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Modeling and optimization of methanol oxidation over metal oxide catalyst in an industrial fixed bed reactor

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ABSTRACT

The main objective of this study is modeling and optimization of methanol oxidation over iron-molybdenum oxide catalyst in a fixed bed reactor. The considered process is modeled based on the mass and energy balance equations at steady state condition. To verify accuracy of the proposed model and considered assumptions, the simulation results are compared with the plant data. Then, the effect of feed temperature, coolant temperature and air-to-methanol molar ratio on the reactor performance is investigated. In addition, considering formaldehyde production capacity and selectivity as objectives, a multi-objective optimization problem is formulated considering feed and coolant temperature, and air to methanol ratio as decision variables. Based on the developed mathematical model of the process and multi-objective optimization model, Pareto optimal front is obtained by non-sorting multi-objective genetic algorithm. Then, the single optimal point is selected from developed optimal Pareto front by TOPSIS decision-making method. The performance of the optimized reactor is compared with the conventional reactor at steady state condition.

1. Introduction

Formaldehyde as the simplest aldehyde is an important compound to produce complex chemicals and polymers such as urea formaldehyde resin, melamine resin, phenol formaldehyde resin and polyoxymethylene plastics [1]. Formaldehyde is produced industrially from methanol through different processes, including partial oxidation and dehydrogenation in the presence of silver crystal or silver gauze with excess methanol, and oxidation only with air in the presence of a modified iron–molybdenum–vanadium oxide catalyst and excess air [2]. The main differences between the production methods are catalyst type, operating condition and the feed concentration.

The methanol oxidation over silver-based catalyst at 600–700 °C is the oldest process to produce formaldehyde commercialized by BASF and ICI [1,3,4]. In this process, reaction temperature and conversion depend on the methanol concentration in feed stream. In Formox process, commercialized by Johnson Matthey Process Technologies, methanol and oxygen react at 300–400 °C in presence of iron–molybdenum oxide catalyst [1]. Generally, the iron–molybdenum oxide catalyst has attracted more attention compared to the silver catalyst due to lower investment and operating costs. However, sensitivity against operating condition is the main disadvantage of iron–molybdenum oxide catalyst [3].

Many researchers have focused on the catalyst synthesis and mechanism of methanol oxidation to formaldehyde [5–14]. Andersson et al. presented a good overview describing the historical and present developments on the methanol oxidation to formaldehyde from 1950s [15]. Generally, vanadium pentoxide catalyst is the first metal oxide used in the methanol oxidation process [1]. Adkins and Peterson introduced iron–molybdenum oxide as methanol oxidation catalyst due to high selectivity and thermal resistance [16]. Galvanin et al. proposed a model-based design of experiments procedure to estimate the kinetic parameters of methanol oxidation on silver catalyst [17]. Chapman et al. showed that the performance of Mo-enriched, bulk ferric molybdate, employed commercially for selective oxidation of methanol to formaldehyde, is limited by a low surface area [18]. The results proved that core–shell, multi-component oxides offer new routes for improving catalytic performance and activity. Windes et al. modeled partial oxidation of methanol considering heterogeneous and pseudo homogeneous models at steady state condition. The results showed that the considered models are capable to predict hot spot position and yield. In addition, it was shown that coolant temperature has a significant effect on the reactor performance compared to the feed temperature [19]. Faliks et al. modeled formaldehyde production over iron–molybdenum oxide catalyst at steady state condition. The results showed that the distribution of heat flux effects

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Nomenclature

a_v	specific surface area of catalyst pellet (m^2/m^3)
A_c	cross section area of each tube (m^2)
C_p	specific heat of the gas at constant pressure (J/mol/K)
C	total concentration ($kmol/m^3$)
D	tube diameter (m)
d_p	catalyst particle diameter (m)
E_i	activation energy for *i*th reaction (J/mol)
D_{ij}	binary diffusion coefficient of component *i* in *j* (m^2/s)
D_{im}	diffusion coefficient of component i in the mixture (m^2/s)
F	total molar flow rate (mol/s)
h_f	gas–solid heat transfer coefficient in reactor ($W/m^2/K$)
h_i	tube side heat transfer coefficient in reactor ($W/m^2/K$)
h_o	shell side heat transfer coefficient in reactor ($W/m^2/K$)
ΔH_i	heat of reaction for reaction i (kJ/kmol)
k_i	reaction rate constant (mol g/cat/h/$kPa^{0.5}$)
K_a	adsorption equilibrium constant in the rate equation ($kPa^{-0.5}$)
L	reactor length (m)
P	total pressure (kPa)
P_i	partial pressure of component i (kPa)
r_i	rate of reaction (mol g/cat/h)
R	Universal gas constant (J/mol/K)
T^g	bulk gas phase temperature (K)
T^c	cooling liquid temperature in shell side (K)
T^s	solid phase temperature (K)
u_g	velocity of fluid phase (m/s)
U	overall heat transfer coefficient ($W/m^2/K$)
y_i^g	mole fraction of component *i* in the fluid phase
y_i^s	mole fraction of component *i* on the catalyst surface
z	axial reactor coordinate (m)

