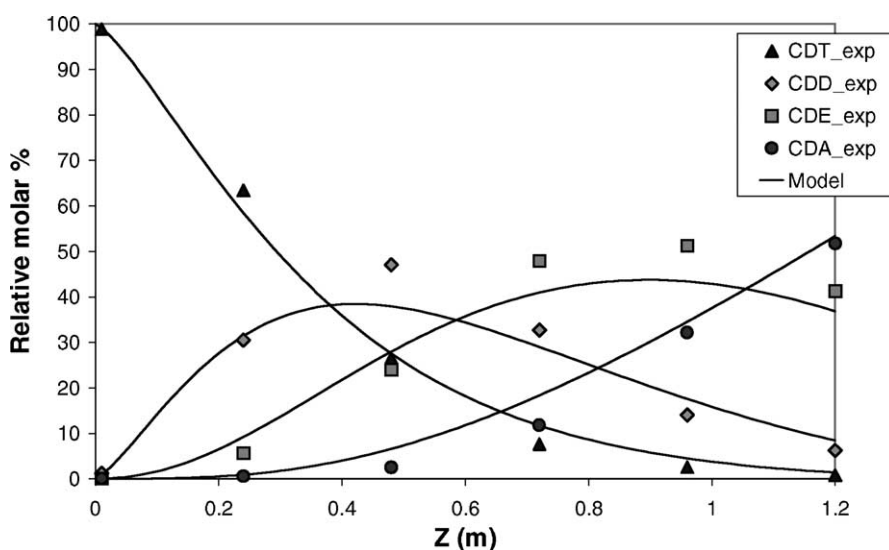


Fig. 2. Axial concentration profiles in up-flow mode ($P = 4$ bar, $T_{\text{wall}} = 100$ °C, $u_{\text{Le}} = 0.53 \times 10^{-3}$ m/s, $u_{\text{Ge}} = 0.042$ m/s).

empirical correlations established by Stüber [11]. It can conveniently predict the axial concentration and temperature profiles (cf. Fig. 2). The relative molar fraction (or %) of CDT is given as the ratio of CDT concentration to the sum of CDT, CDD, CDE and CDA concentrations.

In down-flow mode, coefficients k_{La} , k_{LS} for H_2 , k_{LS} for hydrocarbons, k_{GS} , h_{FS} , and h_{w} are calculated by correlations from the literature [2,4,9,10,13,15]. Only the wetting efficiency (f_{w}) has been used as a fitting parameter.

In the investigated range of fluid velocities, the correlation by El-Hisnawi et al. [3] gives a value around 0.7 for the catalyst wetting efficiency, but as shown in Fig. 3, a small deviation in the estimation of this factor results in dramatically different predictions of the outlet concentrations. However, in the particular case investigated (Fig. 3), this parameter f_{w} was found to have a low influence on the concentration of CDE. In fact as severe hydrogen limitations are governing the reaction rates increasing the dry fraction accelerates similarly all reactions. In any case CDT concentration should decrease and CDA increase, but the behaviour of intermediates depends on the overall hydrogenation advancement.

As the same catalytic bed was used for many runs, a deactivation factor (deact) is also introduced in the model to correct the rate equations measured with

fresh catalyst ($r'_{i,\text{actual}} = \text{deact} \times r'_i$). However the catalyst activity was found to decrease very steeply during the first runs after its loading and then only very gradually [11]. The four previous (consecutive) experiments were performed in the latter conditions, so that a constant deactivation factor could be used: $\text{deact} = 0.85$.

The reaction advancement is calculated by: $\Omega_{\text{H}_2} = (X_{\text{CDD}} + 2X_{\text{CDE}} + 3X_{\text{CDA}})/3$, while selectivity S is defined as the ratio the considered product to the sum of all the reaction products (CDD, CDE, CDA).

3.1.2. Results

Based on the following criteria: $C = \sum_i (X_{i\text{E}} - X_{i\text{C}})^2$ ($i = \text{CDT, CDD, CDE, CDA}$), values of the wetting efficiency were identified for the four experiments (Table 2).

