The Catalytic Pellet: A Very Useful Environment for Engineering Scaling

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Abstract – This contribution focuses on the scaling aspects in the learning of catalytic reactions in pores and pellets. The idea is to identify a systematic approach in the learning process to help students with several concepts related to transport-reactions process and the mathematical description associated with them. Items that are at the heart of the contribution is the integration between math concepts with the physics of the system, the learning of micro and macro levels, and avoiding story telling approaches that are usually utilized in the classical textbooks. In addition, the approach highlights the role of the catalytic pellet as an effective POK introduced by Arce (1994) in learning multiple scales systems. The proposed approach uses a microscopic formulation and an area-averaging process with a closure procedure.

Keywords: Active learning, scaling, catalytic process, averaging, POK.

I. INTRODUCTION AND MOTIVATION

In many widely used textbooks in Chemical Reaction Engineering courses, such as Fogler, Levenspiel, and Carberry, among others the derivation of the conservation equation for the species in the gas mixture is conducted by a "global" approach where many assumptions are hidden in such approach. These assumptions carry significant concepts associated with engineering scaling that, if properly used, offer a powerful learning environment to train students in engineering scaling. This scaling is very useful in current applications of relevant chemical engineering problems and it enhances the readiness of the students in practical problems. In addition, a learning environment that introduces scaling in the learning process lead to a very effective understanding of process at the nano, micro and macro scales; this, in turn offers an economical training of the students since they learn both, fundamentals ad scaling, principles simultaneously.

The catalytic pellet has several aspects that make the engineering description of the fundamentals very challenging for the untrained reader, i.e. the students. Concepts based on transport phenomena are coupled with gas-solid (heterogeneous) catalytic chemical reactions in addition to geometrical parameters. However, the students do not seem to have much difficulty in describing (conceptually) the physics as it happens in the system. Chemical engineering students are familiar with hydrodynamics, diffusion, and chemical reactions from courses at the freshman and sophomore years. Thus, a microscopic (and even a molecular) description is a logical first step for the students when describing the physics of transport with chemical reactions inside a catalytic pellet. What is somewhat difficult to accomplish is a description at the macroscopic level. In fact, identifying the proper mathematical "language" sometimes becomes the "bottleneck" in the learning process. This aspect, perhaps, led to instructors in the past to "simplify" the math so that students can achieve a manageable description. However, the students may easily achieve this when the problem is view from a scaling point of view. Basically, the connection between micro and macroscopic description is an integration of the former over the domain. This approach will produce a mixture of "averaged" quantities and "point" variables. In order to "close" the problem description, a connection between the two is required. These concepts are "rooted" in general principles of scaling and engineering approximations not difficult to be followed logically by students.

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In this contribution, we'll present an overview of the "classical" approach and, then will illustrate the microscopic description to obtain the macroscopic equations based on engineering principles of scaling for the case of a pellet with chemical reactions. The benefits of this approach compared to the shortcoming of the classical will be highlighted. We believe that a very rich learning environment can be uncovered by following this strategy. A by-product of the approach is that concepts from freshman and sophomore math becomes relevant and of enormous practical use for the students leading to a "successful marriage," rather than to a "divorce," between math and physics for the engineer in training.

II. THE CONCEPT OF PRINCIPAL OBJECT OF KNOWLEDGE (POK)

The concept of "Principal Object of Knowledge" or POK's was introduced in the "*Colloquial Approach Environments*" [Arce, 1] to enhance the student learning and to promote a more efficient habit in engineering students to master difficult concepts. The tool was then extended to include a variety of subjects [Arce, 2] in fluid mechanics, mass and energy balances, and continuum theory just to name a few examples. In this article, we highlight the role of the catalyst particle or pellet as a rich example of POK for students interested in learning about transport in porous media and heterogeneous reactions. Moreover, since the pellet is a multiscale-domain environment where diffusion process and heterogeneous reaction take place, the mathematical description of this transport and reaction system is complex and it exemplifies many multiphase and multicomponent systems [Arce, 1] very relevant to many engineering majors including Chemical, Biomedical, and Environmental Engineering. In addition, the pellet domain is an excellent prototype of the various systems of relevancy in current engineering applications such as the microfluidics and nanofluidics systems.

