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Resonance response in the catalytic combustion of methane and propane binary mixture in reverse-flow reactor

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HIGHLIGHTS

- Dynamic simulation of resonance response of reverse-flow reactor is performed.
- Break down of spatial and temporal symmetry is the cause of resonance response.
- Control strategies to minimize negative effects of resonance response are discussed.

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ABSTRACT

A numerical study was performed of the resonance behavior of a reverse-flow reactor that conducts methane and propane binary-mixture catalytic oxidation. A one-dimensional heterogeneous model was used. A resonance response occurs when the periodic inlet concentration variation cycle is the odd part of the flow-reversal cycle, which results in temperature excursion and a sharp increasing in maximum temperature within the reactor. Decreasing in average temperature implies thermal stability of the reactor is impaired. Temperature variation in the reactor is induced by both inlet concentration variation and flow-reversal operation, which may contain low frequency variation. Such resonance behavior is attributed to the breakdown of spatial and temporal symmetry of the reactor. Thus, ways to compensate such asymmetry can be used to maintain stable reactor operation, including adjusting the initial phase difference between the flow-reversal cycle and the inlet concentration variation cycle or the addition of supplemental fuel.

1. Introduction

In the last decades, reverse-flow reactors (RFRs) have drawn much research attention. Such type of reactor has proven to be an effective solution for waste-gas decontamination, such as SO_2 oxidation [1–3], purification of a diluted volatile-organic-compounds gas stream [4–5], coal mine ventilation air methane oxidation [6–7] and the selective reduction of NOx [8–10]. An RFR is a catalytic fixed-bed reactor which operates under forced unsteady state conditions resulting from periodic flow reversals. When exothermic reactions are conducted in the reactor, a temperature wave is generated that creeps with gas flow. By choosing an appropriate flow-reversal cycle, the released heat is trapped inside the reactor that sustains the catalytic reaction. The auto-thermal operation is then possible even with weak exothermic effects and inlet gas feed at ambient temperature. The catalyst at either end acts as a regenerative heat exchanger which is normally substituted by inert materials for economic reasons.

Although an RFR has shown its advantages such as auto-thermal operation and improved performance than steady-state operation, it is difficult to operate because of the inherent non-stationary character that is derived from forced unsteady state operation. Maintaining the auto-thermal operation and construction of corresponding control strategies are of primary interest because only steady-state or pseudo-steady state (PSS) operation has a realistic meaning. For example, a very lean inlet feed would lead to reactor extinction because the heat released is insufficient to maintain catalytic reactions, while a very rich inlet feed would cause thermal run-way and catalyst deactivation due to excessive heat accumulation in local spots. Much effort has been made to establish the dependence of reactor performance on various design and operating parameters both experimentally and numerically [11–15]. Several control strategies have been proposed to maintain the ignition state and have proved effective and efficient [14,16–20]. Detailed reviews on reactor mechanism, operation, mathematical modeling and applications have been provided by Matros [21], Kolios [22]

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Notation

A	pre-exponential factor (s^{-1} for first-order reactions)
a_v	specific interfacial area, $m^2 \cdot m^{-3}$
C_i	molar concentration of *i*th component in gas phase, $mol \cdot m^{-3}$
c_p	specific heat capacity, $J \cdot kg^{-1} \cdot K^{-1}$
D_{eff}	effective diffusion coefficient, $m^2 \cdot s^{-1}$
E_a	activation energy, $J \cdot mol^{-1}$
ΔH	heat of reaction, $J \cdot mol^{-1}$
h	coefficient of gas-solid heat transfer, $W \cdot m^{-2} \cdot K^{-1}$
k_m	mass transfer coefficient, $m \cdot s^{-1}$
k_{eff}	effective thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$
L	reactor length, m
R	ideal gas constant, $J \cdot mol^{-1} \cdot K^{-1}$
T	Temperature, K
ΔT_{ad}	adiabatic temperature rise, K
t	time, s
t_{cycle}	flow-reversal cycle time, s
t_{feed}	cycle time of inlet concentration variation, s
u	gas velocity, $m \cdot s^{-1}$
x	axial position along the reactor, m

Greek letters

ε	void fraction of the bed
η	effectiveness factor
θ	dimensionless temperature
ρ	density, $kg \cdot m^{-3}$
ϕ_1	initial phase difference between the inlet-concentration variation cycle and the flow-reversal cycle, degree
ϕ_2	phase difference between the inlet methane concentration variation cycle and propane, degree

Subscripts

0	initial conditions
in	inlet conditions
G	gas phase
i	*i*th reactant
S	solid phase

and Zagoruiko [23]. A comprehensive survey on RFR performance and model simplification has been given by Marín [24].