The catalyst wetting efficiency is approximately 0.7, as expected by the correlation of El-Hisnawi.

Table 2
Identified values for wetting efficiency

Experiment no.	f_{w}	Criteria
1	0.7	0.0325
2	0.55	0.0068
3	0.7	0.0349
4	0.7	0.0318

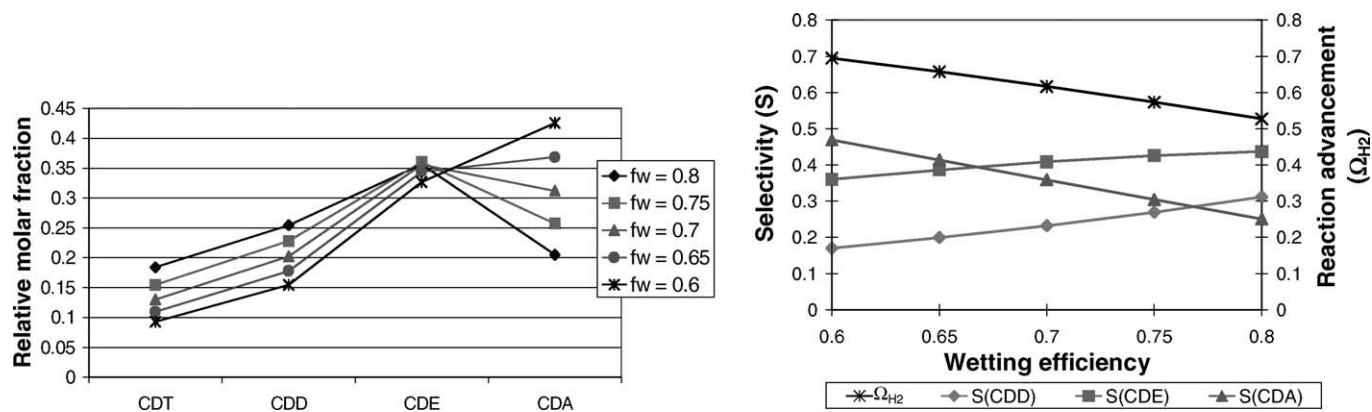


Fig. 3. Influence of the catalyst wetting efficiency.

