A new approach to diagnostics of ideal and non-ideal flow patterns: I. The concept of reactive-mixing index (REMI) analysis

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A new approach is proposed allowing to characterize the hydrodynamic regime in the presence of chemical reactions, through small pulse-response experiments using a reacting component as a tracer instead of inert components which are used in the traditional Danckwerts-type experiment.

Theoretically, our approach is based on the escape time defined as the mean exit age of molecules that escaped all reactions, and uses the original concept of the reactive mixing index (REMI), which is the ratio of the normalized difference between the escape time ($ET(X) = M_1(X)/M_0(X)$) in the presence and in the absence of reaction, to conversion X: $REMI(X) = (1 - ET(X)/ET(0))/X$.

Experimentally, the observed values are the numbers of additional exiting molecules per second as a function of time, $F(t)$ (mol/s). Based on these values, the moments $M_0(X)$ and $M_1(X)$ can be computed and REMI calculated.

This REMI is a global, macroscopic, external, model-free characteristic and to our knowledge has not been introduced or studied before. This value is identical to 1 for perfectly mixed continuous-flow reactors, and identical to zero for ideal plug flow reactors (PFR). For non-ideal PFR, the REMI depends on two independent characteristic dimensionless numbers, the Péclet number and the conversion or, equivalently, the Damköhler number. Expressions for these dependencies are developed.

The smallness of the perturbations allows to use a linearized kinetic model. The theory of this new index is developed; application to experimental data will be the subject of future articles.

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1. Introduction

Since Danckwerts' and Zwietering's classical results (Danckwerts, 1953, 1958; Zwietering, 1959), tracer diagnostics of flow patterns became a traditional tool of chemical engineering. It became a highly developed system of tests which are widely applied to many systems, both laboratory and industrial (see Evangelista et al., 1969; Chella and Ottino, 1984; Chen and Chang, 1989; Choi et al., 2004; Jongen, 2004; Heibel et al., 2005; Singh et al., 2007; Klusener et al., 2007). Many applications outside of the chemical engineering field can be found, particularly for biochemical and nuclear technology systems (e.g., Laquerbe et al., 1998; Escudié et al., 2005).

The main concept of the Danckwerts approach is the residence time distribution (RTD).

First, the concept of fluid element or "point" was introduced by Danckwerts in 1958 to mean a volume small with respect to the reactor vessel size, but still large enough to contain sufficient molecules (Danckwerts, 1958). By definition, this approach is continuous. It can be applied to all systems whose properties can be defined as continuous (particularly, concentration). The "age" of an element of a fluid is defined as the time elapsed since it entered the reactor. The residence time of a fluid element or exit age is defined to be its age as it leaves the reactor. The typical experiment related to this approach is performed with non-reactive tracers, i.e., the flow entering a reactor is marked by a substance that does not participate in the reaction if any, and the reactor outlet stream is then monitored. For example, a radioactive tracer is injected into the reactor inlet. The tracer concentration is then measured at the reactor outlet, and mixing patterns can be determined. In the literature a distinction is made between two types of mixing: the macromixing that refers to the scale of the reactor and the micromixing, i.e., mixing at molecular scale.

The basics of this residence time distribution (RTD) approach can be found in different publications by Danckwerts (1953, 1958) and

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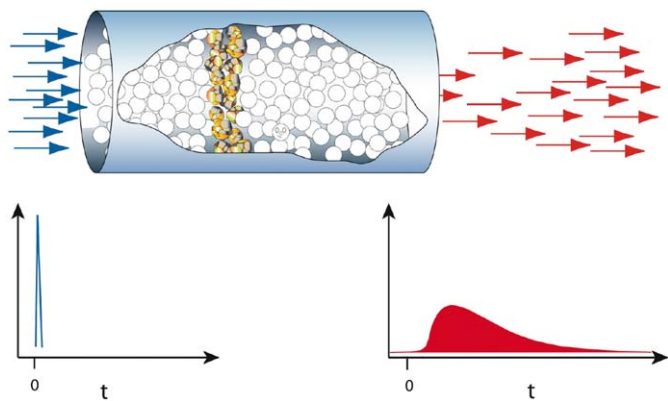
Fig. 1. Scheme of pulse-response experiment.

Zwietering (1959). Summaries are given in several books (Froment and Bischoff, 1990; Thoenes, 1994; Villermaux, 1995; Levenspiel, 1998; Nauman, 2008). The state of the art of the RTD-theory and application is presented recently in Chakraborty and Balakotaiah (2003) and Fox (2003). Also, in the first paper devoted to this approach, Danckwerts presented the solution of the model corresponding to the non-ideal plug-flow reactor, which reflects both convection and diffusion.

