



Article Synthesis and Mathematical Modelling of the Preparation Process of Nickel-Alumina Catalysts with Egg-Shell Structures for Syngas Production via Reforming of Clean Model Biogas

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Abstract: For the work presented herein nickel catalysts supported on γ -alumina extrudates (Ni/Al) with an egg-shell structure were prepared, using a modified Equilibrium Deposition Filtration (EDF) technique. Their performance was compared, for the biogas dry reforming reaction, with corresponding Ni/Al catalysts with a uniform structure, synthesized via the conventional wet impregnation method. The bulk and surface physicochemical characteristics of all final catalysts were determined using ICP-AES, N₂ adsorption-desorption isotherms, XRD, SEM, and TEM. A theoretical model describing the impregnation process for the EDF extrudates, based on the Lee and Aris model, was also developed. It was concluded that following specific impregnation conditions, the egg-shell macro-distributions can be successfully predicted, in agreement with the experimental results. It was shown that the Ni/Al catalysts with an egg-shell structure had a higher H₂ yield in comparison with the ones with a uniform structure. The difference in catalytic performance was attributed to the improved surface and structural properties of the egg-shell catalysts, resulting from the modified EDF technique used for their preparation.

Keywords: biogas reforming; syngas production; nickel catalysts; egg-shell catalysts; surface properties; transport properties; theoretical modeling

1. Introduction

Biogas is one of the most promising renewable fuels, typically generated from the anaerobic digestion of biodegradable organic biomass [1,2]. As the main constituents of biogas are methane (CH₄) and carbon dioxide (CO₂), the atmospheric compounds mostly responsible for the greenhouse gas effect, their transformation into hydrogen rich mixtures and/or synthesis gas (syngas) is a task worth pursuing [3–5].

Biogas typically consists of CH₄ (50–75%), CO₂ (25–50%) and 2–8% other gases i.e., water vapors (H₂O), nitrogen (N₂), oxygen (O₂), and hydrogen sulfide (H₂S) [6,7]. However, the average composition of CH₄ and CO₂ in a molar ratio equal to 1.5 is favorable for the methane reforming reaction, and furthermore, representative of the biogas produced from many facilities [8,9]. The product of this reaction, synthesis gas or syngas, consisting of hydrogen (H₂) and carbon monoxide (CO), is an important industrial raw material, as it can be used for the production of synthetic liquid biofuels and chemicals through the well-known Fischer-Tropsch (FT) process [10–14].

The dry reforming of methane (DRM) process, producing hydrogen rich mixtures or synthesis gas with H_2/CO molar ratios approximately equal to 1, is regarded as one the most suitable paths for the valorization of biogas [15,16]. Moreover, its successful



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). application could lead to the development of small-scale H_2 production units close to the localities where biogas is being produced. Despite its obvious advantages, the commercial development of DRM is for now restricted, due to the lack of effective catalysts resistant to carbon formation and sintering at high temperatures [17–19].

The main network reactions included in DMR process are summarized as follows:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2, CO_2 \text{ reforming}$$
 (1)

$$CO_2 + H_2 \rightleftharpoons H_2O + CO$$
, Reverse water gas shift (2)

$$CH_4 \rightleftharpoons C + 2H_2, CH_4$$
 decomposition (3)

$$2CO \rightleftharpoons C + CO_2$$
, Boudouard reaction (4)

$$C + H_2 O \rightleftharpoons CO + H_2$$
, Carbon gasification (5)

Nickel (Ni) supported on inexpensive and thermally stable metal oxides (e.g., aluminum oxide) has been extensively tested as a catalyst for the DRM reaction, mainly due to its high activity and its relatively low cost [20–26]. However, the nickel-based catalysts usually exhibit high activity at the beginning of the reaction, but then deactivate rather rapidly due to surface carbon deposition [6,11,27]. Thus, the development of nickel catalysts with greater resistance to coking during the dry reforming of biogas is a necessity, if stable long-term operation is to be achieved.

Modification of the catalyst with alkali metal oxides and/or rare earth metal oxides has been shown to greatly enhance catalytic stability [10,11,21,28–31]. In addition, the appropriate macro-distribution of the catalytically active phase within the spherical or cylindrical particles of the supporting material can greatly enhance the performance of the catalyst [32–34].

Usually, the DRM supported Ni catalysts are synthesized by impregnating the support's particles (spheres or cylindrical pellets) with an aqueous solution of nickel nitrate, followed by drying and calcination at high temperatures. This procedure results in a uniform nickel concentration profile (macro-distribution) on the whole body of the support, i.e., across the diameter of the spherical or the cylindrical particle [35]. This is rather expected as it is known that, following the conventional wet impregnation technique, the nickel species deposition on the support surface mainly occurs during drying, which follows the impregnation step by uncontrolled precipitation in the liquid phase inside the pores of the support due to the evaporation of water.

On the other hand, shell catalysts consist of a compact inert support, in the form of rings, spheres, tablets or pellets, and a thin active shell that encloses it, and are ubiquitously used in industrial processes, especially when pellet intraparticle mass and heat transfer limitations have a negative effect on the activity/selectivity and life of porous catalysts. Catalysts with a peripheral macro-distribution (namely egg-shell or core-shell) are very useful for catalytic processes in which the surface reaction proceeds with high rates, and consequently the intraparticle diffusion becomes the limiting step. In these cases, the reactants and the reaction products are more easily transferred between the catalytic active surface and the bulk phase from the periphery of the pellet (egg-shell) than from its inner core (egg-yolk) [35–37]. Thus, a major advantage of the egg-shell type catalysts is short transport or diffusion paths and a better heat transport in the catalyst layer [35,38].

As the elimination of the role of pore diffusion is advantageous to a number of heterogeneously catalyzed reactions, egg-shell catalysts are used, amongst others, for dimethyl oxalate synthesis, Fischer–Tropsch synthesis, selective hydrogenation, methane reforming, and methane partial oxidation etc., as the maximum selectivity and yield to the desired product are obtained when the active phase is located on the external pellet surface. The thickness of the active phase layer also plays a key role. In several studies, supported nickel on alumina catalysts with egg-shell structures showed very good activity and thermal stability in all types of methane-reforming reactions, such as steam reforming (SR) and DRM, as well as the partial oxidation reaction (POX) [39–43].

Egg-shell supported catalysts with transition metals as an active phase can be prepared using different techniques [32,44,45]. Lycourghiotis and co-workers [46–48] have proposed the Equilibrium Deposition Filtration (EDF) technique as an alternative route to achieve the optimization of the size of the supported oxidic nanoparticles. Following this technique, a small amount of supporting material powder is immersed in a considerably large volume of a dilute aqueous solution of the transition metal ionic species (TMIS), ideally at fixed pH and ionic strength experimental conditions. The equilibration of the suspension, under stirring for several hours, is then carried out [24,49]; it is during this step that the TMIS are deposited at the interface developed between the surface of the support and the aqueous solution (interfacial deposition).

The impregnation processes have been described by numerous mathematical models [50–58], which incorporate several factors that determine the active phase's content and the final profile of its macro-distribution, including (i) time of impregnation; (ii) pH, temperature, and initial concentration of the impregnating solution; (iii) the use of additives; and (iv) the previous state of the support [50]. Whereas, historically, many earlier studies were focused on the description of the "diffusion-adsorption" mechanism that controls the active phases profile deposited into formed support material particles adopting simple adsorption mechanisms, later attempts were focused more closely on the physical process of adsorption [7,56,59]. Despite the high number of models available in the literature and the diversity of their complexity, there is still a lack of models that combine detailed descriptions of the imbibition, diffusion, and adsorption processes.

The purpose of this study was to investigate the effect that different active phase macro-distributions, i.e., egg-shell vs. uniform structure, have on the catalytic activity and stability of nickel on γ -alumina (Ni/Al) supported catalysts during the dry reforming of biogas. For this purpose, a modified EDF technique, offering the possibility of tailoring the active phase radial concentration profile (macro-distribution) on the support's cylindrical extrudates (pellets) was applied for the synthesis of egg-shell catalysts, and the conventional wet impregnation technique was used for the synthesis of uniform catalysts. Moreover, catalysts with different active phase loadings (6 and 16 wt%) were prepared using each method. The structural bulk and surface properties of the catalysts, and their dependence on the preparation method, were determined using BET, XRD, ICP-AES, TEM, and SEM. Concerning the biogas reforming reaction, catalytic performance was studied according to the influence of the reaction temperature to CH₄ and CO₂ conversion values, as well as to H₂ yield and to H₂/CO molar ratio, and the role of preparation technique and the active phase macro-distribution type to the final catalyst's properties.

In addition, we present a fundamental model for the preparation of the egg-shell supported catalysts, based on the Lee and Aris model [60]. The model was used to predict the experimental impregnation parameters concerning the radial deposition concentration profiles of Ni species on γ -alumina cylindrical extrudates, derived from the application of the modified EDF technique. Parameters such as time of impregnation, pH and the initial concentration of the impregnating solution were of key importance, whereas the system was thought isothermal and at room temperature. The imbibition process was modelled as a simple one-phase flow in a bundle of identical cylindrical tubes, all having the same pore diameter equal to the average pore diameter of the porous support. Darcy's law for the flow of liquids through porous media under quasi-steady-state conditions was adopted and Laplace's equation was used for the evaluation of the capillary tubes was evaluated using the Washburn approximation [61]. In this way, the model equations that predict the time evolution of the preparation process and the radial distribution of the active components were developed.