The analysis of the literature shows that heterogeneous reactions and catalysis is a very populated subject. There are classical textbooks [Levenspiel, 12] that introduce the students using somewhat simplistic models that quickly convey the information to the student and reach a mathematical description capable of obtaining concentration profiles and effectiveness factors. Others textbooks [Fogler, 11] presents a more "rigorous" introduction to the formulation of models and makes, also, connection with applied aspects such as the effectiveness factor determination and calculation by using "an abstract scaling" approach reaching quickly the "design" equation but missing very significant points of the student training. Textbooks with more sophisticated mathematics [Aris, 5; Aris, 7] concentrate on a beautiful mathematical analysis with implications to practical aspects. Aris [Aris, 8] has also reported useful techniques to obtain information of a reaction-diffusion equation without actually solving the equation.

Based on the brief description presented above, it is a trained reader's choice to select one of these textbooks to read about the subject. It will, probably, be a matter of taste for this class of readers to chose one of these texts and enjoy the journey. Those more interested in the "back of the envelope calculations" will most likely be very comfortable with the simple and "global" type of analysis, i.e., "a Levenspiel's view". Others, with a more mathematical oriented taste will feel at home reading Aris's masterful treatise in diffusion and reaction. The spectrum of contributions could accommodate all levels that places in between these two limits. It looks like that there is nothing to be added to the subject…from the "expert" point of view.

The dilemma, however, does not lead to the same situation for the untrained reader—most likely the students! This class of readers will wonder how a complicated problem in two phases with reaction on the walls may be modeled as a domain with homogeneous reactions. Others may adventure a trial in a more sophisticate description but, perhaps, will not survive the mathematical machinery beautifully crafted in the masterful production by Aris's diffusion and reaction symphony. Therefore, in spite of the fact that the subject of transport and reaction in heterogeneous media is populated with expert contributions, there is a need for a systematic approach to learning, based on first principles and that concludes with the overall or macro transport equations. This approach must follow a complete and logical sequence of steps and it at the heart of the scaling process; these concepts are so important for the training of the future engineer from both the fundamental and practical points of view that disguising them does not seem to be a useful and effective strategy in the training of the students.

In this contribution the authors will present an overall view of the status regarding problem where diffusion and reaction are involved from the point of view of the student learning and then present an "effective" and *progressive* approach to learn (sequentially) fundamental concepts. These will highlight the Catalytic Pellet as a very rich environment and an effective POK to learn about multiples (transport) scales and the role of multiphase process of a current relevancy in Chemical, Biomedical, and Environmental applications. Moreover, the approach will focus on obtaining the "macroscopic equations" useful for the analysis and design of the "micro-reactor" housed in the pellet

domain. In short, by following this approach, students will learn about connecting physics and math, about understanding the role of different scales, and realizing that the new and frontier chemical engineering applications of today technology are not so far from the "classical" ones when they are looked from a different perspective.

III. MORE PROGRESSIVE LEARNING APPROACHES

For systems with more than one phase and the presence of transport and reaction, it is usually a non-trivial task to introduce students to their physical as well as mathematical description. This is exactly the case of a catalytic pellet. It has two main phases, one the gas and the other the solid support with the active material. Instructors tend to use a view that renders the system to a simple case of "homogeneous domain" with just one phase and bulk reaction [Levenspiel, 12]. While this approach leads the engineering equations, the inexpert readers, i.e., the students are left with a number of answered questions and a very confusing picture of the system. Even faculty members, without a familiarity with the subject of catalytic systems, sometimes do wonder about this interpretation as students do. There is, however, a very logical and progressive approach that helps students to understand deeply the nature of systems such as the catalytic pellet and that follows a building block of knowledge (Arce, 1994). Furthermore, the approach "walk" the student through a number of very useful steps that lead to the complete scale up of the pellet conservation equations. It includes the following main steps:

[Realistic physical picture→ rigorous mathematical description→process of homogenization→ engineering model→ macroscopic equation] (1)

This is a very logical and a sequential series of steps that promote understanding of the system, offer an opportunity to the students to review concepts in previous courses, and give the chance to apply mathematical concepts learned in engineering math courses. In addition, the method promotes the overall student confidence in "engineering scaling " to describe the behavior of a complex situation. Several steps related to this progressive approach are detailed below.

