

Analysis of TAP Reactor Procedures using COMSOL

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Abstract: TAP (Temporal Analysis of Products) reactors are powerful instruments to study the kinetics of catalytic reactions¹⁻³. Their basic principle, exposition of evacuated solids of interest to narrow pulses containing very small amounts of gases, and measuring the concentrations (or fluxes) of outgoing molecules permits to study practical catalysts under the conditions approaching those of molecular beam experiments.

However, because of the complex geometry of TAP instruments and intrinsically transient character of TAP experiments, the extraction of kinetic constants from obtained experimental data may present an arduous task. The analytical solutions exist for some special cases, but the conditions to be satisfied (respect of Knudsen diffusion law, constant temperature, uniformity of loading) may be difficult to meet in practical experimental conditions. In most cases numerical methods must be used, with different simplifying assumptions. From other side, computer calculations provide us with knowledge on domains of standard behavior related to analytical solutions.

Since the phenomena occurring in this case include essentially time-dependent gas flow in systems with complex geometries, Comsol is particularly well adapted to simulate these phenomena and to check the validity of particular simplifying hypotheses. Dusty Gas Model may be implemented instead of Knudsen diffusion model using PDE mode, General formulation.

In this study Comsol 3.5a has been used to compare different approaches to the interpretation of TAP results, between 1D modeling of the reactor alone and 3D modeling of the ensemble: reactor and the vacuum chamber (TAP-2).

Keywords: TAP reactors, Knudsen diffusion, dusty gas model

1. Introduction

TAP (“Temporal Analysis of Products”) reactors are special laboratory catalytic reactors, in which a fixed bed of catalyst is maintained in vacuum, typically better than 10^{-6} Pa, and exposed to series of narrow pulses of gases (width of the order of 1 ms) which enter the catalyst bed on its entrance end. The resulting products and unreacted components exiting the bed are analyzed by mass spectrometry.

A pulse series may consist of identical pulses, to determine the diffusion parameters (inert gas) or to study adsorption/reaction of an active gas on the active sites of the solid, or of alternating pulses of two different active species, to study the properties of surface intermediates.

This particular organization of the catalytic process allows studying the rates of catalytic reactions under well-defined conditions difficult to attain in classical steady-state experimental catalytic reactors.

2. Characteristics of a TAP experiment

To achieve the goal of a TAP experiment, some restrictions must be observed. These concern the catalyst sample, gas pulses, and the reactor design.

2.1. Catalyst

The sample represents typically a practical catalyst, containing some active components (metals, oxides etc.) deposited on the surface of a support which may be itself active or not. Typical supports are porous, and the resulting catalyst will be porous too. The amount of active sites (surface species involved in binding one molecule from the gas phase) in the sample in the reactor must be much greater, preferably by a factor of the order 100-1000 than the amount of adsorbing/reacting gas contained in one pulse. This provides for the practical invariability of the catalyst surface when exposed to a series of some tens of pulses.

The sample is contained in a tubular reactor, typically of 5 mm diameter; the typical amount is about 0.1 g (layer of 1 – 2 cm; except in a Thin Zone TAP reactor, “TZT”)⁴. For practical reasons, the granulometry is between 200 and 400 μm. The sample is maintained between two layers of an inert solid with a similar granulometry. The whole charge is maintained by metal grids or quartz wool.

2.2. Gas pulses

The pulses are generated by special computer-driven valves connected to a calibrated volume containing desired gases. The pressure in the source volume may be measured which allows to calibrate the MS responses by comparing the integrated responses with the amount of a gas extracted from this volume.

The amount of a gas in a pulse should be kept identical for all pulses of a series, and as low as possible. The lower limit is determined by the sensitivity of the MS detector used. Typical values are between 10¹² and 10¹⁵ molecules/pulse.

This low pulse sizes are necessary to assure the virtual invariability of the catalyst surface, but also to allow treating the mass transport in the gas phase as the diffusion in the Knudsen domain.

The essential characteristics of this domain are absence of the bulk flow and independent diffusion of each species (collision of molecules in the gas phase may be neglected).