A fixed bed reactor conducting exothermic reactions can exhibit a complex dynamic feature which is resulted from the difference between heat and mass flow rates through the reactor bed and the positive thermal feedback provided by exothermal reactions. It behaves in a more complicated manner with variations in inlet or surrounding conditions. A step change in inlet temperature or concentration can lead to significant qualitative changes in the reactor, such as “wrong-way” behavior, differential-flow instability, multi-steady states or thermal run-away. Owing to the relatively large thermal inertia of the solid packing and flow-reversal operation, an RFR can overcome a temporary change in the inlet concentration and finally recover to previous PSS after the feed has been restored [25–27]· While heat withdraws from an RFR could lead to asymmetric and quasi-periodic states in the reactor [28,29].

For a fixed-bed reactor under steady state operation, dynamic instability will occur when periodic perturbations in inlet feed is introduced. The research works done by Yakhnin and Menzinger [30–33] show that a fixed-bed reactor conducting exothermic reactions tends to amplify periodic inlet temperature perturbation in the reactor, which causes temperature transients in the catalysts packing. The temperature amplification phenomenon depends on the frequencies of inlet temperature variations and such dynamic instability is essentially a resonant phenomenon.

As for fixed bed with forced unsteady state operations, numerical investigations from Cittadini [34] have shown that when the periodic perturbation in inlet concentration or flow rate was introduced, particular ratios between the feed and flow-reversal cycles would endanger reactor stability. In such cases, desynchronizing of inlet perturbation cycle and flow-reversal cycle is a possible way to maintain auto-thermal operation [35].

During the waste-gas decontamination process, the pollutant concentration and compositions often varies. Several control strategies have been proposed to deal with this issue and have proved effective and efficient. However, RFR application to a real process requires an improved understanding of the reactor behavior with a continuous variation in inlet conditions.

Following our previous studies in resonance behavior of RFRs, a numerical simulation was undertaken to explore the causes of resonance behavior and corresponding reactor behaviors when multiple catalytic reactions are conducted in the reactor. Methane and propane are chosen as model reactants because of their differences reaction kinetics. In this study, inlet concentration of these two reactants varies in sinusoid waveform because it is believed that discussion on reactor behavior with continuous inlet variation of such fundamental waveform could reveal some intrinsic nature of RFR. The effects of interactions between periodical inlet concentration variations of the two reactants on resonance behavior are discussed. Possible control strategies to minimize the effect of resonance behavior and to maintain stable reactor operation are discussed as well.

2. Mathematical modeling

A heterogeneous one-dimensional non-steady model of an adiabatic packed bed was applied in this work. A one-dimensional model that considers the axial dimension only is sufficiently accurate to describe the reactor behavior as in this work. The heterogeneous model takes the temperature and reactant-concentration difference between the solid and gas phases into account because of the highly exothermic catalytic reactions. Because of the periodic operation nature of the RFR, a non-stationary term is incorporated into the model, which gives the temperature and reactant concentration distribution evolution. The effectiveness factor (Thiele modulus) is used to incorporate interparticle mass transfer. Given a low methane and propane concentration, the catalytic reaction is considered to be first-order. The kinetic parameters of methane and propane catalytic combustion are adopted from Hevia et al. [36] and Salinger et al. [37] respectively. Methane and propane inhibition on the catalytic surface is neglected because of the low catalyst coverage of these reactants that results from a low concentration and high reaction rate. As Marín et al. [5] have concluded, such assumption would be accurate enough for typical RFR simulation. Homogeneous combustion is ignored at the low reaction temperature of the catalytic reaction. Eqs. (1) to (10) are the energy and mass balances for the gas and solid phase and the initial and boundary conditions. The main physical properties used in the numerical simulation are listed in Table 1.

The energy balance in the gas phase is:

$$\frac{\partial T_G}{\partial t} = -\frac{u_{in}\rho_{G,in}}{\varepsilon \rho_G}\frac{\partial T_G}{\partial x} + \frac{k_{eff,G}}{c_{p,g}\rho_g}\frac{\partial^2 T_G}{\partial x^2} - \frac{h a_v}{\varepsilon c_{p,G}\rho_G}(T_G - T_S) \tag{1}$$

The mass balance in the gas phase is: