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Non-ideal flow in an annular photocatalytic reactor

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ABSTRACT

This study deals with the modelling of non-ideal flow in a tubular photocatalytic reactor with thin layer of TiO_2 photocatalyst. The objective was to analyse different level of mixing in the photoreactor applying basic principles of chemical reaction engineering. For this purpose photocatalytic oxidation of toluene was used as the model reaction. Photocatalytic reactor was operated in two different flow modes: classic type of an annular reactor with basically ideal (plug) flow with some extent of dispersion and annular flow reactor acted as stirred tank reactor with mixing of reaction mixture accomplished by recirculation. A series of experiments with step input disturbance at the entrance of the reactor with different air flow was performed in order to achieve better understanding of the reactor hydrodynamics. Several reactor models are applied, such as one dimensional model of tubular reactor at the steady state conditions, axial dispersion model at non-stationary conditions and the model of the continuous non-stationary stirred tank reactor. Numerical methods necessary for solving model equations and parameter estimation were described.

Keywords: Annular photocatalytic reactor; Toluene oxidation; TiO_2; Reactor models

1. Introduction

Volatile organic compounds (VOCs) represent the important class of pollutants, usually found in the atmosphere of all urban and industrial areas. Photocatalytic oxidation, PCO has become increasingly popular as promising alternative to traditional process for the VOC removal (Ertl et al., 1997; Lasa et al., 2005; Nevers, 1995). The UV based PCO technique for air purification can be implemented even under room temperature and atmospheric pressure. Therefore, it may be more energy efficient than other conventional techniques.

Commercial TiO_2 photocatalysts seems to be well suited for the purification of indoor air. However, there are also some drawbacks associated with their application. This is mostly due to the problems related to deactivation of TiO_2 catalyst after working for a certain period of time (Dezhi et al., 2005; d'Hennezel et al., 1998; Maira et al., 2001; Mendez-Roman and Cardona-Martinez, 1998), as well as due to complex and changeable operating conditions typical for indoor air application. In the past two decades, a lot of investigations have been conducted in this field of research. Catalysts are usually coated on the wall of a photoreactor (thin film reactor) or photoreactor is filled with materials acting as catalyst support. Various supports of TiO_2 are concerned, such as pellets (Bouazza et al., 2008), non-woven fibre textile (Ku et al., 2001), paper holders (Iguchi et al., 2003), metal foam (Ibhadon et al., 2007), zeolite panels (Ichiura et al., 2003) and rashing rings (Quici et al., 2010). Investigation of optimal reactor configurations has also become an important research area in the field of PCO (Lasa and Rosales, 2009). Different designs of laboratory reactors are used, including honeycomb monolith reactor (Du et al., 2008; Nicolella and Rovatti, 1998; Raupp et al., 2001; Huang and Li, 2011.), flat-plate reactor (Salvadó-Estivill et al., 2007a), fixed bed annular reactor (Alberici and Jardim, 1997; Bouzaza et al., 2006; Jeong et al., 2004; Keller et al., 2003), batch reactor (Kim et al., 2002), semi-batch reactor with quartz flat window (Demeestere et al., 2004; Zuo et al., 2006), circulating fluidized bed (CFB) reactor (Dibble and Raupp, 1992; Lim and Kim, 2005; Prieto et al., 2007; Sekiguchi et al., 2008), micro channel reactor (Ge et al., 2005), TiO_2-coated fibre-optic cable reactor (Denny et al., 2009; Peill et al., 1997), annular venturi reactor (Photo-CREC-air) (S. Romero-Vargas Castrillón et al., 2006) and others.

During recent years, various mathematical models describing the flow through photocatalytic reactor, interaction

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Nomenclature

Symbols

a	surface of catalyst per reactor volume, $cm^2\,cm^{-3}$
c_A	toluene concentration, $g\,m^{-3}$
$c_{A,0}$	initial toluene concentration in reactor, $g\,m^{-3}$
$c_{A,s}$	toluene concentration on catalyst surface, $g\,m^{-3}$
D_A	molecular diffusion coefficient of toluene in the air (101,325 Pa, 20 °C), $cm^2\,s^{-1}$
k_A	reaction rate constant of pseudo-first order, min^{-1}
k_g	interphase mass transfer coefficient, $cm\,min^{-1}$
L	full length of reactor, cm
r	dimensionless radius of the annular tube reactor
R_e	the external tube radius of the reactor, cm
R_i	the internal tube radius of the reactor, cm
r_A	reaction rate, $g\,m^{-3}\,min^{-1}$
RH	relative humidity
R	the recirculation ratio, $R = V_r/v_0$
SD	root mean square deviation
t	time, min
t_m	mean time, min
T	temperature, K
X_A	toluene conversion
V	volume of reactor, cm^3
v_0	total volume flow in the reactor, $cm^3\,min^{-1}$
v_R	recirculation flow rate, $cm^3\,min^{-1}$
u	linear velocity of fluid, $cm\,min^{-1}$
y	toluene molar fraction
$\bar{y}_e$	normalized experimental value of dependent variable (c_A)
$\bar{y}_t$	normalized theoretical value of dependent variable (c_A)
z	dimensionless length of the reactor