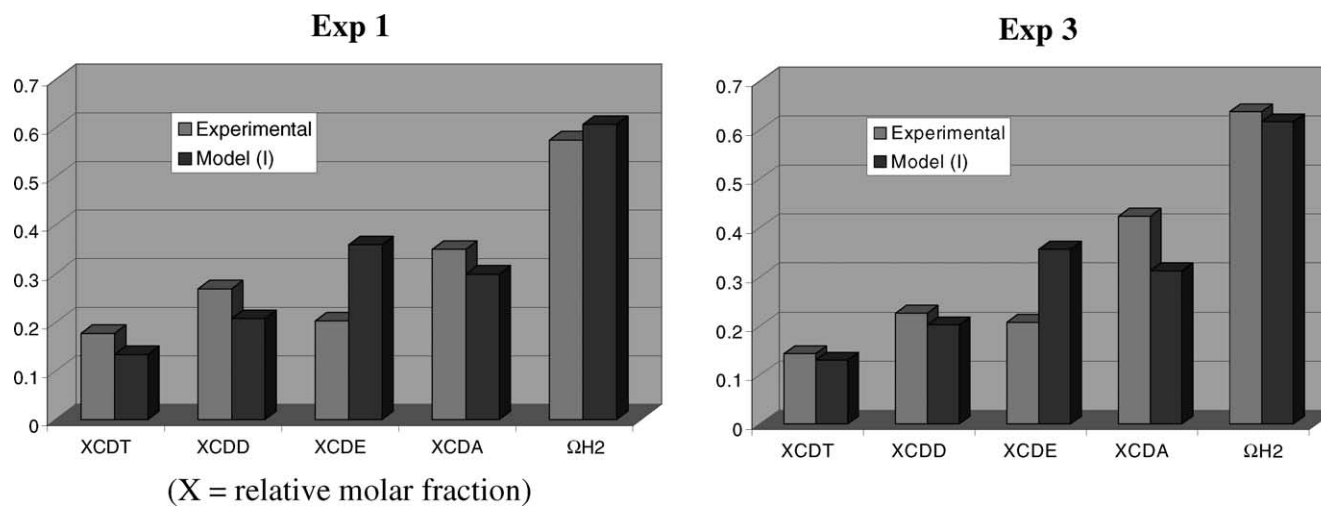


Fig. 4. Distribution of products obtained experimentally and predicted by model (I).

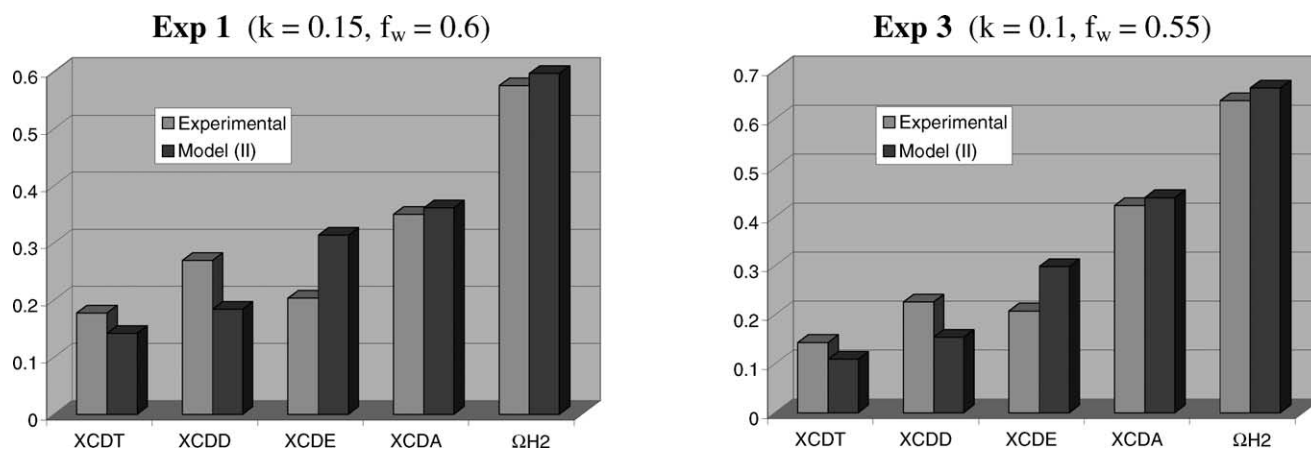


Fig. 5. Results of the model with two parallel reactors.

Nevertheless, in the case of high gas flow rate, predictions can meet experimental hydrogenation rates only for a lower value. This can be explained by the fact that the correlation for f_w does not account for gas flow rate variations.

Even though the model can predict the overall hydrogenation rate, it can never fit the selectivity values for CDE (see Fig. 4). One reason may be that the model assumes the hydrocarbon concentrations inside the catalyst pellets to be uniform. In fact, it seems obvious that the concentrations of the liquid-phase components are not the same everywhere inside the catalyst because hydrogen transfer is greater to the dry surface than to the wetted surface and a diluted reactant is used. This can have in return some effects on the reaction rates, especially when a zero order with respect to hydrocarbons is not still verified.

It is then necessary to differentiate inside the catalyst particle two concentration zones for hydrocarbons corresponding respectively to the wetted and dry surfaces.

Moreover in model (I) the wetting efficiency is supposed to be the same for all the pellets, while in fact channelling of liquid flow has every chance to occur in this long reactor at low liquid velocities, leading to an heterogeneity of the wetting at the bed scale.