A-A Sound Pedagogical Environment: A systematic and progressive approach [Arce, 2; Arce-Trigatti, 4] to derive engineering equations in a catalyst pellet would be a more efficient and far less confusing exercise than those currently introducing the students by a "story telling" about "homogeneous reactions" in a true heterogeneous media. In general, students in engineering majors are quite comfortable with describing (conceptually) basic physical aspects of a problem and, then identifying a mathematical description that mimics closely the physics that they have "visualized". For example, it is quite rational to introduce students to a pore domain, within a catalytic pellet, where diffusion and (heterogeneous catalytic) reactions take place. Diffusion is present as the only transport mechanism inside the pore cavity so that reactants can travel from the bulk to the surface of the pore domain. Since the reaction is catalytic, students based on kinetics or physicochemical concepts have no problem in recognizing that it is located at the walls of the pore domain and, therefore, no reaction is present in the bulk of such pore. Furthermore, students that are familiar with heat surface sources can trivially associate this situation with a process at the boundary of the domain where diffusive fluxes and sources (i.e., reaction) must be involved. It is the equivalent situation to that of the heat conduction and heat generation with heterogeneous sources, a concept already introduced in the heat transfer course!

The physical description offered above is very realistic and strait forward to comprehend. There is no approximation, no "mysterious" concepts involved and no story telling in the presentation. It is, therefore, a sound pedagogical and progressive description of a very complex phenomenon in a non-trivial domain. This description is very appealing to derive a mathematical description of the diffusion-reaction process inside the pore cavity. In fact, students that have already taken heat transfer and mass transfer usually find this situation a simple variation of the examples that they already encountered in the previous courses. What is needed next is the derivation of the differential model that involves the equation and the associated boundary conditions. This description constitutes the basis for the derivation of an engineering model useful for the calculation of the reactant concentration profiles at the "macroscopic domain". This is accomplished below.

B-A Robust and Progressive Approach: Based on the physical description given in section 1, above, the student here recognizes that the reaction in a catalyst pellet takes place at the surface (as it should be) and reactant must diffuse from the porous mouth towards the catalytic surface. Clearly, there is <u>no</u> homogeneous reaction within the domain of the pore cavity. Therefore in the general species continuity equation [Bird, 9]:

$$\frac{\partial C_A}{\partial t} + \vec{\nabla} \bullet \vec{N}_A = R_A(C_A) \tag{2}$$

The reaction term must be dropped; furthermore, if the pellet is under steady-state condition, then the time-derivative is also dropped. Therefore, equation (1) reduces simply to

$$\vec{\nabla} \bullet \vec{N}_A = 0 \tag{3}$$

If the students have been properly introduced to incompressible flows [Bird, 9], equation (3) is of the similar nature to that known as the incompressibility condition. To this point only transport concepts have been used by the student to derive the conservation or engineering equation. At this stage of the analysis, the geometry could be brought to the picture. If the rectangular geometry is the choice, then equation (2) reduces to

$$\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} = 0 \tag{4}$$

Now if, as it was stated before only diffusion is present, by using the Fick's law, equation (4) reduces to:

$$\frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} = 0 \tag{5}$$

Where the x-direction is the axial-direction in the porous cavity and the y-direction is the transversal-direction. Now, the student easily can identify boundary conditions for equation (5). This equation is identical to the Laplacian of the temperature where students focus on conduction heat transfer in a 2-D domain. By recognizing that the only transport mechanism is diffusion, by continuity of fluxes at the wall, and by remembering that the reaction takes place at the wall, the following boundary condition is easily written.

$$-D\left.\frac{\partial C_A}{\partial y}\right|_{wall} = R_A\left(C_{Aw}\right) \tag{6}$$

At this stage of the analysis, chemical engineering reaction concepts may be brought into the analysis. For example, R_A (C_{Aw}) maybe assumed of first order to become

$$R_A\left(C_{Aw}\right) = k(T)C_{Aw} \tag{7}$$

By using the same guidelines as before, the following boundary conditions are easily identified.

$$\left.\frac{\partial C_A}{\partial y}\right|_{center} = 0(symmetry) \tag{8a}$$

$$-D\left.\frac{\partial C_A}{\partial x}\right|_{porousmouth} = kg\left(C_A\big|_{p.m.} - C_A^{\infty}\right) \tag{8b}$$

$$\left.\frac{\partial C_A}{\partial x}\right|_{bottomofpore} = 0(inpermeable) \tag{8c}$$

As mentioned before, the model above is very similar to those derived in heat transfer dominated by conduction where now the source term is explicitly identified as a chemical reaction. This similarity enhances the student understanding of the system and reinforces the concept already described. The differential model (5-8) is a straightforward description of the physics present in the pore. Since the mathematical description follows very closely the physics description of the system under analysis, the students find it very appealing and very attractive

leading to no confusion in the concepts and promoting an excellent understanding of the system. No storytelling is needed to write down such a model in this approach! Just a sound pedagogical environment and a very rational and very rigorous mathematical description will do the job. The model clearly is valid at every point of the domain and, therefore, it is clearly connected with the idea of a "microscopic" scale model of a physical system. Another important point to make is that the mathematics required to in the process is of the same level as the one learned in undergraduate level courses. Thus, a marriage between math and physics has been born in the student's minds. This connection foster an excellent integration of the, otherwise, divorce components or pieces of the engineering curriculum.

C. Process of Homogenization: If all that is needed is a microscopic representation of the physics of transport with reaction in the catalytic pores, all what is remaining is the solution of a differential model either by analytical or computational approaches to obtain the concentration profiles inside the pore domain. This is a typical strategy in an applied math course to obtain the solution of a differential system. However if the objective is to obtain a more "global" view of the problem, *the* question is, perhaps, how can the student simplify the model and have a more "homogeneous view" of the problem? This is a typical question in transport phenomena problems where a more "global or macroscopic view" is desired to achieve meaningful results form either the measurement point of view and or the solution approach to the model stated in section 2, above. In short, what it is required is a Scaling of the Microscopic Model to a Macroscopic Engineering Model. Two approaches will be discussed during the presentation:

a-Simple Averaging Procedure. By applying all area-averaging [Bird, 9] to equation (5), the result will yield an ordinary differential equation in two types of concentration variables. This approach has inherently associated an integration of the microscopic model to reach a macroscopic model in the domain. In short, what the student is looking for is to achieve an elimination of some of the independent variables to obtain a less detail description of the domain. The process mimics closely the concept of average values of a function as oppose to the point or local values for such a function. This another concept already used by the students in applied math or statistics courses.

As result of the area-integration there is an equation that features a "local" concentration, C_A, evaluated at the pore wall and the other one that is the area-averaged concentration variable, $<C_A>$. In principle, this aspect is not trivial for the students and it requires a very intensive but active learning effort from the students to realize that this situation needs a resolution before we can proceed to generate an engineering equation. However, the situation is not different from the "counting equations" processes used in thermodynamic and physical courses. In order to solve the model we need an additional equation and this immediately lead the students to identifying additional constrains. One of such conditions and, in order to solve the model, the student must recognize that the following approximation is a possible "closure" to the problem:

$$C_A\big|_{wall} \approx < C_A > \tag{9}$$

This implies a very specific type of situation within the pore. This aspect will promote an interesting discussion among the students to identify what are these physical situations. Equation (9) is, in fact, one of the simplest "closure" procedures to have an engineering equation of the type [Arce, 3].

$$\frac{d^2 < C_A >}{dx^2} + K_G < C_A >= 0 \tag{10}$$

This is a "homogeneous" differential model for the pore domain where K_G now becomes a "global" constant that is identified with basic parameters of the microscopic model. The concept of introducing global parameters is not new to the students since in kinetics, for example, there exists the concept of elementary and global reactions that parallels the concept identified above.

Students most likely will <u>not</u> have any confusion from where equation (10) was derived. The students will recognize here that equation (10) is a "homogeneous" conservation equation for the pore but in the area-averaged variables, $<C_A>$ rather than the local concentration, C_A, features by equation (5) and with modified or "effective" coefficients (K_G) rather than local coefficients such as the one identified in equation (5). Equation (10) is the basis now for learning additional engineering concepts such as the Effectiveness Factors [Aris, 6]. Within the framework presented here, this concept could be viewed as a further step in the homogenization or *scaling* process in the catalytic pellet. In other words, a "micro-reactor" has been described from a local and macroscopic point of view and both descriptions are sound and valid, however, each one of them involves different parameters and variables.

Students will now be able to connect them by a (physics-based) process of scaling that is intimately related to a (math-related) process of integration of the local equations in the domain to produce the macroscopic or scaled equations.