2. Theory/Calculation

Heterogeneous supported catalyst preparation by impregnating porous carriers with the desired active species solution is a common technique in catalyst manufacturing. In this process, the active species concentration profile within the supporting material pellets can be controlled by the impregnation experimental conditions [62–64]. The catalyst preparation method involves three main steps. First, a porous support is brought into contact with an aqueous solution in which the precursor of a desired catalyst active phase is dissolved. During this process, the aqueous solution is imbibed through the pore space of the porous support, due to capillary forces. At the same time, the active catalyst species are diffused through the pore space already occupied by the aqueous solution and adsorbed on the high internal support material porous surface. The imbibition process is gradually decelerated and eventually stopped as equilibrium between capillary forces and trapped air pressure is established or as the solution approaches the core of the pellet. The second step is the drying of the pellets in order that the imbibed solution to be removed. During this process, the solutes migrate due to capillary flow and diffusion, causing a redistribution of the adsorbed catalytically active species. Finally, calcination and reduction transform the catalyst from its precursor state into its active form [65–68].

However, for a fixed chemical composition, the macro-distribution of the active species on the support extrudates also has critical influence on the performance of the catalyst [69,70]. The first and the second step of the preparation procedure are the key steps for the determination of the final activity profiles of the impregnated catalysts pellets. Several profile types can be established, such as egg-shell (deposition of the active phase in the exterior layer of the pellet), egg-yolk (active phase concentrated in the core of the pellet), and uniform macro-distribution [50,70,71].

A successful methodology to produce egg-shell catalysts has been already presented by Goula et al. [33,34]. Nonetheless, a consistent mathematical model of the catalyst preparation process can help control the preparation process parameters. For this purpose, we developed a one-dimensional transient model to describe radial impregnation in cylindrical pellets. Imbibition, diffusion, and adsorption were the basic mechanisms that were included in the model on the basis of the following assumptions:

- i. The catalyst support consists of distinct, dry, homogenous, and isotropic catalytic particles of cylindrical geometry, non-deformable and not interacting.
- ii. The total amount of the impregnating solution is sufficient to fill the water pore volume of the support.
- iii. The impregnating solution is a Newtonian and incompressible liquid.
- iv. The support pore surface is water wet. The capillary force can be characterized by a single average pore size.
- v. The size of the pores of the support is in the order of several nanometers so that gravity force is negligibly small compared with viscous and capillary forces, but the pores are large enough so that exclusion of the solutes is avoided.
- vi. Inertial forces are negligible and quasi steady-state approximation is justified.
- vii. Air initially filling the pore space is either totally entrapped and compressed in the center of the pellet or totally escaped from it.
- viii. Imbibition can be thought as one-phase radial plug flow through the porous support material with the sharp liquid front separating the advancing liquid and the receding air. The cylindrical pellets are long enough so that edge effects can be ignored. Darcy's law is applicable, and the absolute permeability of the porous support is the pertinent parameter.
- Hydrodynamic dispersion of the active species is taken into account through a dispersion coefficient that combines effective diffusivity and mechanical dispersion.
- x. Non-equilibrium processes such as dynamic contact angle, surface viscosity, and dynamic surface tension are not important. Dynamics of thin liquid films do not influence imbibition flow.
- xi. Surface diffusion of the active species does not take place.
- xii. Deposition of the active species on the supporting material pore surface takes place through isothermal adsorption (sorption and desorption), the overall rate of which is described by a consistent physicochemical deposition model.

The dimensional variables of the problem are defined in the nomenclature at the end of the paper, whereas dimensionless variables and parameters are defined in due course: Mass balances of the active species in the liquid phase (k = 1, 2, ..., n - 1):

$$\frac{\partial \rho_k^f}{\partial t} + \nu \frac{\partial \rho_k^s}{\partial t} - v_p \frac{\partial \rho_k^f}{\partial r} - D_{Lk} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \rho_k^f}{\partial r} \right) = 0$$
(6)

Total mass balance of the liquid phase (continuity equation for incompressible fluids):

$$\frac{\partial(\mathbf{rv}_{\mathbf{p}})}{\partial \mathbf{x}} = 0 \tag{7}$$

Mass balance of the active species in the solid phase (generic equation):

$$\nu \frac{\partial \rho_k^s}{\partial t} = f\left(\rho_k^f, \rho_k^s, v_p, \varepsilon, \text{ solution, inert species, support, etc.}\right)$$
(8)

The last equation represents the adsorption rate of the active species. There are a lot of possibilities for the adsorption rate equation, such as adsorption following Langmuir kinetics,

$$\nu \frac{\partial \rho_k^s}{\partial t} = \frac{a_{\nu} n_k^s}{\varepsilon} \left[k_{1k} \rho_k^f \left(1 - \sum_j^{n_{\gamma}} \frac{\rho_j^s}{n_j^s} \right) - k_{2k} \frac{\rho_k^s}{n_k^s} \right]$$
(9)

or adsorption when mass transfer is the rate limiting step (e.g., mass transfer through a stagnant film),

$$v \frac{\partial \rho_k^s}{\partial t} = \frac{\alpha_v}{\varepsilon} k \left(\rho_k^f - \rho_k^{f*} \right)$$
(10)

In this study, we choose to work with Langmuir kinetics, since its parameters allow for a more meaningful physical interpretation. Momentum balance (Darcy's equation for Newtonian one phase flow through homogeneous and isotropic porous solids):

$$\varepsilon v_{\rm p} = \frac{k}{\mu} \frac{\partial P}{\partial r} \tag{11}$$

An additional equation that describes the motion of the sharp front that separates the advancing liquid, and the receding air must supplement the system of the four independent equations of the model, i.e., Equations (6), (7), (9) and (11). Actually, the following equation defines the frontal position, r_f , as a function of time:

$$\frac{\mathrm{d}\mathbf{r}_{\mathrm{f}}}{\mathrm{d}\mathbf{t}} = -\mathbf{v}_{\mathrm{pf}} \tag{12}$$

A system of initial and boundary conditions suitable for the aforementioned system of partial differential equations is the following:

Initial conditions:

$$t = 0, \ \forall r \in 0, R, \ \rho_k^t(0, r) = 0, \ \rho_k^s(0, r) = 0$$
 (13)

Boundary conditions:

$$\mathbf{r} = \mathbf{R}, \ \forall \mathbf{t} \in (0, \mathbf{t}_{e}), \ \mathbf{v}_{p} \left(\rho_{k}^{f,0} - \rho_{k}^{f} \right) = \mathbf{D}_{Lk} \frac{\partial \rho_{k}^{t}}{\partial \mathbf{r}}, \ \mathbf{P} = \mathbf{P}_{a}$$
(14)

$$\mathbf{r} = \mathbf{r}_{f}, \ \forall t \in (0, t_{e}), \ \mathbf{v}\mathbf{v}_{p}\boldsymbol{\rho}_{k}^{s} = D_{Lk}\frac{\partial \boldsymbol{\rho}_{k}^{f}}{\partial r}, \ \mathbf{P} = P_{a}\frac{R^{2}}{r_{f}^{2}} - P_{c} \text{ or } \mathbf{P} = P_{a} - P_{c}$$
(15)

Definition of dimensionless variables and problem parameters:

$$u_{k} = \frac{\rho_{k}^{f}}{\rho_{k}^{f,0}}, \ \theta_{k} = \frac{\nu \rho_{k}^{s}}{\rho_{k}^{f,0}}, \ \xi = 1 - \left(\frac{r}{R}\right)^{2}, \ \tau = \frac{2r}{R^{2}} \int_{0}^{t} v_{p} dt$$
(16)

$$\eta_{k} = \frac{vn_{k}^{s}}{\rho_{k}^{f,0}}, K_{pk}' = K_{pk}\rho_{k}^{f,0} = \frac{k_{1k}}{k_{2k}}\rho_{k}^{f,0}, Pe_{k} = \frac{v_{p}r}{D_{Lk}}, St_{k} = \frac{k_{k}r}{v_{p}},$$

$$\widetilde{v}_{p} = \frac{v_{p}}{v_{pc}}, v_{pc} = \frac{kP_{a}}{\mu\epsilon R}, \widetilde{P} = \frac{P}{P_{a}}$$
(17)

where, u_k is the dimensionless impregnating solution concentration of the k-th component (active species), θ_k is the dimensionless surface concentration, ξ is the dimensionless space variable, τ is the dimensionless time variable, η_k is the relative adsorption capacity, K'_{pk} is the dimensionless adsorption equilibrium constant, Pe_k is the (time dependent) Péclet number, St_k is the (time dependent) Stanton number, \tilde{v}_p is the dimensionless interstitial pore velocity, v_{pc} is the characteristic dimensionless interstitial pore velocity of the impregnating liquid that flows through a porous medium with absolute permeability, k, when the driving pressure difference is equal to the atmospheric pressure, P_a , and \tilde{P} is the dimensionless pressure. Finally, it is useful to define the dimensionless position of the imbibition front, $\xi_f = 1 - \left(\frac{r_f}{R}\right)^2$, the dimensionless capillary pressure, $\sigma = \frac{P_c}{P_a}$, and the inverse measure of the capillary force, $b = \frac{1}{1+\sigma}$, whereas capillary pressure is given by $P_c = \frac{2\gamma \cos \theta_e}{d_{av}}$, where, γ is the surface tension of the active catalyst solution, θ_e is the equilibrium contact angle, and d_{av} is the average pore diameter.