The flux of a species „j“ may then be written as

$$F_i = -D_i \frac{\partial c_i}{\partial x} \quad (1)$$

Where

$$D_i = D^0 (T / M_i)^{1/2} \quad (2)$$

D⁰ is a constant for the milieu through which the transport is taking place, T is the temperature in kelvins, and M_i is the molar weight of the diffusing species¹³.

If M_i is expressed in its usual units g/mol, then D⁰ is in m²g^{1/2}s⁻¹mol^{-1/2}K^{-1/2}.

The experiments with inert gases allow determining the constants D⁰ for each layer

(subdomain) in the reactor, which can be then used in the modeling of the transport combined with adsorption/reactions:

$$\varepsilon \frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} + \rho_b n_s r_i \quad (3a)$$

for gas-phase species, and

$$\frac{\partial \theta_j}{\partial t} = r_j \quad (3b)$$

for immobile adsorbed species. ε is the porosity of the bed (layer), ρ_b is its density in kg/m³, n_s is the concentration of active sites in mol/kg of the catalyst, θ_j is the degree of coverage of active sites by species „j“, and r_i, r_j are rates of formation of species „i“ and „j“, respectively, (negative for reactants/adsorbing species) in s⁻¹.

2.3 Organization of the process

The first version of the apparatus TAP (“TAP-1”)¹, contains three chambers connected by coaxial openings. The first chamber contains the reactor described previously, and the third one is evacuated by a powerful vacuum pump, and contains the MS detector placed on the axis of the reactor and the openings. The later versions (TAP-2, TAP-3) have only one cylindrical chamber evacuated on one end and receiving the flow of gases exiting the reactor on the opposed wall (Fig. 1). All versions have been described in detail in the literature¹⁻³.

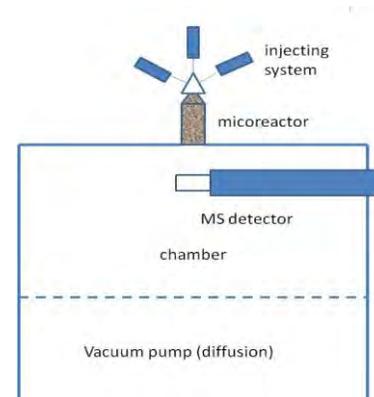


Figure 1. Schema of a TAP-2 reactor.

2.4 Interpretation of the TAP results

The usual quantitative exploitation of TAP experiments is based on simplified models of presented above systems and processes. In particular, a “simple model”⁵ is based on the following assumptions: (1) Knudsen diffusion everywhere, (2) influence of the solid porosity negligible, (3) homogeneity of the solid layer (temperature, coverages), and (4) ideal boundary and initial conditions, i.e. entrance flux or concentration well represented by Dirac $\delta(t)$ or $\delta(x)$, respectively, exit concentration equal to zero, and initial concentration equal to zero everywhere. The equations of this model may be solved analytically which reduces the computation times and allows studying the kinetics without specifying the reaction mechanism⁴. However, all these assumptions are approximations, so the question arise, how the deviations influence the precision of the modeling. The application of Comsol to appreciate the use of the Dirac function as the entrance boundary condition in practical TAP experiments, to model alternative-pulse experiments, and to analyze the influence of the catalyst porosity have been addressed before⁶. In this paper a TAP facility (TAP-2) will be modeled to compare the concentrations in the TAP chamber with exit fluxes of an injected gas, and the dusty gas modeling will be compared with that using Knudsen model, for isothermal and non-isothermal cases.

2.4.1 Mass transport in the layers of the reactor (“subdomain properties”). The difficulties may arise from different sources: non-respect of the Knudsen regime, presence of the free volume between the injection valves and the (first) solid layer in the reactor, temperature in the reactor variable with the position ($,x'$), in particular the thermal transpiration effects.