Greek letters

κ	ratio of inner and outer reactor diameter
ρ	density, $g\,cm^{-3}$
τ_0	residence time, min
τ_m	mean residence time, min
$\bar{\bar{\tau}}$	stress tensor

Dimensionless parameters

Pe	Peclet number, $Pe = uL/D_A$
Re	Reynolds number (modification for annular reactor), $Re = (2R(1-\kappa)u\rho)/\eta$
Sc	Schmidt number, $Sc = D_A\rho/\mu$
Sh	Sherwood number, $Sh = 0.705[Re(d/L)]^{0.43}Sc^{0.56}$

between the light, polluted air and catalytic surface are used and several research strategies are described. Nicolella and Rovatti (1998) presented distributed parameter model for photocatalytic oxidation of air contaminants in monolith reactors. Tomasic et al. (2008) developed and compared one dimensional (1D) and two dimensional (2D) heterogeneous models of an annular photocatalytic reactor based on assumed ideal and laminar flow through the reactor. Imoberdorf et al. (2007) described a proposal for scaling-up of photocatalytic reactors designed as catalytic walls coated with a thin layer of titanium dioxide. Interesting approach to the modelling of PCO reactors is reported by Zhang et al. (2003). Based on the analogy between heat and mass transfer for heat exchangers they developed reactor model with two parameters, the fractional conversion and the number of mass transfer units as the main parameters influencing the photo oxidation performance of PCO reactors. In general, simplified hydrodynamic models, such as plug flow or completely mixed flow are proposed and discussed in the literature. Obviously, by using such approach it is impossible to correctly describe the reactor hydrodynamics and to make conclusions about the performance of the photoreactor which can be greatly influenced by the reactor hydrodynamics. As known, the computational fluid dynamics (CFD) is emerging engineering tool which can be used for design and optimization of chemical reactors due to coupling the reactor geometry and reaction mixture flow thorough reactor. Thus, several researchers use CFD to simulate UV-reactor performance through the integration of reactor hydrodynamics, radiation distribution and UV reaction kinetics (Taghipour and Mohseni, 2005; Salvadó-Estivill et al., 2007b; Queffeulou et al., 2010).

Generally, the performance of an annular photocatalytic reactor used for removal of volatile organic compounds from the gas phase can be affected by operation parameters, such as reactor configuration (reactor geometry, the shape of the reactor inlets and outlets with respect to the reactor axis) and reaction conditions (initial concentration of reactant(s), humidity, the light source and intensity, total flow rate of the reaction mixture, etc.). Obviously, the overall performance of an annular reactor is greatly influenced by the reactor hydrodynamics due to the fact that the reacting fluid usually flows through the reactor with various degree of mixing. However, little work has been done in this field, especially with regard to the reactors used for photocatalytic oxidation in the gas phase. As well known, three main characteristics can be used to describe non-ideal reactors: distribution of residence time in the system, the quality of mixing and the model used to describe the system. The objective of this work was to carry out a detailed computational and experimental study of hydrodynamics in the annular photoreactor, to develop appropriate mathematical models as well as to compare the results with experimental measurements.

2. Experimental

Detailed description of the experimental set-up and procedure can be found elsewhere (Tomasic et al., 2008). In short line, high purity synthetic air (20.5% O_2 in N_2, *Messer*) was used as oxidant and carrier gas. The appropriate concentrations of the toluene (*Aldrich*) and water were obtained by the vaporization of the organic compound and water at the specified flow rates of the gas carrier through the saturators. The flow rates were regulated using the mass flow controllers (*Cole Palmer*). The secondary flow of the air was introduced into the mainstream to dilute the reaction mixture and finally to obtain desired concentration of the reactant at the reactor inlet. The temperature of the liquid containing saturators (toluene and water) was maintained at 20 °C. All measurements were carried out at the room temperature, atmospheric pressure, at the initial concentration of toluene of $2.68{\cdot}10^{-3}\,g\,dm^{-3}$ and the relative humidity RH of 50%. The total flow rate of reaction mixture was in the range from $(41–123){\cdot}10^{-3}\,dm^3\,min^{-1}$. The membrane peristaltic pump was applied to circulate a