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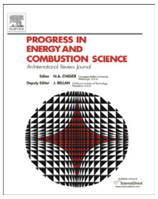

Review

Interpreting chemical kinetics from complex reaction–advection–diffusion systems: Modeling of flow reactors and related experiments

Frederick L. Dryer [a],*, Francis M. Haas [a], Jeffrey Santner [a], Tanvir I. Farouk [b], Marcos Chaos [c]

[a] *Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544-5263, USA*
[b] *Department of Mechanical Engineering, University of South Carolina, Columbia, SC 29208, USA*
[c] *FM Global, Research Division, Norwood, MA 02062, USA*

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ABSTRACT

The present discourse is directed toward the community that wishes to generate or use flow reactor data from complex chemical reactions as kinetic model development and validation targets. Various methods for comparing experimental data and computational predictions are in evidence in the literature, along with limited insights into uncertainties associated with each approach. Plug flow is most often assumed in such works as a simple, chemically insightful physical reactor model; however, only brief qualitative justifications for such an interpretation are typically offered. Modern tools permit the researcher to quantitatively confirm the validity of this assumption. In a single complex reaction system, chemical time scales can change dramatically with extent of reaction of the original reactants and with transitions across boundaries separating low temperature, intermediate temperature, and chain branched (high temperature) kinetic regimes. Such transitions can violate the underlying assumptions for plug flow interpretation. Further, uncertainties in reaction initialization may confound interpretation of experiments for which the plug flow assumption may be appropriate. Finally, various methods of acquiring experimental data can also significantly influence experimental interpretations. The following discussions provide important background for those interested in critically approaching the relatively vast literature on the application of flow reactors for generating kinetic validation data. The less frequently discussed influences of reactor simulation assumptions on modeling predictions are addressed through examples for which the kinetic behavior of specific reactant combinations may cause experimental observations to depart locally from plug flow behavior.

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* Corresponding author. Tel.: +1 609 258 5206.
E-mail address: fldryer@princeton.edu (F.L. Dryer).

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1. Introduction

Flow reactors are used extensively in the chemical process industry, and their configuration and integration with other types of reactors are discussed widely in introductory chemical reaction engineering texts, see for example [1–3]. Such tutorials consider fundamental principles, and discussions typically proceed in the context of industrial design, application, and optimization for chemical processing. These discussions generally assume simplified chemical kinetics using first or second order reactions, or perhaps empirical chemistry composed of a small number of reaction steps. An idealized plug flow reactor analysis is introduced, and using the above chemistries, sources of departure from ideal behavior are examined toward offering "corrections" to the predictions of ideal performance. Such treatment with engineering examples is useful, but not particularly informative for those in the combustion chemistry community interested in elucidating chemical kinetics by generating or modeling flow reactor data. Instead, exploitation of flow reactor data depends upon an appreciation of the coupling among the chemical species, momentum, and energy fields that comprise the chemically reacting flow, and how this coupling may be affected by the specific detailed reaction system of interest. In the present work, we tailor the standard departure-from-ideality discussion to focus directly on several such issues that bear on scientific interpretation of flow reactor experiments for complex reaction systems. Though our discussion focuses primarily on flow reactors, generalizations also extend to other experimental reacting flow configurations such as shock tubes, laminar flames, rapid compression machines, etc., as suggested in this paper and elsewhere (e.g., [4–12]).

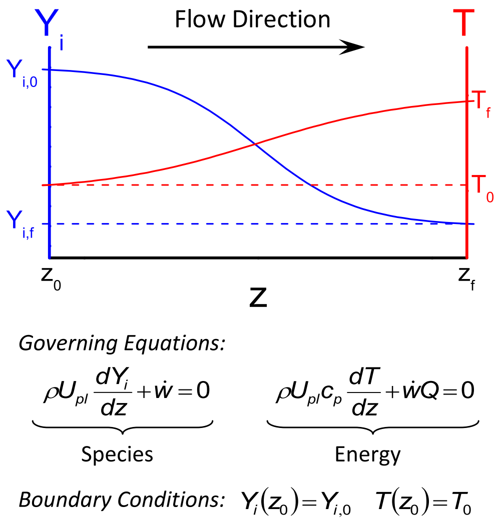
Historically, a large body of literature (see for example [13–21]) has been generated on the use of tubular flow reactors in the "direct" characterization of reaction parameters either for a single reaction or a system of a few elementary reactions. Many of these works implement experimental design considerations to approximate plug flow conditions, discuss the possible departures from ideality, and present interpretive, quantitative methods to correct for the non-idealities. We encourage the specialist interested in flow reactor design and interpretation to become familiar with this material. However, for those interested in using flow reactor data, especially for development and validation of *detailed chemical kinetic models*, a more general appreciation of flow reactor assumptions, experimental characteristics, and operational modes is of additional value. We offer several literature-based examples illustrating common, representative situations where chemistry–facility interactions may drive experimentally observable behavior to depart from otherwise ideal assumptions of reactor physics. This in turn may lead to significant interpretive uncertainties for experiments and modeling. These examples have not been singled out to intentionally criticize particular research, but to demonstrate in concrete terms the significance of a particular aspect to kinetic interpretations of results.

Our discussion cannot comprehensively consider the vast physical and chemical parameter space accessible to the experimental facilities considered here, nor do we intend on providing explicit criteria and parameters for reactor design and operation. Nevertheless, the present discussions should provide a basis from which to assess these more general topics. We begin by considering an ideal plug flow reactor, represented conceptually and mathematically in Fig. 1. Using this canonical basis for comparison, we illustrate the effects of varying (A) initial conditions and (B) boundary/interior conditions on the ideality of the flow reactor response. Techniques for interpreting measurements of downstream reactor conditions at specific residence times or spatial locations are discussed throughout. Finally, we close with an illustration of the coupling among these non-idealities, which is more representative of real flow reactor experiments.

2. The ideal plug flow reactor

Fig. 1 schematically shows the reaction of a species *i* in an isobaric plug flow reactor (PFR) as a function of the axial reactor coordinate z. Initial conditions $Y_{i,0}$ and T_0 (species fraction and temperature, respectively) are addressed in the following section, but for now are assumed to be easily attained and well-characterized, as are the final conditions $Y_{i,f}$ and T_f. The species fraction Y_i may be mass- or molar-based without loss of generality in the following discussions.

Under steady-state conditions, the associated conservation equations are written for a simple global chemical reaction that describes the rate of overall reactant conversion $\dot{w}$ and an



$$\underbrace{\rho U_{pl}\frac{dY_i}{dz}+\dot{w}=0}_{\text{Species}} \qquad \underbrace{\rho U_{pl}c_p\frac{dT}{dz}+\dot{w}Q=0}_{\text{Energy}}$$

$$Y_i(z_0)=Y_{i,0} \qquad T(z_0)=T_0$$

Fig. 1. Species and energy conservation equations and boundary conditions for a simple exothermic chemical reaction in a one-dimensional adiabatic, steady flow.