3.2. Model (II): reactor split into two portions operating in parallel under different flow conditions

To account for wetting heterogeneities at the reactor scale, a very simple model was derived from model (I), assuming the reactor to be a linear combination of two reactors working in parallel under different wetting conditions: one (volume fraction k) in which the catalyst is totally wetted (wetting efficiency = 1) and the other one (volume fraction $(1 - k)$) in which the wetting efficiency value is ranging between 0.5 and 0.8.

After a trial and error procedure, the following results have been obtained, showing that model (II) predictions can be closer to experimental data, especially when regarding the outlet concentration of the final product CDA. This is due to lower values of the wetting efficiency used in the partially wetted section: in this part, the reaction proceeds quickly leading to com-

plete hydrogenation. However the gaps for CDD and CDE are still significant (Fig. 5).

3.3. Model (III): uniform catalyst wetting, concentration heterogeneities in the particle for liquid-phase compounds

As the previous models could not predict the selectivity values, a new model was derived to improve the description of the catalyst scale phenomena under partial wetting conditions. As the first model, model (III) assumes that the external wetted fraction is the same for all the pellets, but it accounts for concentration heterogeneities of the liquid-phase components inside the catalyst: each particle is divided into two distinct concentration zones corresponding respectively to the wetted and dry catalyst surfaces (see Fig. 6).

Hydrocarbons are supplied to the catalyst through the wetted surface only, while hydrogen passes both through the liquid-phase and directly at the dry surface. Mass transfer between these two zones is described by a simplified diffusion mechanism, using arbitrarily the dry surface as a reference:

$$F_i = (1 - f_w)a_c \frac{D_{Li}}{L_{cd}} (C_{Sw,i} - C_{Sd,i})$$

for $i = \text{CDT, CDD, CDE, CDA, H}_2$

where L_{cd} is the diffusional characteristic length.

These considerations lead to modify Eqs. (3)–(5): two zones (wetted and dry) and thus two sets of concentration are now considered for hydrocarbons

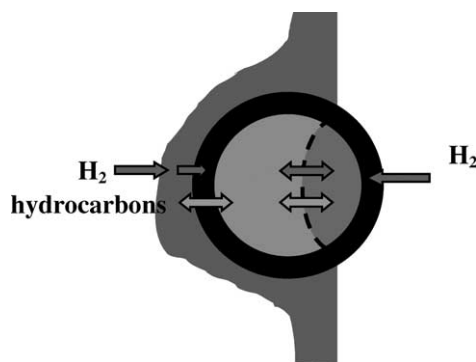


Fig. 6. New model involving different hydrocarbon concentrations in the two zones (wetted and dry).

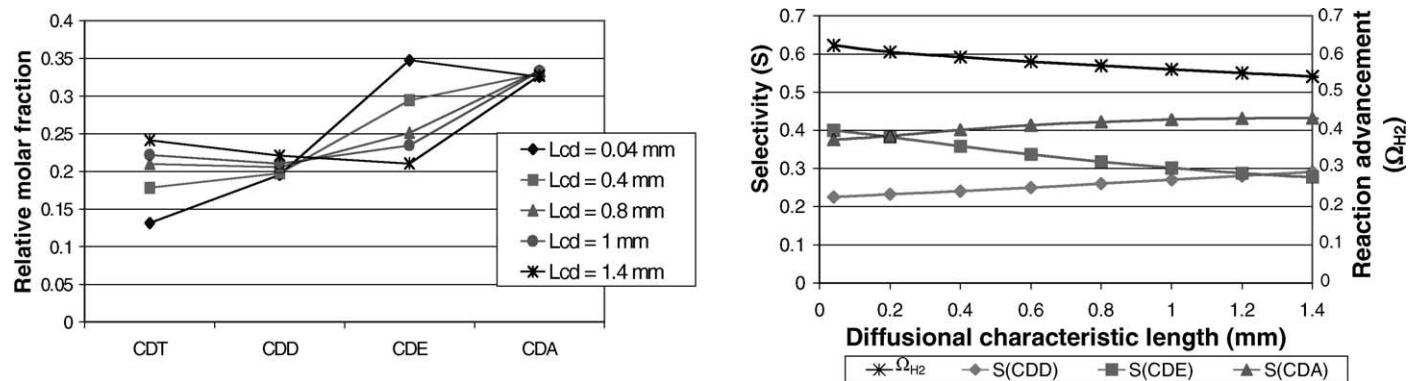


Fig. 7. Influence of the diffusional characteristic length on the product distribution.

