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Simulation of a large methanol-to-olefins fluidized bed reactor with consideration of coke distribution

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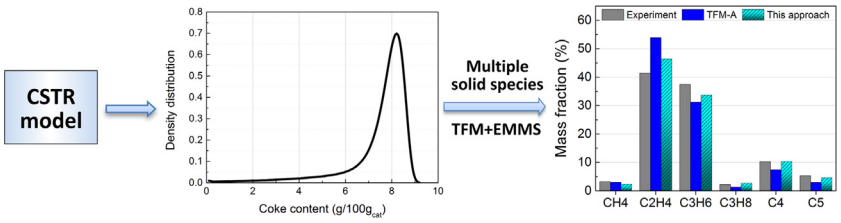
HIGHLIGHTS

- A CSTR model considering the content distribution is established.
- The solid phase is treated as a mixture of a series of solid species with different coke contents.
- This approach requires 36% more computation time compared with the previous study.
- The predictions of reaction quantities are improved using this approach.

GRAPHICAL ABSTRACT



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ABSTRACT

In the methanol-to-olefins (MTO) process, coke deposition is closely related to the selectivity of light olefins. Previous simulations of different-sized MTO reactors using two-fluid model (TFM) combined with the EMMS (energy minimization multi-scale)-based drag well predict the hydrodynamic behaviors but poorly predict the product distribution of large reactors due to the unreasonable prediction in coke distribution. In this study, the TFM integrated with the EMMS-based drag is still employed, but the solid phase is treated as a mixture of a series of species with different coke contents. Because the coke content depends on the age of catalyst particles inside the reactor, a continuous stirred tank reactor (CSTR) model mimicking turbulent fluidization while considering the age distribution of catalysts is established to predict the initial coke distribution for speeding up simulation. Compared with the previous simulation without consideration of coke distribution, this approach increases the computational time by a factor of 36% and shows no influence on hydrodynamic predictions, but the reaction quantities such as methanol conversion, mass fractions of gaseous products and selectivity of light olefins, are better predicted.

1. Introduction

The methanol-to-olefins (MTO) process creates a new route to produce light olefins such as ethylene and propylene (Tian et al., 2015). Methanol can be readily obtained from oil and non-oil feedstock including coal and natural gas (Amghizar et al., 2017), thus diversifying the production of light olefins and making the MTO process attractive, especially in China. At present, there are several successful MTO techniques brought into stream, such as the processes developed from Dalian Institute of Chemical Physics (DICP), SINOPEC, UOP and ExxonMobil (Keil, 1999, Chen et al., 2005, Tian et al., 2015, Ye et al., 2015), respectively. In 2010, the World's first commercial unit (1800 kt/a methanol feedstock) using the DICP's MTO (DMTO) technique was successfully operated in Baotou plant of Shenhua group (Tian et al., 2015). The MTO process is expected to be the primary route for producing light olefins in the future.

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Nomenclature

C	concentration, mol/L
C_{D0}	standard drag coefficient for an individual particle
d_p	particle diameter, m
$\boldsymbol{g}$	gravitational acceleration, kg/m^2/s
G_s	mass flow rates of the recycled catalysts, g/s
H_D	heterogeneity index
k_i	reaction rate constant, L/(g_{cat}·s)
M	molecular weight, g/mol
p	pressure, Pa
Q	volumetric flow rate of gas phase, L/s
R_i	reaction rate, g/(g_{cat}·s)
$\boldsymbol{u}$	real velocity, m/s
v	stoichiometric number
w_c	coke content, g/100g_{cat}
Y	mass fraction

Greek letters

β	drag coefficient with structure in a control volume, kg/(m^3·s)
Γ	interphase mass transfer, kg/m^2/s
ε	volume fraction
μ	viscosity, Pa·s
ρ	density, kg/m^3
τ	stress tensor, N/m^2
φ	deactivation function
η	methanol conversion

Subscripts

g	gas phase
s	solid phase
i, j	lump in reaction kinetics/interval

The design of the MTO process originates from the concepts of modern fluid catalytic cracking (FCC) units, but it has distinctive characteristics (Ye et al., 2015), taking the DMTO process as an example: first, the SAPO-34 catalysts used in MTO have much smaller pores (<2 nm) than the zeolite Y catalysts in FCC, so the coke deposition which could decrease the pore size shows a close relation to the selectivity of ethylene (Li et al., 2016); second, because long residence time of catalysts (on the order of tens of minutes) is required to achieve the optimum coke content, dense fluidized bed such as a turbulent bed is preferred in the MTO process while a riser reactor is often used in modern FCC units. Hence optimization of the current MTO technology calls for further fundamental research to fully understand the hydrodynamics and reaction behaviors in the reactor.

In early research, classic reactor models were widely applied to describe the simplified hydrodynamics (Bos et al., 1995, Schoenfelder et al., 1996, Soundararajan et al., 2001, Alwahabi and Froment, 2004, Kaarsholm et al., 2010). Alwahabi and Froment (2004) coupled chemical kinetics with three reactor models (the multi-tubular quasi-isothermal reactor model, multi-bed adiabatic reactor model and bubbling fluidized bed model) separately to search for the optimal reactor type. Soundararajan et al. (2001) employed a core-annulus two-phase model with a lumped kinetic model to investigate the reaction performance. Generally, reactor models have been found to be suitable for predicting mean quantities and steady state behaviors. In recent years, the rapidly developing Computational Fluid Dynamics (CFD) has been extensively used to investigate complex hydrodynamics and reactions in fluidized beds. Chang et al. (2013) applied the TFM with a lumped kinetic model to simulate a small fast bed reactor and analyzed the effects of operating conditions including gas velocity, solid circulation rate, temperature and coke content. Zhuang et al. (2014) employed the discrete particle model (DPM) and the kinetic model of Bos et al. (1995) to simulate a very small two-dimensional (2D) reactor and obtained detailed hydrodynamic quantities. Zhao et al. (2013) used the TFM and the EMMS/bubbling drag to simulate a demo-scale DMTO turbulent reactor and found a good prediction in pressure distribution. Zhu et al. (2016) re-simulated this turbulent reactor by changing the drag model and studied the effects of reaction kinetic models on the results. These studies are more focused on model validation.

To further develop and optimize the MTO process, DICP cooperated with Institute of Process Engineering (IPE) to conduct a series of CFD simulations of DMTO reactors ranging from the micro to commercial scale. Simulations of different-sized reactors pose a big challenge to CFD modeling in the following aspects: (i) because DMTO reactors are operated at dense fluidization with long residence time, even simulations using coarse-grid resolution require formidable computational cost. Hence speeding up the simulation is very necessary; (ii) because the flow regime changes from the bubbling fluidization to turbulent fluidization on upscaling the DMTO reactor (Tian et al., 2015, Lu et al., 2017), these changes should be taken into account in drag modeling which is a key factor of CFD simulations of fluidized beds (Li & Kwauk, 2003, Yang et al., 2003, Wang & Li, 2007, Stroh et al., 2016, Kraft et al., 2017, Luna et al., 2017); (iii) the chemical kinetic model was obtained from experiments on the micro-scale reactor (Ying et al., 2015, Yuan et al., 2017), so the applicability of this model to simulations of larger reactors having different hydrodynamic behaviors needs to be further investigated. Lu and coworkers conducted a series of researches (Lu et al., 2016, 2017, Luo et al., 2017): first, a continuous-stirred tank reactor (CSTR) model was established to predict mean coke content. It was found that using the mean coke content as the initial value, the reactive simulation of a pilot-scale bubbling fluidized bed can quickly reach the pseudo-steady state (Lu et al., 2016); second, the EMMS/bubbling model which is more suitable for bubbling fluidization was extended to a two-step version whose heterogeneity index depends on both voidage and slip velocity. The relevant simulations show a weak dependence on grid size and better predictions for the turbulent fluidized bed (Luo et al., 2017); third, a series of simulations of different-sized DMTO reactors were conducted by using the TFM and the two-step drag model in conjunction with the lumped kinetics from the experiments on the micro-scale reactor. It was found that hydrodynamic behaviors in these MTO reactors are successfully captured, but there is a big discrepancy between reaction quantities from simulations and experimental data for large reactors (Lu et al., 2017).

Ye et al. (2015) reported that there is a wide distribution of coke content in large MTO fluidized bed reactors because of the significant circulation of catalysts and the formation of meso-scale structures, whereas our previous work (Lu et al., 2017) predicted uniform coke distribution in the reaction zones of large reactors. Lu et al. (2017) pointed out that the coke content depends closely on the residence time of catalysts, while the TFM simulation averages different coke contents in a computational cell and is thus unable to capture the realistic change of coke content.

In this study, we aim to improve the reactive simulations of large MTO reactors by differentiating catalysts with different coke contents under the TFM framework. The basic governing equations and chemical kinetic model are first presented. Then a CSTR model is extended by considering the age distribution of catalysts to