Classically, the variance of the exit time distribution in the absence of reaction was taken as a measure for the degree of macromixing (Danckwerts, 1958). The goal of this paper is to present an alternative approach to characterize macromixing. Rather than admitting a non-reactive tracer, a small perturbation of one of the reactant concentrations is imposed at the reactor inlet. The experimentally observed values are the numbers of additional exiting molecules per second as a function of time, $F(t)$ (mol/s). Based on these values, the moments M_0 and M_1 can be computed,

$$M_0 = \int_0^{+\infty} F(t)\,dt, \quad M_1 = \int_0^{+\infty} tF(t)\,dt.$$

In a typical case, the conversion can be presented as $X = 1 - \bar{M}_0$, where $\bar{M}_0$ is the pulse-normalized zeroth moment. In our paper we propose to use of the so-called reactive mixing index, REMI(X), defined as

$$\text{REMI}(X) = \frac{1 - \dfrac{\text{ET}(X)}{\text{ET}(0)}}{X}, \tag{1}$$

where ET(X) denotes the so-called escape time in terms of the conversion X, i.e., the average exit time of "surviving" molecules, the ones that do not react, when the total conversion is X: ET(X)$= M_1/M_0$. The value ET(0) corresponds to the case where no reaction occurs. We shall only consider reactors for which ET(0) is a finite value, excluding e.g., laminar tubular reactors where the slowness of transport near the wall leads to infinite ET(0). This REMI is a global, macroscopic, external, model-free characteristic and to our knowledge has not been introduced or studied before. In general, the REMI(X) value can be obtained experimentally, using the pulse technique, which allows to perform small perturbations of the same reactants, instead of inert gases as a tracer in the Danckwerts procedure, and measure the pulse response at the reactor outlet (see Fig. 1). The smallness of the perturbations allows to use a linearized kinetic model.

We shall show subsequently that the value REMI(X) $= 1$ corresponds to a continuously stirred tank reactor (or CSTR, i.e., perfect mixing) and REMI(X)$=0$ to a plug-flow reactor (PFR). For a non-ideal PFR (where diffusion cannot be neglected), the REMI(X) value will lie between these two values of 0 and 1, and the actual value will depend on two independent dimensionless characteristics, e.g., the Péclet number Pe and the conversion X.

Methodologically, our approach was sparked by the temporal analysis of products (TAP) experiment, in which a reactor is run at vacuum conditions and an *insignificant* injection of chemical reactants is performed at the reactor inlet; subsequently the resulting response at the outlet is analyzed particularly based on the moment technique (see Gleaves et al., 1997). In this case Knudsen diffusion is the only transport mechanism and the mathematical model is linear.

The mathematical apparatus of the new approach is based on moment analysis as well. The residence time distribution is analyzed in the presence of reaction for some basic reactor models of macromixing and both ideal and non-ideal plug flow. In these models ideal micromixing is implicitly assumed. It should be stressed, however, that experimentally the REMI(X) can be determined in any situation, including cases with possible micromixing effects.

To present our approach conceptually, we shall analyze the one-substance case, in which the reaction rate is linear (or pseudo-linear) regarding one measured substance. In the next paper, these results will be generalized for other linear (pseudo-linear) kinetic models, including models with reversible reaction (e.g., reversible adsorption) and models with multi-route complex reactions. This will be done using a similar formal apparatus.

Nevertheless, the results obtained in this paper for the one-substance case can be directly used for understanding one-substance transient behavior in multi-substance systems. It can be realized in many special situations, particularly in the analysis of the transient behavior of complex linear (or pseudo-linear) reactions with "irreversible fragments" labeled by one substance, e.g., the consecutive scheme $A \rightarrow B \rightarrow C$, or the parallel scheme $A \rightarrow B$, $A \rightarrow C$ in which the only measured substance is A, or the fragment of the presented consecutive scheme $B \rightarrow C$, in which the only pulsed substance is B. In general, the comparison of escape times of different substances can provide information on the structure of the reaction network.

2. Problem formulation

The mass balance of an open, i.e., continuous-flow, chemical reactor can be presented qualitatively as follows:

Temporal change of the substance amount = change caused by transport + change caused by reaction.

It expresses that the change of the substance amount, i.e., its accumulation, is caused by the substance motion and its reaction.

Rigorously, this equation is presented as the equation of change for multicomponent system composition (the equation of continuity) see the classical monograph by Bird et al. (1960).

In general, at least three time scales should be taken into account in dynamic analysis:

(1) the "residence time" scale, i.e., the average time required to reach the outlet from the inlet;
(2) diffusion time scale(s), more than one if different length scales occur;
(3) the reaction time scales, e.g., $1/k$ (s) for first-order reactions.

In the models we consider, the reaction may be fast or slow, but its time scale should be comparable with the other two. Otherwise, such macroscopic models make no sense. We shall see, in the development of the theory, that in the very high conversion domain ($X > 0.95$) the sensitivity of characteristics breaks down and diagnostics cannot be performed.