In addition, D_{Lk} is the dispersion coefficient of the k-th component (active species) and $k_k = \frac{a_U k_{2k}}{1-\varepsilon}$ is a generalized mass transfer coefficient based on Langmuir isotherm and desorption kinetic constant, k_{2k} .

With these definitions the problem equations read now:

Mass balances of the active species (k = 1, 2, ..., n - 1):

$$\frac{\partial u_k}{\partial \tau} + \frac{\partial \theta_k}{\partial \tau} + \frac{\partial u_k}{\partial \xi} - \frac{2}{Pe_k} \frac{\partial}{\partial \xi} \left[(1 - \xi) \frac{\partial u_k}{\partial \xi} \right] = 0$$
(18)

Total mass balance (continuity equation):

$$\frac{\partial}{\partial \xi} \left(\sqrt{1 - \xi} \widetilde{\mathbf{v}}_{\mathbf{p}} \right) = 0 \tag{19}$$

Mass balance of the active species in the solid phase (Langmuir adsorption):

$$\frac{\partial \theta_{k}}{\partial \tau} = \frac{St_{k}}{2(1-\xi)} \left[K'_{pk} u_{k} \left(\eta_{k} - \sum_{j}^{n_{s}} \frac{\eta_{k}}{\eta_{j}} \theta_{j} \right) - \theta_{k} \right]$$
(20)

Momentum balance (Darcy's equation):

$$\tilde{\mathbf{v}}_{\mathrm{p}} = -2\sqrt{1-\xi}\frac{\partial\tilde{\mathbf{P}}}{\partial\xi} \tag{21}$$

Equation of motion of the sharp imbibition front:

$$\frac{\mathrm{d}\xi_{\mathrm{f}}}{\mathrm{d}\tau} = 1 \tag{22}$$

Initial conditions:

$$\tau = 0, \ \forall \xi \in 0, 1, \ u_k(0, \xi) = 0, \ \theta_k(0, \xi) = 0, \ \xi_f(0) = 0$$
(23)

Boundary conditions:

$$\xi=0,\;\forall\tau\in(0,\tau_e),\;\frac{2}{\mathrm{Pe}_k}\frac{\partial u_k}{\partial\xi}=u_k-1,\;\widetilde{P}=1 \tag{24}$$

$$\xi = \xi_{f}, \ \forall \tau \in (0, \tau_{e}), \ \frac{2}{Pe_{k}} \frac{\partial u_{k}}{\partial \xi} = -\frac{1}{1-\xi_{f}} \theta_{k}, \ \widetilde{P} = 1 + \frac{1}{1-\xi_{f}} - \frac{1}{b} \text{ or}$$

$$\widetilde{\widetilde{P}} = 2 - \frac{1}{b}$$
(25)

The above system of partial differential equations constitutes a moving boundary value problem, the solution of which can be greatly facilitated by the observation that Equations (19), (21), and (22) can be solved separately for interstitial pore velocity, \tilde{v}_p , liquid pressure, \tilde{P} , and position of the sharp front between liquid and air, ξ_f . The two remaining Equations (18) and (20) can be solved using the previous results for the two remaining variables, bulk concentration, u_k , and surface concentration, θ_k , of the active species. This way, the system of differential equations is simplified considerably. Essentially, this was the work done by Lee and Aris [60] for spherical pellets, which was followed closely here for cylindrical pellets and radial impregnation.

First, there are two choices in Equation (25) concerning the boundary condition imposed on the liquid pressure at the moving right boundary, according to whether receding air filling initially the pore space of the catalytic pellet is entrapped totally in the center of the pellet or totally escapes from it.

Accordingly, the major result of the first part of the solution is the expression for the dimensionless interstitial pore velocity, \tilde{v}_p , as a function of the dimensionless liquid front position, for the two extreme cases examined here, namely total air entrapment within and total air escape from the catalyst pore space. The two results are given below:

Total air entrapment

$$\widetilde{v}_{p} = -\frac{1-b-\xi_{f}}{b(1-\xi_{f})(\ln\sqrt{1-\xi_{f}})}\frac{1}{\sqrt{1-\xi}}, \ 0 \le \xi_{f} \le 1-b$$
(26)

Total air escape

$$\widetilde{v}_{p} = -\frac{1-b}{b\left(\ln\sqrt{1-\xi_{f}}\right)}\frac{1}{\sqrt{1-\xi}}, \ 0 \le \xi_{f} \le 1$$

$$(27)$$

From Equations (26) and (27), it becomes obvious that the solution to the problem lasts for a certain time period, which is denoted by τ_e , and it corresponds to the time needed for the imbibition process to be completed, i.e., until interstitial pore velocity becomes zero. In dimensionless form, τ_e , it is equal to ξ_e , the final position of the liquid front (see also Equation (22)), and it is given by $\tau_e = \xi_e = 1 - b$ in the case of total air entrapment, whereas, in the case of total air escape the same time is given by $\tau_e = \xi_e = 1$ (catalyst center of the cylindrical pellet). At first sight, it seems that it is not necessary to calculate the dimensional relation between t_e and r_e to actually achieve the final solution. However, when attempting to evaluate the time span that is needed for the completion of the imbibition process in dimensional form, it is realized immediately that an infinite time is needed in both cases. Depending on the fate of the receding air during imbibition, the time for imbibition completion can be evaluated either analytically or numerically, according to:

Total air entrapment

$$t_{e} = -\frac{b}{2} t_{c} \int_{0}^{\xi_{e}} \frac{(1-\xi_{f}) \left(\ln \sqrt{1-\xi_{f}} \right)}{1-b-\xi_{f}} d\xi_{f}$$
(28)

Total air escape

$$t_{e} = -\frac{1}{2} \frac{b}{1-b} t_{c} \int_{0}^{\xi_{e}} (1-\xi_{f}) \left(\ln \sqrt{1-\xi_{f}} \right) d\xi_{f}$$
⁽²⁹⁾

where, $t_c = \frac{L}{v_{pc}} = \frac{\mu \epsilon R^2}{k P_a}$ is a characteristic dimensional time.

With the help of the expressions for the interstitial pore velocity, Equation (26), or Equation (27), the definition of the key dimensionless parameters of the problem, Pe_k and St_k , is complete, and the solution of Equations (18) and (20) can be achieved, with the appropriate initial and boundary values given in Equations (23)–(25).

However, a more stable solution for the moving boundary problem is achieved by converting it to a more tractable fixed boundary value one. Defining a new dimensionless space coordinate, $y = \frac{\xi}{\xi_f}$, as the fraction of the dimensionless frontal position, and using the chain rule, the equations of the new problem are written as:

Before imbibition completion: $\tau \leq \tau_e$

$$\frac{\partial u_{k}}{\partial \tau} - \left(\frac{y-1}{\tau} - \frac{1}{\tau} \frac{2}{\operatorname{Pe}_{ck} \widetilde{v}_{p} \sqrt{1-y\tau}}\right) \frac{\partial u_{k}}{\partial y} - \frac{1-y\tau}{\tau^{2}} \frac{2}{\operatorname{Pe}_{ck} \widetilde{v}_{p} \sqrt{1-y\tau}} \frac{\partial^{2} u_{k}}{\partial y^{2}} + f_{k} = 0 \quad (30)$$

$$\frac{\partial \theta_{k}}{\partial \tau} - \frac{y}{\tau} \frac{\partial \theta_{k}}{\partial y} - f_{k} = 0$$
(31)

$$\begin{aligned} &\tau = 0, \; \forall y \in [0,1], \; u_k = 0, \; \theta_k = 0 \\ &y = 0, \; \forall \tau \in (0,\tau_e), \; \frac{1}{\tau} \frac{2}{\Pr_{e_k} \tilde{v}_p \sqrt{1-y\tau}} \frac{\partial u_k}{\partial y} = u_k - 1 \\ &y = 1, \; \forall \tau \in (0,\tau_e), \; \frac{1-\tau}{\tau} \frac{2}{\Pr_{e_k} \tilde{v}_p \sqrt{1-y\tau}} \frac{\partial u_k}{\partial y} = -\theta_k \end{aligned}$$
(32)

After imbibition completion: $\tau > \tau_e$

$$\frac{\partial u_k}{\partial \tau} + \frac{1}{\tau_e} \frac{2}{Pe_{ck}} \frac{\partial u_k}{\partial y} - \frac{1 - y\tau_e}{\tau_e^2} \frac{2}{Pe_{ck}} \frac{\partial^2 u_k}{\partial y^2} + f_k = 0$$
(33)

$$\frac{\partial \theta_{k}}{\partial \tau} - f_{k} = 0 \tag{34}$$

$$\begin{split} &\tau = \tau_e, \ \forall y \in [0,1], \ u_k = u_k(y,\tau_e), \ \theta_k = \theta_k(y,\tau_e) \\ &y = 0, \ \forall \tau \in (\tau_e,\infty), \ u_k = 1 \\ &y = 1, \ \forall \tau \in (\tau_e,\infty), \ \frac{\partial u_k}{\partial v} = 0 \end{split} \tag{35}$$

where, f_k is the rate of adsorption of the k-th active species given by Equation (20) according to Langmuir adsorption

$$f_{k} = \frac{St_{ck}}{2\widetilde{v}_{p}\sqrt{1-y\tau}} \left[K_{pk}' u_{k} \left(\eta_{k} - \sum_{j}^{n_{s}} \frac{\eta_{k}}{\eta_{j}} \theta_{j} \right) - \theta_{k} \right]$$
(36)

and Pe_{ck}, St_{ck} are the characteristic (time independent) Péclet and Stanton numbers, defined as:

$$Pe_{ck} = \frac{v_{pc}R}{D_{Lk}}$$
(37)

$$St_{ck} = \frac{k_k R}{v_{pc}}$$
(38)

Special provisions were taken in order to extend time integration beyond imbibition completion, in order to take into account possible redistribution of active species on the catalytic surface that is taking place in times after the completion of imbibition process, during evaporation step of catalyst preparation. In Lee and Aris [60], integration started at a time instant greater than zero but arbitrarily close to it, chosen in such a way that integration results were left unaffected. The same practice was followed also here, to circumvent divergence of interstitial time dependent pore space velocity at time zero, as can be seen in Equations (26) and (27). In the same manner, closely following the practice of Lee and Aris [60], it was assumed that imbibition eventually stops at a finite time instant

before its actual completion at infinite time, when liquid front, ξ_f , has reached close to its final position, but it is still away from it by a small but discernible distance. This distance was chosen in a similar way as was done previously at the onset of liquid imbibition, so that the results of integration remain unaffected as well. Finally, total integration time was chosen so that an unaltered solution was achieved.