If the pressure (concentration) in some parts of the reactor exceeds that corresponding to the Knudsen regime, a model known as Dusty Gas Model (DGM)⁷ may be used to represent the gas flow. For a one-component flow, the flux is expressed as

$$F_i = -\left(D_i + \frac{BRTc_i}{\mu_i}\right) \frac{\partial c_i}{\partial x} + \frac{\alpha_i}{c_i RT + 2\alpha_i} \frac{c_i D_i}{T} \frac{\partial T}{\partial x} \quad (4)$$

In this equation, D_i is the effective Knudsen diffusivity, B is the permeability of a layer or of the free volume in the reactor, μ_i is the bulk viscosity of the gas $,i'$ (low pressure limit), and

$$\alpha_i = \frac{3}{4} \frac{\mu_i}{M_i} \beta RT / D_i \quad (5)$$

β is the porosity-tortuosity ratio. The second term on the right-hand side of the equation (4) represents so-called thermal transpiration.

In practical TAP reactors the temperature in the layers of inert solid and of the catalyst is always a function of the position $,x'$. If the reactor is treated in 1D approximation, for the Knudsen domain the equation (3) should be rewritten as

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left(D_i \frac{\partial}{\partial x} \right) c_i + \rho_b n_s r_i \quad (6)$$

and the influence of temperature on the reaction rates should be taken into account. In the case of huge temperature gradients, thermal transpiration should be taken into account, too.

2.4.2 Initial conditions. Most qualitative work was performed with so-known Single-pulse experiments (SP) in which the catalyst suitably pretreated is exposed to a short series of pulses of an active gas. The lapse of time between pulses is usually long enough for the gas phase initial condition $c = 0$ to be acceptable. The initial state of the surface of the catalyst corresponds typically to a “proper” surface for which the coverage by active sites, θ_0 , is taken as one. As already stressed, the amount of active molecules in one pulse is much lower than the total amount of active sites in the catalyst sample, so that the assumption of $\theta_0 = 1$ may be retained for all pulses.

In multipulse experiments (MP) the catalyst is exposed to much longer series of pulses, to suppress the consequences of previous SP experiments (e.g., to reduce the catalyst) or to modify the catalyst (“state-modifying experiments”). In the later case, the homogeneity of the modification (local coverage of active sites by the modifying agent, initial condition for successive SP experiments) may not be respected. The same question arises for Alternating Pulse (“Pump-Probe”) experiments

where short series of alternating pulses of different active gases are applied to the catalyst. Finally, as the reaction temperature usually exceeds 500 K, and the injection valves cannot be heated, there is an important temperature gradient between the entrance of the reactor and its part maintained at the reaction temperature. A term containing such a gradient will intervene in the flux expression if the gas pressure in the reactor demands the use of the dusty gas model.

2.4.3. Boundary conditions. Most basic theoretical analyses (e.g., see ¹⁻⁵) were performed assuming that these fluxes can be represented as Dirac δ -functions normalized to match the amounts of injected gases. The advantage of this hypothesis is the possibility to obtain analytical solutions of PDE systems (equations 3 for all participating species). The adequacy of such assumption for practical pulses of about 1 ms width can be discussed. Zou et al.⁸ speculated that the correct entrance condition is a non-steady state flux, i.e. the temporal dependence of the flux time for all gaseous components injected by the valves. The presence of a free volume between the injection system and the reactor particles has to be taken into account as well.

The measured exit data produced by the MS detector are obviously proportional to the concentrations of the outgoing species at the place where the detector is placed. Typically, the boundary condition at the exit is taken as $c_i = 0$ for all gas phase species. Following Zou et al.⁸, the exit data should be taken as proportional to the exit fluxes of species. The assumption about zeroth exit gas concentrations was criticized recently by Gao et al.⁹

3. Studied models

3.1 The reactor

The (micro)reactor is assumed to be a cylindrical tube with inner diameter of 4 mm containing a layer of 4 cm of length of an inert solid with following properties: porosity $\varepsilon = 0.5$, Knudsen diffusivity constant $D^o = 10^{-3} \text{ m}^2/\text{s} (\text{mol}/\text{kg K})^{1/2}$, permeability $B = 10^{-10} \text{ m}^2$.

There is no free volume between the valves and the solid.