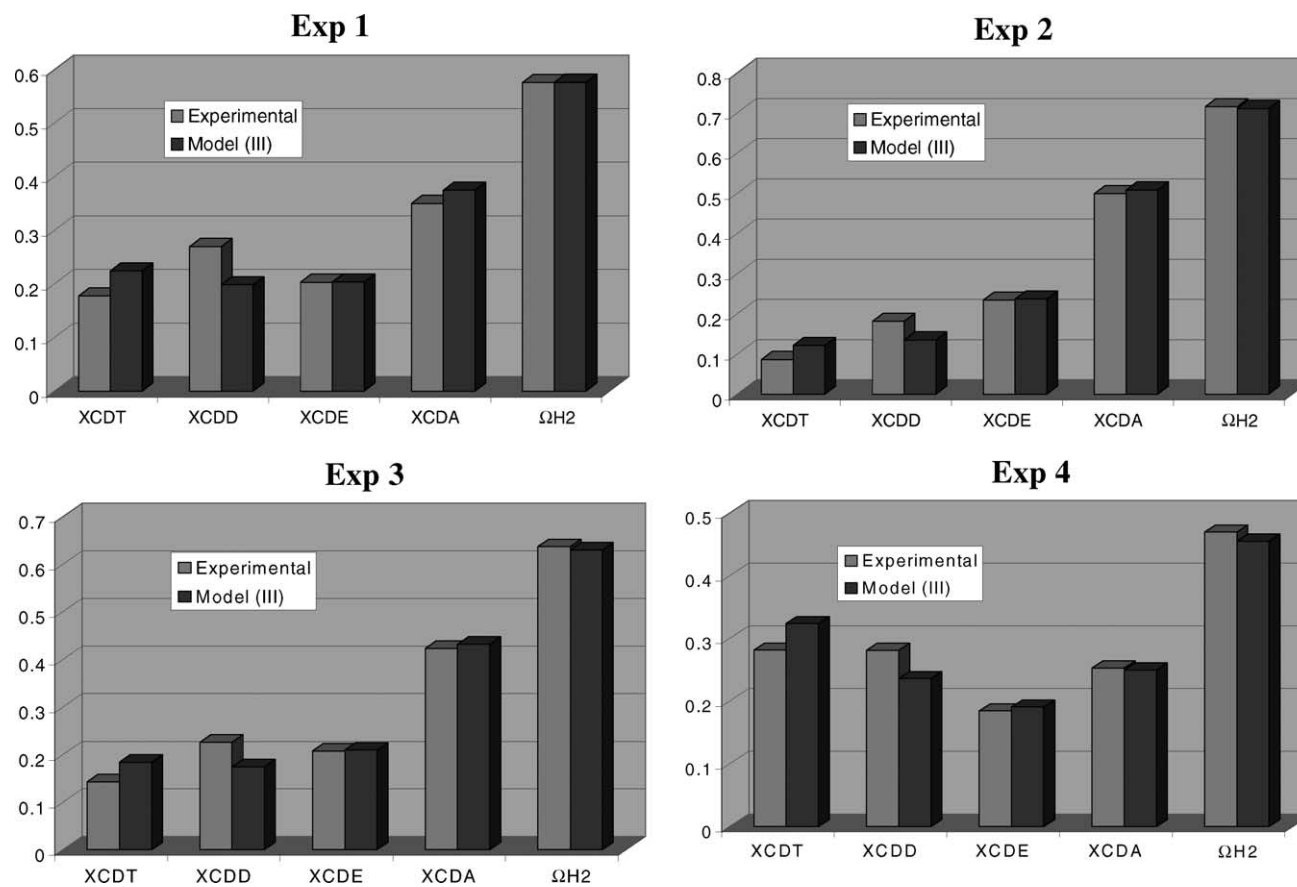


Fig. 8. Distribution of the products predicted by the model (III) and obtained by experiments.

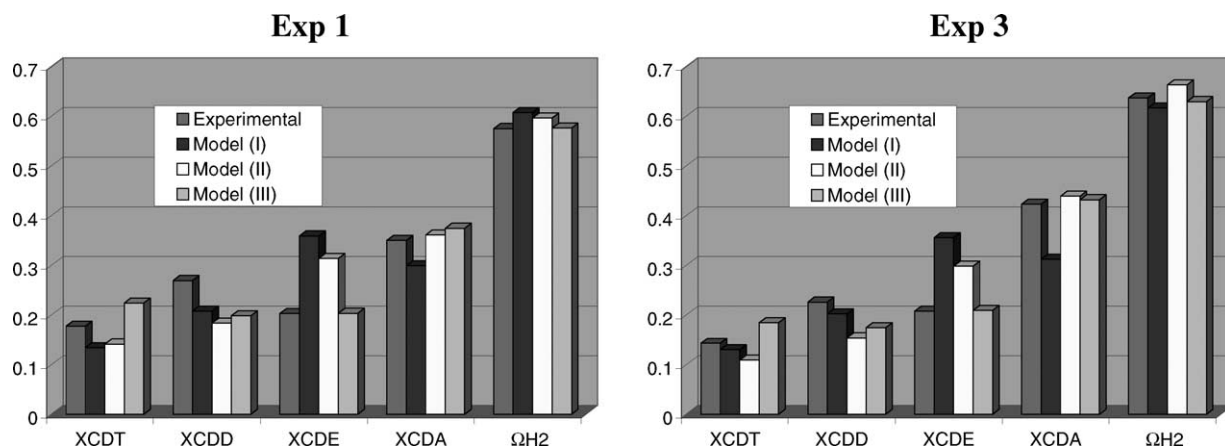


Fig. 9. Distribution of products predicted by the three models and obtained experimentally.

and the exchange term between the two zones is also added.

3.3.1. Influence of model parameters

This model involves one more parameter than model (I): the diffusion characteristic length L_{cd} . As in model (I), the wetting factor has a significant effect on the overall hydrogenation rate and on the selectivity.

The increase of the diffusional characteristic length reduces the reaction rate because it reduces the hydrocarbon fluxes towards the catalyst dry zone. This parameter has thus a major effect on selectivity (Fig. 7).

3.3.2. Optimal parameters

Table 3 shows the optimised values of the wetting efficiency and diffusional characteristic length for the new model. As expected, the wetting efficiency was found to increase with the liquid flow rate, and less obviously to decrease with the gas flow rate. Its order of magnitude is near to the one predicted by the correlation of El-Hisnawi.

Table 3

Optimised values for wetting efficiency and diffusional characteristic length

Experiment no.	f_w	L_{cd} (mm)	Criteria
1	0.65	1.16	0.0078
2	0.55	0.44	0.0034
3	0.6	0.96	0.0044
4	0.65	1.20	0.0038

For a constant liquid velocity, the diffusional characteristic length decreases when the gas flow rate increases. An increase of the gas flow rate should result in a better spreading of the liquid at the catalyst surface so that the catalyst dry fraction would not correspond to a single region, but to several ones. The real exchange surface between dry and wetted zones increasing, this leads in the model to a decrease of the diffusional characteristic length. On the other hand increasing the liquid flow rate would result in less dry zones then in higher diffusional characteristic length.

3.3.3. Results

This model predicts the molar fractions of CDE and CDA correctly, but there are still small differences for CDT and CDD. Nevertheless, this model predictions are very close to the experimental values (Fig. 8).

4. Comparison of the different models

In Fig. 9 the graph compares the different models for each experiment. The model with two parallel reactors always predicts the fraction of CDT and CDA at the outlet of the reactor correctly, but model (III) fits the experimental results more precisely.

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