3. Results and Discussion

3.1. Catalysts Characterization

3.1.1. Physicochemical Properties

Table 1 presents the physicochemical properties of xNi/Al-edf and xNi/Al-wet catalysts. In all cases, the specific surface area values are significantly lower than that of the supporting material (γ -Al₂O₃, 195 m² g⁻¹), which is because the internal surface area of the pore system of the support is gradually covered by Ni species that are adsorbed on alumina active sites, forming a layer [23,24]. As this process continues, and a monolayer is being formed, nickel species are no more deposited through adsorption, and thus the micropores are blocked. These results are in line with those obtained by Rahmani, et al. [72] for a similar Ni/Al₂O₃ catalyst system. Thus, the catalysts with the lower nickel loadings (6 wt%) exhibit higher surface areas and smaller nickel species particle sizes, in comparison with the ones with higher metal loadings (16 wt%). However, especially at low metal loadings, the reduction in the specific surface area is higher for the catalysts with the uniform nickel concentration profile. This finding is attributed to the fact that for the catalytic samples prepared by the modified EDF technique, the Ni species were mostly adsorbed at the surface γ -Al₂O₃ adsorption active sites during the impregnation step, which means that the proportion of Ni species deposited during the drying process was rather small. As for the ICP results, Table 1 shows that the Ni concentration was approximately 6 and 16 wt%, for the low and high loading, respectively, i.e., very close to the nominal one.

Catalyst	S_{BET} (m ² g ⁻¹)	ICP (Ni, wt%)	Crystalline Phase (XRD)	Ni Species Particle Size (nm)
6Ni/Al-edf	173	5.90 ± 0.9	γ-Al ₂ O ₃ , NiAl ₂ O ₄ +	12.1 ± 1.2
16Ni/Al-edf	137	16.80 ± 0.8	γ -Al ₂ O ₃ , NiAl ₂ O ₄ +++	17.2 ± 1.9
6Ni/Al-wet	163	5.91 ± 0.3	γ -Al ₂ O ₃ , NiAl ₂ O ₄ ++	14.1 ± 1.7
16Ni/Al-wet	141	15.87 ± 0.7	γ -Al ₂ O ₃ , NiAl ₂ O ₄ ++++	25.1 ± 2.1

Table 1. Structural and physicochemical properties of the Ni/Al catalysts used herein.

3.1.2. Crystal Structure

The XRD patterns of the nickel on γ -alumina catalysts calcined at 800 °C, for low and high Ni loadings, are shown in Figure 1. Characteristic diffraction peaks at $2\theta = 45.9^{\circ}$ and 67.0° assigned to γ -Al₂O₃ can be observed for all samples [73,74]. Moreover, according to the XRD analysis, no reflections belonging to transition aluminas, θ -alumina (25.6° and 43.3°), or alpha-alumina (31.2° and 36.6°) were observed, indicating that alumina transformation was not promoted at the temperature used for calcination [24]. The spinel nickel aluminate phase (NiAl₂O₄) was identified by diffraction peaks at $2\theta = 19.0^{\circ}$, 37.0° and 59.6°, for all the calcined catalysts, [75,76]. On the other hand, no diffraction peaks corresponding to the nickel oxide phase (NiO) were identified, which indicates either that these structures are smaller than the typical XRD detection limit or that they are nearly amorphous [24,76,77]. The presence of NiAl₂O₄ on the calcined catalysts surface was also corroborated via TEM analysis (discussed below). The increase in the metal loading from 6 to 16 wt%, irrespective of the preparation method used, is accompanied by increasing intensities of the peaks at $2\theta = 37.0^{\circ}$ and 59.6°, probably related to an increase in NiAl₂O₄ concentration in the final catalysts [24].



Figure 1. XRD patterns for (i): (a) γ -alumina, (b) 6Ni/Al-edf, and (c) 16Ni/Al-edf, and (ii) (a) γ -alumina, (b) 6Ni/Al-wet, and (c) 16Ni/Al-wet. All samples calcined at 800 °C.

3.1.3. Electron Microscopy

SEM micrographs of the calcined catalytic samples were recorded in order to analyze their surface composition, as well as the nickel species concentration profile. These micrographs, presented in Figure 2, reveal that by preparing supported catalysts using the modified EDF technique, as proposed by the authors, an egg-shell nickel phase concentration profile along the cylindrical pellet diameter can be accomplished.



Figure 2. SEM images of calcined: (**a**) 6Ni/Al-edf catalyst, (**b**) 16Ni/Al-edf catalyst, (**c**) 6Ni/Al-wet catalyst, and (**d**) 16Ni/Al-wet catalyst.

The atomic percent of the nickel phase measured at the external pellet surface (periphery) for the egg-shell catalysts was found to be 7.8% and 19.9%, and at the center of the catalyst cylindrical particle, 4.5% and 4.8%, for nickel loadings 6 and 16 wt% Ni, respectively (Table 2). The higher nickel species concentration on the periphery of the catalysts cylindrical pellets (extrudates) is likely a result of the strong interactions existing between the nickel particles and the supporting material surface active sites, as a result of the modified EDF technique used for their preparation. It should be mentioned that the SEM-EDS analysis was performed not only at the periphery and at the center of the pellet, but also along the catalyst particle diameter. Thus, the results presented in Table 2 reveal the difference of the atomic percent of nickel in the periphery and the center for the two different macro-distributions. In order to explain this observation, we should consider that the deposition of the nickel species on the γ -alumina surface may be affected through the following two processes: (i) adsorption of the nickel species on alumina surface active sites during the impregnation step, and (ii) precipitation of these species during the step of drying. The ratio of the adsorbed nickel to the precipitated nickel (Ni_a/Ni_p), depends on the value of the impregnation parameters, mainly on pH and concentration of the impregnating solution. For our case, high pH values are related to relatively high density of adsorption sites, whereas low nickel concentration values do not favor precipitation. These conditions, encountered in the preparation of the egg-shell profile catalysts, resulted in the increase of the Ni_a/Ni_p ratio, and thus of the nickel amount which interacted strongly with the support surface.

Table 2. SEM-EDS results of calcined catalysts.

Element	Atomic (%) Periphery, 6Ni/Al-wet	Atomic (%) Center, 6Ni/Al-wet	Atomic (%) Periphery, 6Ni/Al-edf	Atomic (%) Center, 6Ni/Al-edf	Atomic (%) Periphery, 16Ni/Al-wet	Atomic (%) Center, 16Ni/Al-wet	Atomic (%) Periphery, 16Ni/Al-edf	Atomic (%) Center, 16Ni/Al-edf
Al K	91.68	92.38	92.18	95.47	80.65	86.11	80.05	95.20
Ni K	8.32	7.62	7.82	4.53	19.35	13.89	19.95	4.80
Total	100	100	100	100	100	100	100	100

Following EDF it is probable that more than one of the modes of interfacial deposition [33] take place simultaneously during the equilibration of the suspension. This depends on the nature of the support surface and the species to be deposited mainly on the nature of the ligand of the TMIS, as well as on the impregnation parameters. The most important parameters are the pH, the concentration of TMIS, the ionic strength, the impregnation temperature, and the impregnation time; these parameters determine the relative contribution of each process to the whole interfacial deposition. It is well established that an increase of concentration value causes an increase to the extent of the TMIS deposition and thus to its surface concentration. In our case, the nickel profiles were obtained using two different values of concentration for the impregnation solution and keeping constant all other experimental conditions of catalyst' synthesis procedure (e.g., temperature, impregnation time, initial pH). An increase in the concentration of the precursor ions is expected, which results in an increase of the saturation surface concentration of the adsorption sites value [34].

Furthermore, the nickel species layer on the periphery of the catalytic samples can be clearly seen in Figure 2a,b, and its thickness could be estimated at 0.028 mm for the 6Ni/Al-edf and 0.046 mm for the 16Ni/Al-edf. This observation, i.e., that with increase in the catalyst Ni loading, the thickness of the nickel layer also increases, has been also confirmed by Kim et al. [40] for nickel-alumina egg-shell catalysts that were prepared by the multibubble sonoluminescence (MBSL) technique. A final observation that can be made regarding the results presented in Table 2 is that the catalysts prepared using the wet impregnation technique show no significant difference on nickel species concentration between the periphery and the center of the cylindrical pellets, indicating a uniform nickel concentration profile.