Diffusing gas is argon, molar mass $M = 40 \text{ g/mol}$; its viscosity μ is expressed by Sutherland equation

$$\mu = C_1 T^{1.5} / (T + C_2) \quad (7)$$

with the constants $C_1 = 2.0521 \cdot 10^{-6} \text{ Pa s K}^{-1/2}$ and $C_2 = 171.3 \text{ K}$, obtained by adjusting equation (7) to the values computed from a more complex equation¹⁰.

Initial condition is $c = 0$ at $t = 0$ for all „x“, the entrance boundary condition is taken as „Flux“:

$$F_0 = N_0 / (N_A A) t / \tau^2 \exp(-t/\tau) \quad (8)$$

where N_0 is pulse size in molecules (between 10^{12} and 10^{17}), N_A is the Avogadro constant, $6.02 \cdot 10^{23}$ and A is reactor cross section^{6,11}. Parameter „ τ “ was taken as 1 ms.

3.2 Diffusion: influence of the pulse size.

The dusty gas model of the diffusion is not included in the standard models of Comsol 3.5a, so the diffusion in this reactor was modeled using 1D, PDE Modes > General Form (g) > Time-dependent analysis, with the DGM expression for the flux given by equation (4). The boundary condition for the entrance is eq. (8), Neumann condition, and for the exit it is taken as $c = 0$ (Dirichlet condition). The desired result is the flux at the exit of the reactor.

To check this modeling using PDE Mode, the results obtained for the pulse size of 10^{12} molecules were compared with those obtained with the mode „chdi“: Chemical Engineering Module > Mass Transport > Diffusion > Transient analysis, for the same pulse size, assuming Knudsen diffusion, with expression (2) for „D“ (Fig. 2).

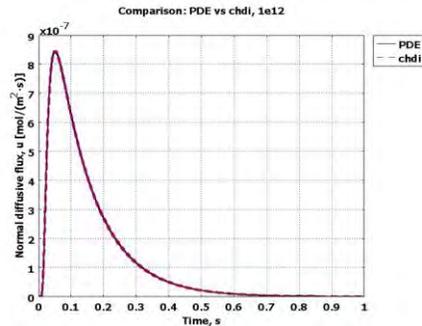


Figure 2. Exit flux computed using PDE-General form (g), and Diffusion (chdi) modes. $T = 300 \text{ K}$, $N_0 = 10^{12}$.

An excellent agreement of the results is evident. For such a low pulse size, DGM reduces to Knudsen model.

3.2 Modeling of the TAP-2

A simplified model of the TAP-2 facility consist of a reactor as described in 3.1, attached by its exit to a cylindrical vacuum chamber, which is evacuated at the opposed end by a vacuum pump (see Fig. 1). The ensemble chamber – reactor has been modeled by adjoining a cylinder of a diameter $d_0 = 24$ cm and of a height 30 cm (chamber, Subdomain 1) to a reactor as in 3.1 (Subdomain 2).

The model is: 3D, Chemical Engineering Module > Mass Transport > Diffusion > Transient analysis (chdi). In both subdomains Knudsen diffusion was assumed, using the equation

$$D_K = \frac{2d_0}{3} \sqrt{\frac{2000RT}{\pi M}} \quad (9)$$

for the diffusivity in the chamber.

The entrance boundary condition was as in 3.1, while for the exit of the chamber toward the pump, condition „Flux“, $F_0 = -(V_p/A_0)c$ with V_p = pumping speed in m^3/s and A_0 = chamber cross-section.

The model was meshed using free mesh with 112377 degrees of freedom.

The researched results were the concentrations in the chamber, on the axis of the ensemble chamber – reactor, considered as proportional to the indications of a MS detector placed at these points. It is evident that the detector measures the local concentration c_i of a selected species, but usually this MS signal is considered as proportional to the exit flux of this species, while the boundary exit condition is taken as $c_i(\text{exit}) = 0$. This approach was criticized recently⁹.

4. Results and discussion

4.1 The influence of the pulse size (Dusty Gas Model). The influence of N_0 in an isothermal reactor ($T = 300$ K) is shown in Fig. 3 for N_0 between 10^{12} and 10^{17} molecules ($1.66 \cdot 10^{-12}$ – $1.66 \cdot 10^{-7}$ mol).

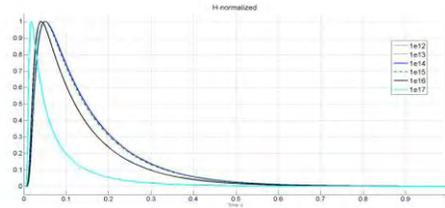


Figure 3. Height-normalized exit flow from the microreactor (model 3.1) for various pulse sizes.

It can be seen that up to $N_0 = 10^{15}$ the curves are practically identical (and identical with that obtained with the Knudsen model). The differences increase strongly for larger pulse sizes. This agrees quite well with the results of Delgado et al.¹² On the other hand, this result correlates well with a comparison of two terms of eq. (4), $RTBc/\mu$ and D , Fig. 4. The maximum values of $RTBc/(\mu D)$ obtained for $N_0 = 10^{13}$, 10^{15} , 10^{16} and 10^{17} are respectively 0.0022, 0.21, 1.55 and 8.7: the values larger than 1 are associated with significant deviations from the Knudsen model.

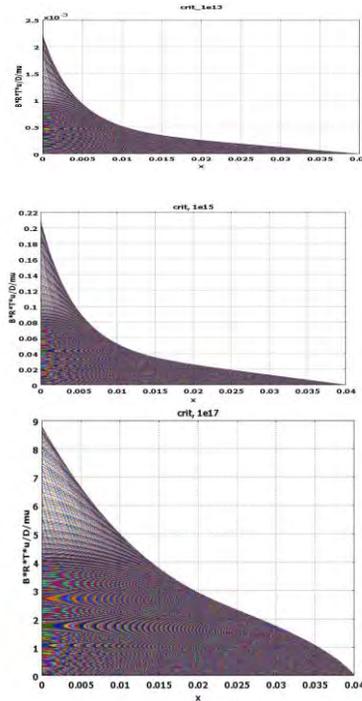


Figure 4. Comparison of bulk diffusion and Knudsen terms in eq. (4), for all time and all „x“ values, in function of the pulse size.

4.2 The influence of the thermal transpiration term was studied on the same model, with the flux in the subdomain 2 (microreactor) given by equation 4, assuming the temperature of the injection system T_0 as 300 K and that of the reactor T_r as 800 K. The temperature was supposed to vary linearly between T_0 and T_r over a distance of 5 mm.

The results are shown in Fig. 5. It should be stressed that the thermal transpiration term does not vanish as the pressure (concentration) approaches 0, so it should be taken in the consideration even in Knudsen domain, as far as the DGM may be considered as correct.

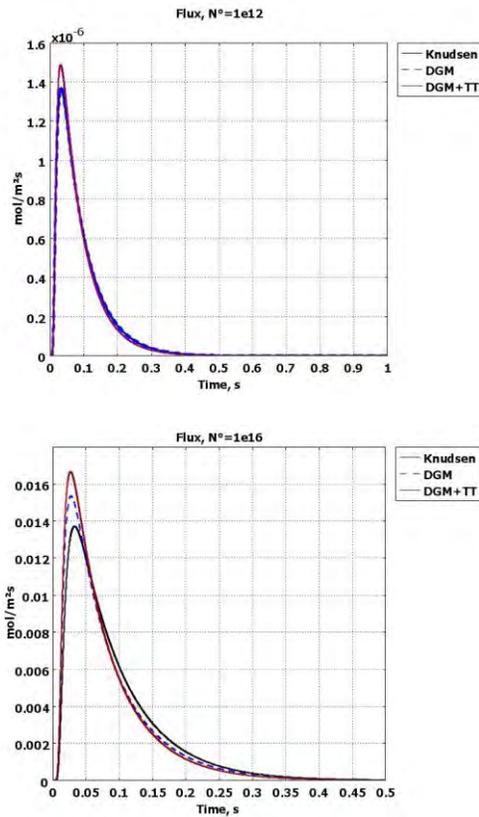


Figure 5. Knudsen model vs. DGM, for $N_0 = 10^{12}$ and 10^{16} , without and with thermal transpiration term.