In summary, the significance of (10) may be immediately appreciated. This equation is, in fact, a macroscopic equation for the pore domain and, in fact, a scaled up version of the microscopic model. The equation has been obtained by a scaling up, i.e. homogenization, that is logical, sequential and has prominent practical implication for the engineering in training.

b-A Rigorous Averaging Procedure. By applying the procedure suggested, for example, by Whitaker (Whitaker, 13; Whitaker, 14], a more involved area-averaging procedure can be applied [Arce, 3]. This procedure yields an "effective" or "global" reaction rate with a constitutive equation that features various parameter involved in the problem. This procedure, however, will not change the basic idea of the procedure identified in a, above. It only will identify a more rigorous equation for the K_G macroscopic parameter identified in equation (10). By studying this equation, the student is able to identify the various physical conditions capable of being represented by the "homogeneous" or area-averaged model. Details about this approach may be found in Whitaker [Whitaker, 14] and Arce [Arce, 3]. A procedure such as this is perhaps more likely suited for an advanced senior or graduate level course.

IV. ASSESSMENT

The assessment of the implementation of this approach in two different courses at the FAMU-FSU College of Engineering has shown a very promising trend. The students have been able to clearly perform better in exercises that involved conceptually the identification of quantities related to "global" parameters such as averaged concentration and "effective diffusion" as oppose to "local" concentration values and molecular diffusion. Students' interviews at the end of the course have confirmed the mastering of the concepts and that they have achieved, in general, a deeper understanding of the different aspects in a heterogeneous system with diffusion and reaction. A similar outcome was observed in the kinetic course taught at Tennessee Tech. Students felt very comfortable in obtaining the description of the system and in identifying boundary conditions for the model. In addition, they welcomed the discussion of the closure process and the implication to the approximations involved in applying the results of the model. Furthermore, the platform of knowledge developed seems to be a very good tool to attack other more sophisticated systems such as a collection of pores in a catalytic particle. In addition, students have expressed their satisfaction in using concepts of engineering mathematics to develop "applied" models that are efficient in handling complex situations in transport and reaction. One aspect that would be useful to determine is how much the approach has increase their ability to handle system with transport and heterogeneous reactions and with several scales involved. This aspect is a subject matter for future assessment.

V. CONCLUSION

The article presents an analysis of the importance of a pellet as an environment where multi-scale transport process take place and introduces a systematic and progressive approach to derive differential models of the homogeneous type in a catalyst pellet. The approach avoids the storytelling methods followed in many classical textbooks. The same approach can be extended to include engineering equations valid for the entire pellet.

Once this approach has been introduced, the student in a rational fashion can extend the analysis from one-single porous cavity to a complete pellet. The procedure has shown that enhances the chances of the students to understand how a "homogeneous" type of description can be used as a useful approximation for describing the process of diffusion and reaction in a heterogeneous domain at the macroscopic level. Students, however, do not seem to show any confusion about the assumptions and limitations of the macroscopic model once they have followed a systematic approach for the derivation and averaging of the microscopic model.

Some of the key benefits introduced by the approach presented here from the students point of view include: a- A realistic description of the physics of the situation, b- A clear identification of the role of the molecular diffusion and surface reaction, c- A chance to reinforce concepts already learned in previous courses, d- The opportunity for the students to apply math concepts learned in the engineering math courses, e-A clear chance of building blocks of knowledge in a sequential approach and f- Avoiding the use of story-telling arguments to derive engineering equations.

This approach also allows the students to enjoy the activities to "find things out" as Feynman used to say [Feyman, 10]. In fact, based on what we saw in our courses, the process of connecting the basic physics with the mathematical description creates a learning environment that will help the students to become a confident and alert individual. In many instances, the mathematical level required does not go beyond the one reached by the student in an undergraduate engineering math course. This approach differs in a remarkable way to that of "believe me this is the way that you must analyze this problem." Within this framework, the instructor tells the student a story about considering a "homogeneous" reaction with an effective diffusion coefficient and proceeding to write equations of change by using (usually) a shell balance for a "homogeneous" system! In contrast, the approach shown here follows a systematic procedure to derive conservation (engineering) equations in heterogeneous media that are useful for a macroscopic description of the catalytic process. The approach is the same for any change of scale that is needed in the engineering work force!

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