TEM images of the nickel on γ -alumina catalysts after calcination are shown in Figure 3. As a first observation, the TEM analysis corroborates the formation of the nickel aluminate spinel phase (NiAl₂O₄) identified by the XRD results discussed above. EDS analysis confirms the presence of nickel, oxygen (O) and aluminum (Al) in all analyzed regions, while some nickel aggregates can be observed on the catalyst surface.



Figure 3. (a) 6Ni/Al-edf, (b) 16Ni/Al-edf, (c) 6Ni/Al-wet, and (d) 16Ni/Al-wet calcined catalysts TEM micrographs and the analyzed composition by EDS.

The nickel species particle size was determined by the characteristic TEM images, where discrete enough Ni particles were detected. As expected, for the catalysts with the low nickel loading, a smaller mean Ni species particle size was determined in comparison to the ones with the high nickel loading, irrespective of preparation method (Table 1). Specifically, the nickel particle size was 12.1 nm for the 6Ni/Al-edf (Figure 3a), lower than the 17.2 nm estimated for the 16Ni/Al-edf (Figure 3b). For the catalysts prepared with the wet impregnation method, the mean Ni particle size was 14.1 nm for the 6Ni/Al-wet (Figure 3c) and 25.1 nm for the 16Ni/Al-wet (Figure 3d). Significantly, the nickel particle sizes are lower for the catalysts with the egg-shell structure, prepared applying the modified EDF technique, in comparison to those with the uniform structure, prepared using the conventional wet impregnation technique.

This finding is in agreement with the theory underpinning EDF synthesis, i.e., that the deposition of the active phase occurs almost exclusively during the equilibration via adsorption on sites created by the charged surface hydroxyl groups and/or reaction with the neutral hydroxyl groups of the carrier surface [78–82]. As mentioned above, during

EDF synthesis, the support is immersed in a large volume of a very dilute aqueous solution of TMIS, ideally at a fixed pH and ionic strength. Equilibration of the suspension then follows for several hours under stirring. During equilibration, the TMIS are deposited at the interface developed between the support surface and the aqueous solution. This mode of deposition is called interfacial deposition. As reported in the literature [46-49,78,81-84], the mode of deposition (bulk vs. interfacial) strongly affects the physicochemical characteristics and results in supported catalysts with very high dispersion of the active phase. This has been attributed to the fact that their size is controlled by the size and the physicochemical characteristics of the interface. Moreover, the relatively high dispersion reported also by other studies following EDF (i.e., where the interfacial deposition predominates), is frequently reflected in the relatively high activity of the resulting catalysts [78,83,85]. This is in contrast to the wet impregnation synthesis, where, the deposition takes place mainly in the step of drying, which follows the impregnation step, by uncontrolled precipitation in the liquid phase inside the pores of the support due to water evaporation. Lycourghiotis and co-workers [48,86] argued that the characteristics of the supported phase, and thus the amount and the size of the crystallites, in respect to the synthesis technique followed for mounting active metal species on the γ -Al₂O₃ surface, depend on two crucial parameters: (i) on the ratio 'amount of active metal species deposited in the impregnation step to that remaining in the liquid phase inside the pores precipitating thus in the drying step' closely related with the ratio 'amount in the deposited phase (isolated surface inner sphere complexes and surface precipitates)/amount in the precipitated phase formed in the drying step', and (ii) on the composition of the precipitated phase.

For the catalytic systems presented herein, the application of the wet impregnation method resulted into low values for the above ratios, and thus to the formation of a precipitated phase that is rather unstable; this, upon calcination, was transformed into loosely bounded crystallites of relatively big size. On the other hand, the application of the EDF preparation technique resulted into high values for the above-mentioned ratios. As a result, the deposited phase was predominant and, upon calcination, it was transformed to well dispersed catalytically active phases that were bound strongly with the support surface. In other words, following wet impregnation, the deposition does not take place during the impregnation step but rather during drying, i.e., by uncontrolled precipitation in the liquid phase inside the pores of the support, due to the evaporation of water. However, during EDF synthesis, the deposition takes place in the step of the long-time equilibration of the quite dilute impregnating suspensions via adsorption, which in certain cases is followed by surface oligomerization, polymerization, or surface (more precisely interface) precipitation [46–49,78–82,84,85].

3.2. Model Implementation

The model was implemented and solved in an ATHENA Visual Studio process modelling environment (AthenaVisual Studio, 14.0, AthenaVisual Inc., Chicago, IL, USA, 2020). The problem contains four dimensionless parameters, namely the characteristic Péclet number, Pe_c , the characteristic Stanton number, St_c , the surface active sites to active Nickel ions ratio, η , and the Nickel modified Langmuir isotherm adsorption constant, K'_p , for which a certain degree of uncertainty is contained.

To this end, a four-parameter estimation problem for the Nickel deposition was established, by forming an estimation parameter vector including those parameters of the model which are unknown or uncertain to some degree, according to, $\theta = (Pe_c \ St_c \ \eta \ K'_p)^T$. In this manner, a statistical investigation of the model is performed and the values of the unknown or uncertain parameters are estimated from observations. Furthermore, the variances of the resulting parameter estimates are calculated, and it is made possible to refine their posterior density function and add confidence interval estimates. For the solution of the nonlinear parameter estimation problem with single response data, the Bayesian estimator of the GREGPLUS solver of ATHENA Visual Studio software [23,87,88] was adapted to the numerical solution of PDAPLUS solver. From the estimated values

of the unknown parameters, the Nickel dispersion coefficient, D_L , the saturation surface concentration, n^s , and the adsorption and desorption kinetic constants, k_1 and k_2 , and therefore the Langmuir isotherm adsorption constant, K_p , were easily evaluated.

The single response data corresponded to experimental nickel surface concentrations for the two catalysts with nickel content 6 and 16 wt%, prepared by the modified EDF technique, respectively as functions of the dimensionless radial coordinate. Only the case of total air escape was studied hereby, because it represents physically a more realistic situation, supported by the experimental data, according to which substantial nickel deposition occurred on the entire catalytic surface along the radial coordinate towards the center of the cylindrical extrudates.

The conclusion was that following the modified EDF method at constant pH = 7.0, the egg-shell nickel species macro-distribution profiles can be predicted, in accordance with the experimental results. The experimental and theoretical concentration profiles are shown in Figure 4 for the 6Ni/Al-edf and 16Ni/Al-edf samples, respectively, whereas the estimated values of the parameters derived from the model application, were compared with values in the literature from previous studies (Table 3). Confidence intervals of the estimated parameter values were included in Table 3, as well.



Figure 4. Experimental and theoretical distributions for: (**a**) 6Ni/Al-edf at pH = 7.0, and (**b**) 16Ni/Al-edf at pH = 7.0.

Study	Ref. [54]	Ref. [46]	Ref. [89]	This Study (6Ni/Al-edf)	This Study (16Ni/Al-edf)
Solution Properties	$C^{\circ} = n/a$	$C^{\circ} = 0.0012 - 0.003 M$	$C^{\circ} = 0.002 M$	$C^{\circ} = 0.17 M$	$C^{\circ} = 0.34 M$
Estimated Parameters	pH = 5.2	pH = 6.2	pH = 10.6	pH = 7.0	pH = 7.0
$K_p (l mol^{-1})$	326	408	1422	715 ± 842	781 ± 226
$n^{s} (\mu mol m^{-2})$	0.50	0.60	1.82	46.45 ± 19.16	133.71 ± 8.51
$D_L (m^2 s^{-1})$	-	-	-	$\begin{array}{r} 2.93 \ 10^{-8} \ \pm \\ 1.66 \ 10^{-8} \end{array}$	$\frac{2.50\ 10^{-8}\ \pm}{8.28\ 10^{-1}}$

Table 3. Parameters derived from model application and from bibliography.

Note: n/a = not available.

In most of the previous studies, the procedure used for catalyst preparation was based on the conventional EDF technique as described in the introduction. Thus, the deposition of the nickel species was taking place through adsorption on and/or surface reaction with the receptor sites that were developed on the support surface (surface oxygen and surface hydroxyls) during the equilibration step. Therefore, the n^s values corresponded to the maximum amount of the active phase that was deposited through adsorption on the alumina surface. On the other hand, in the modified EDF method proposed by the authors, not only a major portion of the Ni²⁺ ions is deposited by adsorption on and/or reaction with the solid surface on a single adsorption layer, but a significant portion of them is also deposited by precipitation on multiple deposit layers during the evaporation of the water. As a result, the n^s values estimated by the modified EDF technique corresponded to the total amount of the active phase that can be adsorbed and/or deposited on alumina surface, either by adsorption on a single layer during the equilibration step or by adsorption/precipitation on multiple layers during the evaporation step.

Nevertheless, the n^s value is strongly affected by the precipitation of the active phase, as it can be expressed as the total amount of the metal ion deposited on the support surface either on a single or multiple layers. Note again that applying the unmodified EDF technique, this amount corresponds mainly to the one that is deposited by single layer adsorption alone. Furthermore, n^s is affected by the type of the catalytic support, the pzc of the support, the pH value and the catalyst preparation procedure. Therefore, due to the fact that the active species (nickel) solution concentrations used in our study were considerably higher than those used in the other studies, the estimated values of the saturation surface concentration, n^s, were also reasonably higher than those in the other studies. Additionally, they include the amount of the active phase that is deposited by precipitation as well and not only by adsorption on a single adsorption layer on the catalytic surface.