Greek letters

μ	viscosity of gas phase (Pa s)
η	catalyst effectiveness factor
ρ	gas density (kg/m^3)
ρ_b	catalytic bed density (kg/m^3)
ε	porosity factor

on the formaldehyde yield [20]. Yang et al. modeled a packed-bed membrane reactor for partial oxidation of methanol to formaldehyde. The simulation results showed that the membrane reactor presents a higher selectivity compared to the conventional process [21]. Moustafa simulated a formaldehyde reactor considering diffusion-reaction kinetic model [22]. The effectiveness factor of reactions was selected as fitting parameters and calculated based on the plant data.

Process optimization is the discipline to adjust process condition to operate at desired performance without violating operational, safety and other constraints. Operating the chemical processes at optimal point could decrease cost, energy and risk in the system. There are many researches in the literature that have focused on the optimization of chemical process particularly chemical reactors [23]. Elnashaie et al. developed a heterogeneous model to simulate and optimize an industrial ammonia reactor [24]. The results showed that applying the optimal condition on the system increases ammonia production capacity about 6–7%. Kordabadi and Jahanmiri optimized methanol production in an industrial fixed bed reactor by genetic algorithm [25]. This optimization approach enhanced 2.9% additional yield throughout 4 years. Farsi and Shahhosseini optimized the steam reforming of methane in a fixed bed reactor considering a multi objective optimization problem [26]. The single optimal solution was selected from developed Pareto frontier by various decision-making methods such Shannon Entropy, LINMAP and TOPSIS.

The main objective of this study is to optimize the operating condition of methanol oxidation process over iron–molybdenum oxide catalyst to achieve maximum formaldehyde production and selectivity considering a multi-objective optimization model. The Pareto front is developed and the single optimal point is selected from developed optimal Pareto front by TOPSIS decision-making method. In Section 2, Formox process to produce formaldehyde is explained. In Sections 3–5 the considered reaction kinetic, developed mathematical model and selected procedure to find the optimal process condition are presented, respectively. The results and discussion section consist of the model validation, simulation results, sensitivity analysis and results of optimized reactor subsections.

Table 1
Reactor characteristics and catalyst specification of the conventional process.

Parameter	Value
Feed condition	
Coolant temperature (K)	540
Methanol feed flow rate (kmol/h)	102.96
Air to methanol ratio	8.325
Inlet pressure (bar)	2.16
Inlet temperature (K)	467
Reactor characteristics	
Catalyst bed length (m)	0.77
Tube internal diameter (m)	0.025
Number of tubes	7700
Bed void fraction	0.45
Catalyst particle characteristics	
Catalyst shape	Ring
Density (kg/m^3)	1000
Diameter (m)	0.0048
Height to diameter ratio	1

2. Process description

Methanol oxidation over the iron–molybdenum oxide catalyst is one of the main methods to produce formaldehyde. In the considered domestic Iranian plant, the methanol oxidation reaction occurs in a multi-tubular fixed-bed reactor. The tubes of reactor are filled by the catalyst plates and light oil as the cooling liquid flows inside the shell side to remove heat from the reaction and keeps the tube surface at a uniform temperature. The used catalyst in the reactor is in the form of rings, with the diameter and height of about 5 mm. Methanol is mixed with excess air, preheated and fed to the reactor. Feed is converted to the formaldehyde over the catalyst surface and product stream is fed to the distillation section. In the separation section, formaldehyde is separated from reactor effluent. The specification of reactor and feed of considered industrial reactor are tabulated in Table 1.

3. Reaction scheme and kinetics

Methanol oxidation reaction is highly exothermic. Through the oxidation reaction, methanol reacts with oxygen and formaldehyde is produced.

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