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Modelling residence time distribution in chemical reactors: A novel generalised *n*-laminar model Application to supercritical CO_2 and subcritical water tubular reactors

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Abstract

A new two-parameter RTD model based on the one-parameter laminar flow model has been proposed. The model, '*n*-laminar model', is defined in time domain and considers a generalization of the parabolic velocity profile across radial direction; its mathematical deduction is presented in text. The model has been validated for both supercritical and near critical CO_2 and near critical H_2O. It is shown how the proposed two-parameter model works much better than the classical models with one, two or even three parameters for both CO_2 and H_2O under near critical and supercritical conditions. A range of experiments at 10–30 MPa and 100–250 °C at different flowrates are presented. Traditional models, such as *n*-tanks in series or a combination of *n*-tanks with a plug flow resulted in a poor explanation of the behaviour in most cases with average errors over 100%. Laminar flow has shown the best results within all these classical models, with a mean average error of 50%. The proposed model predicts with an average error of less than 10–20%. Thus the generalization of the laminar flow to *n*-laminar is a significant improvement over traditional models. This model is the first successful attempt for the modelling of RTD curves at high pressures.

Keywords: Residence time distribution; Supercritical fluid; Flow pattern; Model; Laminar flow

1. Introduction

Supercritical fluids, SCFs, have emerged as an alternative environmentally friendly solvent for performing synthetic reactions, and have received much attention recently [1]. Supercritical carbon dioxide, $scCO_2$, is one of the more popular choices as it possesses relatively attainable critical parameters, it has a large density range and hence a tuneable solubility, is inexpensive, non-toxic and it can be available in large quantities if required. The use of $scCO_2$ as a solvent for a wide range of synthetic transformations, including hydrogenation, dehydrogenation, etherification, Friedel-Crafts alkylation and hydroformylation has been extensively reviewed [2–4]. Supercritical water was also successfully used for waste water treatment [5].

Near critical and supercritical water have also been used to perform a wide range of organic and inorganic processes. The dielectric constant and the ionic product of water can be easily tuned by changes in pressure and temperature. These properties have a drastic effect on the polarity and on the acid/base characteristics of the water allowing a relatively simple optimization of the reaction conditions.

The use of SCFs presents some additional advantages compared to "traditional" solvents. An increase in selectivity, catalyst lifetime and easily separation and recovery of catalyst product as well as processes intensification (higher productivity) has been reported using SCFs. Both batch and continuous flow processes have been developed [2–6]. Besides, selectivity and conversions of laboratory-scale reactions were also found to be

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Nomenclature

c_A	tracer concentration (mol m^{-3})
D	pipe diameter (m)
E	residence time distribution function (s^{-1})
f	fraction of fluid
F	concentration distribution function
Flow	flowrate (mL min^{-1})
L	characteristic length (equal to diameter, D, if the cross-section is circular; m)
$\dot{m}$	fluid mass flowrate (kg s^{-1})
n	model parameter related to velocity profile shape
$nt = N = M$	model parameter number of tanks
P	pressure (Pa)
r	radial coordinate (m)
R	pipe radius (m)
Re	Reynolds number
t	time (s)
$\bar{t} = \tau$	mean residence time (s)
t_n	model parameter tank residence time (min)
t_p	model parameter plug flow residence time (min)
T	temperature (°C)
u	fluid velocity (m s^{-1})
$\bar{u}$	average fluid velocity in radial direction (m s^{-1})
u_{max}	maximum fluid velocity, equal to velocity at $r = 0$ (m s^{-1})
$\dot{v}$	fluid flowrate (m^3 s^{-1})
V	reactor volume (m^3)
z	axial coordinate (m)

Subscripts

0	standard conditions, 1 atm and 25 °C
max	maximum
in	inlet conditions
out	outlet conditions
real	experimental
fit	modelled

Greek letters

ε	void volume fraction (m^3 m^{-3})
μ	actual (absolute) dynamic fluid viscosity (Pa s)
ρ	density (kg m^{-3})
σ^2	standard deviation (s^2)

close to identical on the large-scale, showing that the reactors behave in a similar manner regardless of the size. As a matter of fact, Thomas Swan & Co. Ltd. developed first Europe's multi-purpose $scCO_2$ pilot-scale showing that the change from the laboratory-scale to plant does not involve some of the common issues related to scaling-up process [7,8].

The residence time distribution (RTD) of a reactor is one of the most informative characterizations of the flow pattern in a chemical reactor. It provides information on how long the various elements have been in the reactor [9]. It is a quantitative measure of the degree of backmixing within a system [10] and allows for an accurate kinetic modelling of the system helping to achieve or preserve a desired flow pattern during reactor design. Besides, RTD allows for a more thorough comparison between systems having different configuration of the reactor, being an extraordinary tool for a successful process scale-up.

The residence time distribution was determined by modelling the time dependent transport of a neutral tracer species, where the concentration of the tracer at the reactor exit is monitored over time. However, little information is available about RTD curves in reactors working at supercritical conditions, so far. Fauvel et al. [11] estimated that such a study is difficult to perform in such conditions because of the compressibility of near critical and supercritical fluids. They concluded that this is possibly the reason of the lack of reported RTD experiments in supercritical fluids. RTD theory requires a constant-volume flow rate in the reactor and that is difficult to achieve when dealing with compressible gases. In addition to this, in some cases like supercritical water, the extreme pressure and temperature conditions (over 22.1 MPa and 374.1 °C) causes damage to most of the detectors and cannot be easily measured directly [11].

RTD curves can be modelled by simple models of ideal reactors (*i.e.* CSTR, plug flow and laminar flow) or conjugated models (considering simple models in series or in parallel) [10,12–15]. When RTD behaviour cannot be explained by simple or conjugated models some authors have successfully solved hydrodynamic equations and mass balance equations [16,17].

Fauvel et al. have applied three different convection models presented by Levenspiel [13] to study the RTD curves obtained in a porous reactor for supercritical water oxidation [11]. They found that the 'axially dispersed-plug flow model' and 'tanks in series model' could be used to adequately describe their reactor.

In summary, the literature regarding the RTD experimental measurement and modeling of reactors operating at supercritical conditions is very sparse at the current time. Screening results obtained by the authors (presented in this paper) suggested the necessity of a modified model that could explain easily and precisely RTD for supercritical tubular reactors.

A new RTD model based on the one-parameter laminar flow model is proposed in this paper for tubular reactors working under near critical and supercritical conditions. The model is validated using experimental results for both CO_2 and H_2O at high pressures and temperatures.

2. Model formulation

2.1. Background information

Some necessary concepts about residence time and ideal or non-ideal behaviour of flow patterns in reactors, such as basic definitions, $E(t)$ and $F(t)$ curves, mean residence time and standard deviation of $E(t)$ used in this work are listed and comprehensively explained in Supplementary Data attached [13–15].

Three main types of ideal flow patterns have been considered within this work. First, backmixing flow (BMF) which is the flow model employed for a continuous stirred tank reactor (CSTR). BMF implies perfect mixing and, hence, uniform fluid properties throughout the vessel due to efficient stirring. It also implies a