From Table 3 it can be seen that the equilibrium constant, K_p , which is defined as the ratio of the adsorption to the desorption kinetic constants, $K_p = \frac{k_1}{k_2}$, is not influenced by the percentage of the active phase that is deposited by adsorption/precipitation and increases with a parallel increase in the pH of the impregnating solution, assuming Langmuir type of single layer adsorption isotherm. Therefore, by keeping a constant pH value in the present study (pH = 7.0), selected to be close to the point of zero charge (pzc) of the γ -alumina used here, the estimated values for the Langmuir equilibrium constant, K_p , were also nearly the same and in good agreement with the value expected according to the experimental values reported in previous studies and their dependence on pH. In other words, the K_p values calculated in this study fall within the K_p , values calculated in the studies reported in refs. [46,89] (Table 3), as the pH of our solution (7.0) was also between the pH values of these studies (6.2 and 10.6, respectively).

Finally, the estimated values of the dispersion coefficient of the nickel species were also included in Table 3. It is remarkable that essentially the same value of the dispersion coefficient, $D_L = 2.5 \times 10^{-8} - 3.0 \times 10^{-8} \text{m}^2 \text{s}^{-1}$, was estimated for the two catalysts with nickel content 6 and 16 wt%, respectively, as it was anticipated, since all other process parameters were kept constant, including imbibition flow parameters. This fact supports the applicability of the proposed model.

In summary, the model presented herein is capable of capturing the characteristics of the impregnation stage of the modified EDF method proposed by the authors for supported catalyst preparation.

By applying the model, the egg-shell macro-distributions of the nickel species on γ alumina cylindrical extrudates were predicted in agreement with the experimental results under the same experimental conditions. Moreover, reasonable values for the key parameters of the model, namely dispersion coefficient, D_L, and saturation surface concentration, n^s, were estimated, whereas the constants of the Langmuir adsorption isotherm, namely adsorption and desorption kinetic constants, k₁ and k₂, and therefore Langmuir isotherm adsorption constant, K_p, were also estimated in good agreement with previous studies.

3.3. Biogas Reforming over Ni/Al₂O₃ Catalysts

3.3.1. Catalytic Activity

To test the reproducibility of the experimental results the 6Ni/Al-edf experiments were repeated three times. From these, 95% confidence intervals for the mean value were calculated, and the results in the form of error bars are depicted in Figure 5. As can be seen, individual experimental values lay well within the corresponding confidence intervals, showing a very good reproducibility of the repeated experiments.



Figure 5. Repeat experiments for the 6Ni/Al-edf catalyst. (a) Conversion of methane (X_{CH4}), and (b) Hydrogen yield (Y_{H2}) (CH₄:CO₂ = 1.5).

The influence of the reaction temperature to the CH₄ and CO₂ conversion values from 700 to 900 °C for the biogas reforming reaction and for the nickel on alumina catalysts, with egg-shell and uniform macro-distribution, are shown in Figure 6. A general observation is that an increase in temperature led to an increase in CH₄ and CO₂ conversion, which is expected due to the endothermicity of the reaction. Moreover, as the CH₄/CO₂ ratio at the inlet of the reactor was higher than unity, methane conversion values are lower than the carbon dioxide ones for the whole range of reaction temperatures studied. In the work reported by Yasyerli et al. [90], using feed mixtures containing a CH₄/CO₂ ratio higher than one, coke formation was excessive and reactor blockage occurred in a short period of time. In contrast, we observed stable conversion during the tests, which may be due to the high active phase dispersion of our catalysts. Serrano-Lotina and Daza [91] reported that when CH₄/CO₂ > 1, methane conversion is lower, but the selectivity to H₂ is higher.



Figure 6. Effect of reaction temperature on the conversion of methane (X_{CH4}) and carbon dioxide (X_{CO2}) for the catalysts with: (**a**) low (6 wt%), and (**b**) high (16 wt%), nickel loading (CH₄:CO₂ = 1.5).

Turning our attention first to the low nickel catalysts (Figure 6a), it is clear that the 6Ni/Al-edf catalyst exhibits significantly higher CH₄ and CO₂ conversion in comparison with the 6Ni/Al-wet catalyst up to 860 °C. Over this temperature, although the egg-shell catalyst retains higher X_{CH4} and X_{CO2} , the difference is minimized. It is noted that above 750 °C, the reactions of CH₄ decomposition and steam reforming of methane can also occur, to a varying extent, affecting the methane and carbon dioxide conversion values [92]. Concerning water production, it has been reported [93] that the hydrogenation of carbon dioxide (CO₂ + 2H₂ \leftrightarrow C + 2H₂O) and of carbon monoxide (CO₂ + 2H₂ \leftrightarrow C + 2H₂O),

both exothermic reactions, are associated with carbon formation, as well as with water production. Furthermore, the methanation reactions ($CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$ and $CO + 3H_2 \leftrightarrow CH_4 + H_2O$), both exothermic, may also produce water. The extent of the above mentioned reactions decreases as the temperature increases.

Furthermore, from our results, conversion values for both reactants increase as the nickel loading increases from 6 to 16 wt% (Figure 6). It is noted that these experiments were performed over a shorter temperature range, i.e., between 780 and 900 °C. The value of CH₄ conversion for the 16Ni/Al-edfreaches about 92% and 89% for the 16Ni/Al-wet catalyst at reaction temperature equal to 900 $^\circ$ C,. According to thermodynamic analysis, the CH_4 equilibrium conversion for the biogas reforming reaction, when using a feeding mixture with CH_4/CO_2 molar ratio equal to 1.5, is about 99% for temperature 860 °C [10]. Additionally, the CO₂ conversion values reach 95% for the 16Ni/Al-edf catalyst and 91% for the 16Ni/Al-wet at reaction temperature equal to 900 °C, very close to the ones predicted by thermodynamic analysis (equilibrium carbon dioxide conversion value, at 860 °C, equal to 98%). A further observation is that the performance of the high metal loading catalysts is not significantly different between the two preparation methods used herein (modified EDF versus wet impregnation). This is attributed to the high metal loading, which means that the conversion values are very close to the ones predicted by the thermodynamic analysis. This finding is in agreement with the works carried out by Ko and co-workers [43,45], who investigated the performance of egg-shell type catalysts in the steam reforming of methane. The somewhat higher methane conversion observed for the 16Ni/Al-edf catalyst in comparison to the 16Ni/Al-wet one is probably due to the extent of the main reforming and methane decomposition reaction.

Egg-shell catalysts are considered useful in processes where the reaction has a very high rate and the intraparticle diffusion becomes the limiting step. This is because the reactants and the reaction products are more easily transported to the surface from the egg-shell, i.e., the thin layer of active component placed on the outer surface of the catalyst particles, than from the catalyst inner core [35,94]. Intraparticle diffusive limitations are especially important for processes taking place in packed beds, as is the case with the methane reforming reaction [36,95]. A number of literature reports have proven the advantage of using egg-shell catalysts as they have shown that the reaction mostly occurs on the outer region of pellet (where most of the active sites are located), due to its extremely low effectiveness factor [43,45,96,97].

The results presented herein regarding the catalysts prepared via the EDF method are explained by their physicochemical properties. In particular, as shown in Table 1 above, for both low and high Ni loadings, the Ni species particle size was lower for the EDF catalysts, in comparison with those prepared via conventional wet impregnation i.e., the NiO and NiO_x species were better dispersed. Moreover, EDF synthesis also led to the presence of Ni⁺² ions, interacting strongly with the support in the interfacial layer. Thus, it is likely that the adverse effects caused by coke formation and the sintering process were less severe during the reforming reaction [46,86,98]. This is in agreement with other investigators reported work, where the supported Ni on γ -alumina catalysts with the egg-shell structure exhibited good performance in biogas reforming reactions [40–42,99].

The H₂ yield values for the biogas reforming reaction, carried out at temperature values ranging from 700 to 900 °C, for the 6Ni/Al-edf and the 6Ni/Al-wet catalysts, are shown in Figure 7a. As can be observed, the H₂ yield values below 750 °C are rather low for both catalysts, most probably due to the limited extend of the reforming and decomposition reactions and the function of the reverse carbon gasification reaction. However, over 750 °C, the H₂ yield values start to increase for both catalysts, but above 820 °C they become significantly higher for the 6Ni/Al-edf catalyst compared to the ones for the 6Ni/Al-wet catalyst. The reactions that predominate in this temperature range are the main reforming reaction (Equation (1)) and the methane decomposition reaction (Equation (3)), resulting in higher hydrogen production. Figure 7b presents the Y_{H2} for the nickel on alumina catalysts with high metal loading. Again, although the catalyst prepared via the EDF



method presents higher Y_{H2} , the high metal loading means that no substantial differences are observed with the 16Ni/Al-wet catalyst.

Figure 7. Effect of reaction temperature to hydrogen yield (Y_{H2}) for the catalysts with: (**a**) low (6 wt%), and (**b**) high (16 wt%), nickel loading (CH₄:CO₂ = 1.5).