4.3 Reactor exit flux vs. concentration in the chamber of TAP-2.

The objective of this part is to verify the validity of the modeling of TAP reactors considering the indications of MS detector in the chamber as proportional to the fluxes of the molecules

leaving the bed in the reactor modeled with the exit boundary condition $c = 0$.

The concentrations in the chamber were computed for different pumping speeds and for different distances from the exit of the reactor, height-normalized, and compared with the height-normalized exit fluxes for the microreactor alone modeled in a 1D, Knudsen domain approach (3.1). For the pumping speed of $1 \text{ m}^3/\text{s}$, the shapes of the curves change little with the distance, but differ markedly from that of the exit flow curve (Fig. 6).

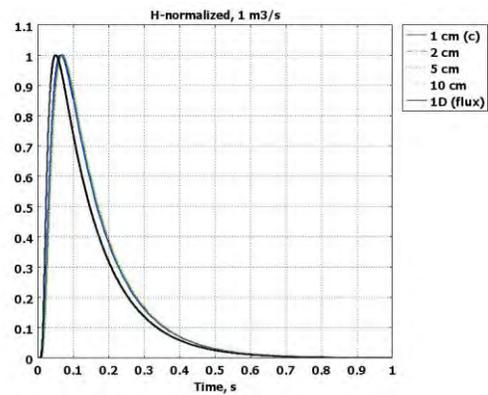


Figure 6. Concentrations c^* at various distances from the exit of the microreactor (model 3D) and Exit flow from the microreactor (model 1D, Knudsen). All curves height-normalized. $N_0 = 10^{12}$.

These differences depend mostly on the pumping speed, Fig. 7, at least for the examined model which represents obviously an important simplification of the real TAP-2 instrument.

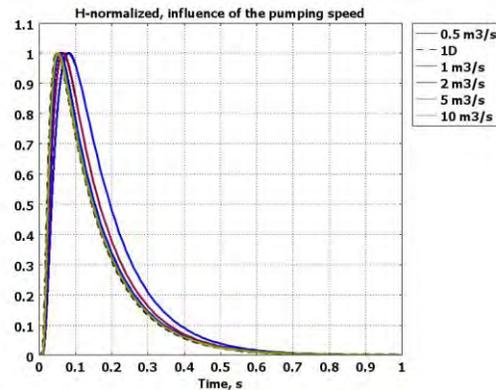


Figure 7. Influence of the pumping speed: the difference between the curves disappears at about $5 \text{ m}^3/\text{s}$; distance from the exit 1 cm. $N_0 = 10^{12}$.

However, it appears to confirm the results of Gao et al.⁷ who found that the pumping speed of 1.5 m³/s may be insufficient.

Constales et al.⁵ have shown that exit fluxes are not influenced by the limited variation of the pressure in the chamber. Indeed, the exit flux integrated over the interface microreactor – chamber in the 3D model examined here is not modified by the pumping speed, Fig. 8. So, the source of the differences shown in Figs. 6 and 7 is not due to the inadequacy of the exit boundary condition $c = 0$, but to the flow phenomena in the chamber.

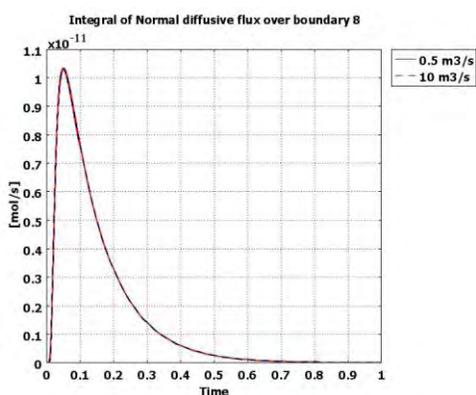


Figure 8. The exit flux of the microreactor integrated over the exit area for two pump speeds. $N_0 = 10^{12}$.

5. Conclusions

The flexibility of Comsol is well adapted to the study and control of the models of TAP reactors. Such models are necessary to interpret quantitatively experimental results. In some cases, the hypotheses of these models may lead to important errors. The Comsol modeling may help to detect such situations for particular studied systems (geometry, solid phases, processes present), or, better, improve the models by including new features to obtain better estimation of kinetic or diffusion parameters.

6. References

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