This improved catalytic performance of the 6Ni/Al-edf arises mainly from its optimum physicochemical properties, such as the higher surface area, the lower nickel particle size and thus the higher active phase dispersion, as well as the egg-shell nickel concentration profile (macro-distribution), accomplished by the application of the modified EDF technique. Indeed, the interfacial nickel species deposition on the alumina surface related to the EDF method results in catalysts with smaller nano-particles and thus in higher dispersion of the supported nickel phase compared to the ones prepared by the wet impregnation method.

3.3.2. Catalysts Stability

In order to examine catalytic stability in the targeted reaction, short time-on-stream experiments (5 h) were performed. It is noted that these experiments were carried out only for the catalysts with the low Ni loading, i.e., the 6Ni/Al-edf and 6Ni/Al-wet. The results obtained, at a reaction temperature of 860 °C and for feedstock consisting of a $CH_4/CO_2 = 1.5$ mixture diluted with helium (He), are depicted in Figure 8. It is obvious that the 6Ni/Al-edf was more stable than the 6Ni/Al-wet, for the duration of the time-on-stream experiment. For the former catalyst, X_{CH4} , X_{CO2} , and Y_{H2} took the values (start of the experiment, and in parenthesis, the end of the experiment): 80% (75%), 95% (92%), and 78 (75%), respectively (Figure 8a). For the 6Ni/Al-wet catalyst, the corresponding values were: 71% (62%), 85% (76%), and 67% (59%). Moreover, these results are also in agreement with the ones presented above, confirming that the 6Ni/Al-edf was more active due to its the egg-shell nickel concentration profile (macro-distribution).

As discussed above, biogas reforming is also accompanied by several side reactions that determine the selectivity of the process, such as the reverse water gas shift (RWGS) reaction (Equation (2)), Boudouard reaction (Equation (4)) and the methane decomposition reaction (Equation (3)). The RWGS reaction increases CO_2 conversion and the yield of CO, while the Boudouard decreases CO_2 conversion and the yield of CO. On the other hand, the CH_4 decomposition reaction increases methane conversion and the hydrogen yield. Previous studies [100,101] have also reported that fuel (CH_4) activation/conversion is independent from the amount of co-reactant (CO_2) and is generally considered as the rate determining step in CH_4 - CO_2 reforming reaction. Hence, CH_4 concentration in the feed stream determines the methane reforming rate, while on the other hand CO_2 concentration affects the extent of RWGS reaction. A higher CO_2 concentration seems to help shift the RWGS reaction towards its equilibrium composition.



Figure 8. (a) CH₄ and CO₂ conversion and H₂ yield, and (b) H₂/CO ratio, during stability tests for the 6Ni/Al-edf, and 6Ni/Al-wet. Reaction conditions: $T = 800 \degree C$, WGHSV = 1200 h⁻¹.

Within the tested temperature range, the calculated H_2/CO ratio was stable at 1.1 for the 6Ni/Al-edf, and around 0.6 for the 6Ni/Al-wet (Figure 8b). According to thermodynamics [93], a H_2/CO ratio in the order of 1 can be obtained at high reaction temperatures and high CO₂ conversion, indicating high activity and selectivity of the catalyst towards CO_2 reforming of methane (as is the case with the 6Ni/Al-edf catalyst). However, elevated H_2/CO values also imply pronounced occurrence of the methane cracking reaction and/or the Boudouard reaction, which enrich the reformate gas with H_2 but are also responsible for carbon formation [16,19,102]. On the other hand, lower than unity value of the H_2/CO molar ratio can be caused by the RWGS reaction and oxidation of carbon deposits by CO_2 [103]. Therefore, the present results may indicate that the 6/Ni/Al-edf catalyst probably inhibited the reverse water gas shift (RWGS) reaction. Das et al. [104] argued that the synthesis method has an effect on the distribution of acidic and basic sites. The EDF, being a more controlled synthesis method, could provide a more uniform distribution of these sites and positively affect DRM. On the other hand, when acidic and basic sites are distributed randomly, then higher surface acidity and basicity is expected, promoting side reactions like RWGS.

These results may also indicate that increased carbon deposition occurred on 6/Ni/Aledf, in comparison with the 6Ni/Al-wet catalyst, without, however, an accompanying loss in catalytic performance. Literature reports [105] suggest that for catalysts with a uniform distribution of metallic nickel particles, coke deposition occurs both on the outside and on the inside of the pellets. As coke accumulates inside the pellets, the stress induced might cause their fragmentation. On the other hand, it has been reported [45] that in the egg-shell-type catalyst, where the metallic nickel particles were selectively located in the outer region of the pellets, coke was only deposited and grown on the outer regions of the pellets. Although coke accumulation also occurred, the stress induced by coke accumulation appeared to dissipate by the location of Ni particles on the outer region of the pellets. The excellent stability of the 6Ni/Al-edf catalyst can be attributed to its egg-shell structure, as well as from its bulk and surface properties, i.e., its high surface area and active phase dispersion.

4. Materials and Methods

4.1. Catalysts Preparation

The supporting material of all the nickel-based catalysts consisted of γ -Al₂O₃ extrudates (cylindrical pellets), supplied by Akzo Nobel. The physicochemical properties, i.e., surface area, pore volume, bulk density, and mean pore diameter, before treatment, have been previously presented in ref. [10]. Prior to catalyst synthesis, the γ -Al₂O₃ support was calcined at 800 °C, resulting in an S_{BET} of 195 m² g⁻¹. Ni(NO₃)₂·6H₂O, purchased from Sigma Aldrich, was used for the catalyst preparation. Two different concentrations (x wt%) were used, c₁ = 0.17 M and c₂ = 0.34 M, so that the Ni content of the final catalysts would be 6 and 16 wt%, respectively. The water used for the solutions was distilled and de-ionized (NANOpure Diamond UV unit, Barnstead International). Two different preparation methods were used, i.e., a modified EDF technique [24,46] and wet impregnation.

For the preparation of the egg-shell type nickel on γ -alumina catalysts (xNi/Al-edf) via EDF synthesis, a thermostated vessel (250 mL), equipped with a pH adjusting and controlling device and a glass/saturated calomel electrode (Metrohm 703 Ti Stand), was used. The EDF samples were prepared at a constant temperature (T = 25 ± 0.1 °C) and at a pH value equal to 7.0, which is the point of zero charge (pzc) of the γ -alumina used, i.e., the pH value at which the negatively and the positively charged sites on the γ -Al₂O₃ surface are equal. The pH of the impregnating solution was adjusted and controlled by adding small amounts of ammonium hydroxide via an NH₄OH aqueous solution (c = 0.1 M) to the preparation vessel. During the preparation process, nitrogen gas was bubbled into the vessel to prevent dilution with atmospheric CO₂ and subsequent change in the pH. The pH was kept constant for approximately 2.5 h.

The nickel on γ -alumina catalysts with uniform structure (xNi/Al-wet) were synthesized applying the wet impregnation technique, where a pre-weighed amount of the cylindrical support (w = 10 g) was added to 100 mL of aqueous solution of the metal salt under continuous stirring. The volume of the impregnation solution was approximately 15 times higher than the pore volume (Vp) of the γ -Al₂O₃ used herein.

For all catalysts, the water was evaporated using a rotary evaporator at temperature value equal to 60 °C, and for a period of time equal to 4 h. In addition, all the final catalyst samples were air-dried overnight and were calcined at 800 °C for 5 h. The samples were labelled as xNi/Al-edf and xNi/Al-wet, where x is the active phase concentration (wt%).

4.2. Catalysts Characterization and Testing

The bulk and surface physicochemical characteristics of all final catalysts were determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), N_2 adsorption-desorption isotherms, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM). In brief, (i) ICP-AES was used for the determination of the metal loading (wt%) of the final catalysts, and was performed on a Perkin-Elmer Optima 4300 DV. To avoid any dissolution issues the following procedure was used: an acid digestion procedure involved the weighting of an appropriate amount of the catalyst in a Teflon beaker. The exact weight of the sample was recorded to the nearest 0.0001 g. The sample was transported to the fume hood, where 1 mL of concentrated sulphuric acid was added. The mixture was heated to dryness at low heat on a hot plate overnight. Then, 2 mL of concentrated hydrochloric acid and 2 mL of concentrated nitric acid were added to the beaker. The heating was terminated after 5–10 min, when the reaction of dissolution was completed. At that point, approximately 2 mL of de-ionized water was added and the beaker was left to cool. The resulting clear solution was loaded into a 50 mL volumetric flask in order to make up an accurate fixed volume adding deionized water. (ii) N_2 adsorption-desorption isotherms were used for the determination of the specific surface area (SSA) via the BET technique, and the experimental work was performed on a Micromeritics Tristar apparatus, with Micromeritics VacPrep 061 Sample Degas System; (iii) XRD was used for the determination of the crystalline phases of the calcined catalysts, and was carried out on a Siemens D500 diffractometer using Cu-Ka radiation; (iv) SEM was used for the determination of nickel distribution along the cylindrical pellet diameter (macro-distribution), and was performed on a JEOL 6300 instrument, equipped with a microanalysis device; (v) TEM was used to determine the morphology of the catalytic surface and the particle size of the surface nickel species, and was carried out on a JEOL JE-2010 instrument.

The catalytic testing was carried out in a fixed bed continuous flow reactor, at atmospheric pressure. The experimental rig and procedure followed has been described previously in ref. [10]. Succinctly, a quartz glass reactor was used, operating at between 700 to 900 °C. The feed consisted of CH₄/CO₂ in a molar ration 1.5 and was further diluted with He (200 mL min⁻¹ in total, of which 50% was He). The amount of catalyst used in the catalytic bed was 10 cm³, diluted with an equal amount of inactive γ -Al₂O₃ extrudates; thus, the Gas Hourly Space Velocity (GHSV) value was equal to 1200 h⁻¹. Prior to performing any catalytic reaction measurement, catalysts were in situ activated by flowing pure H₂ for 2 h at 700 °C. Catalytic stability was examined at 860 °C, during short (5 h) tests. The gaseous reaction products were analysed on-line by gas chromatography in a CG-Agilent 7890 A gas chromatographer. The instrument utilised parallel HP-Plot-Q (19095-Q04, 30 m length, 0.530 mm I.D.) and HP-Molesieve (19095P-MSO, 30 m length, 0.530 mm I.D.) columns, and was equipped with TCD and FID detectors at the exit. Methane conversion (X_{CH4}), carbon dioxide conversion (X_{CO2}), hydrogen yield (Y_{H2}), carbon monoxide yield (Y_{CO}), and H₂/Co molar ratio were determined according to the following equations:

$$X_{CH_4}(\%) = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100$$
(39)

$$X_{CO_2}(\%) = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100$$
(40)

$$Y_{H_2}(\%) = \frac{F_{H_2}}{2F_{CH_4,in}} \times 100$$
(41)

$$Y_{CO}(\%) = \frac{F_{CO}}{F_{CH_4,in} + F_{CO_2,in}} \times 100$$
(42)

$$Molar ratio = \frac{F_{H_2,out}}{F_{CO,out}}$$
(43)

5. Conclusions

Nickel supported on γ -Al₂O₃ catalysts with different types of the active phase concentration profiles were prepared, characterized, and tested for the biogas reforming reaction. We were able to show that the interfacial deposition, related to the application of the modified EDF method, results to catalysts with slightly smaller nano-particles, and thus, to a higher dispersion of the nickel supported phase, compared to the ones prepared by the wet impregnation method. Concerning the biogas reforming reaction, at high metal loadings, the catalysts revealed similar catalytic performance, resulting in high conversion rates above 800 °C. On the other hand, at low metal loadings, the catalyst with an egg-shell structure showed increased methane conversion and hydrogen yield. We also concluded that the catalysts with the egg-shell structure, especially for low metal loadings, probably inhibit the reverse water gas shift reaction, which is related to H₂ consumption and CO production. Succinctly, the improved catalytic performance of the 6Ni/Al-edf catalyst, is due to its unique properties, including a higher surface area and active phase dispersion, and its egg-shell structure that is generally considered to be beneficial in reforming reactions.

Concurrently, a theoretical model was developed and applied to the impregnation stage of the nickel supported on the cylindrical γ -alumina extrudates catalysts preparation process (modified EDF technique), where the active ions were adsorbed on the active sites of alumina and precipitated forming multiple layers. The model was able to predict that a pH = 7.0 would produce catalytic materials with nickel egg-shell macro distributions, in agreement with the experimental results.

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Nomenclature

$b = \frac{1}{1+\sigma}$	inverse measure of the capillary force, dim/less
c	concentration of aqueous solution of ammonium hydroxide, $\mathrm{NH_4OH}$, M
d _{av}	average pore diameter, m
c^0, c_1, c_2	initial concentration of the impregnating liquids, M
D _{Lk}	dispersion coefficient of the k-th active species, m^2/s
D _L	Nickel dispersion coefficient, m ² /s
f _k	rate of adsorption of the <i>k</i> -th active species, dim/less
k	absolute permeability, m ²
$K_{pk} = \frac{k_{1k}}{k_{2k}}$	Langmuir isotherm adsorption constant of the <i>k</i> -th active species,
$K_p = \frac{k_1}{k_2}$	Nickel Langmuir isotherm adsorption constant,
$K'_{pk} = rac{k_{1k}}{k_{2k}} ho_k^{0,f}$	modified Langmuir adsorption constant of the k -th active species, dim/less
$K'_p = rac{k_1}{k_2} ho_{Ni}^{0,f}$	Nickel modified Langmuir adsorption constant, dim/less
$k = \frac{a_{\upsilon} k_{2k}}{1-\varepsilon}$	generalized mass transfer coefficient based on Langmuir isotherm of the
	<i>k</i> -th active species, dim/less
k _{1k}	adsorption kinetic constant of the k-th active species, m^3 pore volume
k ₁	Nickel adsorption kinetic constant, m ³ ·pore volume m solid volume/kg·s
k _{2k}	desorption kinetic constant of the k -th active species, m solid/s
k ₂	Nickel desorption kinetic constant, m solid/s
$K_p = \frac{k_1}{k_2}$	Nickel Langmuir isotherm adsorption constant,
L	pellet average length, m
$\eta_k = \frac{\mathrm{vn}_k^s}{\rho_{\mathrm{b}}^{f,0}}$	relative adsorption capacity of the <i>k</i> -th active species, dim/less
$\eta = \frac{vn^{s^{\kappa}}}{\rho^{f,0}}$	Nickel relative adsorption capacity, dim/less
n ^s	saturation surface concentration of the <i>k</i> -th active species, kg/m ³ solid volume
n ^s	Nickel saturation surface concentration, kg/m ³ solid volume
$\tilde{P} = \frac{P}{P_a}$	dimensionless pressure
Pa	atmospheric pressure, N/m ²
Pc	capillary pressure, N/m ²
$Pe_k = \frac{v_p r}{D_{Lk}}$	local (time dependent) Péclet number of the <i>k</i> -th active species, dim/less
$Pe_{ck} = \frac{v_{pc}R}{D_{Lk}}$	characteristic (time independent) Péclet number of the k-th active
	species, dim/less
$Pe_c = \frac{v_{pc}R}{D_L}$	Nickel characteristic (time independent) Péclet number, dim/less
r	radial coordinate, m
r _f	liquid front position, m
R	pellet radius, m
S _{BET}	pellet surface area, m ² /kKg
$St_k = \frac{k_k r}{v_p}$	local (time dependent) Stanton number of the <i>k</i> -th component, dim/less
$St_{ck} = \frac{k_k R}{v_{pc}}$	characteristic (time independent) Stanton number of the k-th
r-	component, dim/less

$St_c = \frac{kR}{v_{pc}}$	Nickel characteristic (time independent) Stanton number, dim/less
t	time, s
$t_c = \frac{L}{v_{pc}} = \frac{\mu \epsilon R^2}{k P_a}$	characteristic imbibition time, s
te	imbibition termination time, s
u _k	impregnating solution concentration of the <i>k</i> -th component, dim/less
v_P	local (time dependent) interstitial liquid pore velocity, m/s
$\widetilde{v}_p = \frac{v_p}{v_{pc}}$	local (time dependent) interstitial liquid pore velocity, dim/less
V _{pc}	characteristic (time independent) interstitial liquid pore velocity, dim/less
Vp	pellet pore volume, m ³ pore volume/kg
a	mean pore radius, m
a _v	specific catalytic surface, m ² solid surface/m ³ total volume
γ	surface tension, N/m
ε	porosity, m ³ pore volume/m ³ total volume
θ_{e}	equilibrium contact angle, radian
$\theta_k = \frac{\nabla \rho_k}{\rho_k^{f,0}}$	dimensionless surface concentration of the <i>k</i> -th component
$ heta = rac{ u ho_{ m Ni}^{ m s}}{ ho_{ m Ni}^{ m f,0}}$	dimensionless Nickel surface concentration
μ	viscosity of the impregnating solution, Pa s
$\nu = \frac{1-\varepsilon}{\varepsilon}$	ratio of solid to pore pellet volume, m ³ solid volume/m ³ pore volume
$\xi = 1 - \left(\frac{r}{R}\right)^2$	dimensionless radial space coordinate
$\xi_{\rm f} = 1 - \left(\frac{r_{\rm f}}{R}\right)^2$	dimensionless liquid front position
ξ _e	termination liquid front position, dim/less
ρ _B	pellet bed density, kKg/m ³
$ ho_k^r$	mass concentration of the k -th active species in the liquid (fluid) phase, kg/m ³ pore volume
ρ_k^{f*}	equilibrium mass concentration of the <i>k</i> -th active species in the liquid
K	(fluid) phase, kg/m ³ pore volume
$ ho^{\rm f}_{ m Ni}$	Nickel mass concentration in the liquid (fluid) phase, kKg/m ³ pore volume
$\rho_k^{f,0}$	initial mass concentration of the <i>k</i> -th active species in the impregnating
	liquid, kKg/m ³ liquid volume
$\rho_{Ni}^{t,0}$	Nickel initial mass concentration in the impregnating liquid,
	kKg/m ³ liquid volume
$ ho_k^{s}$	mass concentration of the <i>k</i> -th active species in the solid phase,
0	kKg/m ³ solid volume
$\rho_{\rm Ni}^{\rm s}$	Nickel mass concentration in the solid phase,
P.	kg/m ³ solid volume
$\sigma = \frac{\Gamma_c}{P_a}$	dimensionless capillary pressure
$ au = rac{2r}{R^2} \int_0^t v_p dt$	dimensionless time variable
τ _e	imbibition termination time, dim/less
$y = \frac{\xi}{\xi_f}$	dimensionless radial space coordinate with respect to liquid
	front position

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