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Dynamic analysis on methanation reactor using a double-input–multi-output linearized model☆

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ABSTRACT

A double-input–multi-output linearized system is developed using the state-space method for dynamic analysis of methanation process of coke oven gas. The stability of reactor alone and reactor with feed-effluent heat exchanger is compared through the dominant poles of the system transfer functions. With single or double disturbance of temperature and CO concentration at the reactor inlet, typical dynamic behavior in the reactor, including fast concentration response, slow temperature response and inverse response, is revealed for further understanding of the counteraction and synergy effects caused by simultaneous variation of concentration and temperature. Analysis results show that the stability of the reactor loop is more sensitive than that of reactor alone due to the positive heat feedback. Remarkably, with the decrease of heat exchange efficiency, the reactor system may display limit cycle behavior for a pair of complex conjugate poles across the imaginary axis.

1. Introduction

The research on alternative fuel is highly attractive with the concern of environmental protection and growing energy demand. Natural gas, mainly containing methane, is considered as one of the most promising alternative fuels because of its excellent combustion characteristics such as high octane number, good antiknock property and less emission [1,2]. However, it is reported that natural gas will be exhausted in 40–60 years, so a sustained effort has been made to convert various coal-based and biomass feedstock into synthetic natural gas [3,4]. As a by-product in the coke production, the coke oven gas (COG), most of which is either discharged directly into the atmosphere or committed to flames, is considered as an important hydrocarbon resource to the synthesis of natural gas through methanation process [5].

The methanation of COG most likely occurs in adiabatic fixed bed reactors with nickel-based catalysts. The inherent distribution nature in the reactor (variables change with axial position), interaction of heat, mass transport and reaction, and thermal inertia of catalysts may give great challenge to the study on dynamic behavior, where significant dynamic lags, multistability, and sudden loss of stability could be induced [6,7]. The COG methanation reactor is also sensitive to disturbances of CO concentration and temperature, because COG from different coking furnaces varies in components and enormous reaction heat will bring about a large temperature rise in the adiabatic bed. Furthermore, the feed gas is always preheated with the product gas from the viewpoint of energy cascade utilization, which could introduce a feedback mechanism and make the reactor stability worse and the anti-interference ability poor [8]. Therefore, it is necessary to analyze these dynamic characteristics in the methanation process of COG.

Up to now, many methods have been adopted to address the dynamic model of distributed parameter system. With the finite difference method, Kordabadi and Jahanmiri [9], and Rahimpour [10] carried out a dynamic simulation on a dual-stage reactor for methanol synthesis in the face of catalyst deactivation. Baldea and Daoutidis [11] computed the singular perturbation of an autothermal fixed bed reactor for methane steam reforming, where reactor extinction may arise. With the orthogonal collocation method, Margarida and Rosa [12] simulated the start up and the wrong way behavior of a fixed bed reactor with two distinct zones for methanol oxidation. Continillo *et al.* [13] characterized the dynamic behavior of a self-ignition reactor by considering the diffusion effect, where the period-doubling bifurcation could be found. Other methods such as polynomial approximation, wavelet-like collocation method and piecewise linearization method are also developed to deal with the distributed parameter system [14–18]. These methods can describe the transient behavior of the fixed bed reactors well, while lacking of a complete system identification that characterizes the input–output relationship of a reactor loop. Furthermore, double

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perturbation may also occur, but the counteraction and synergy effects caused by simultaneous variation of concentration and temperature were seldom taken into account in above researches.

In this paper, a double-input–multi-output (DIMO) linearized system based on a simple dynamic model is developed for dynamic analysis of a methanation reactor with feed-effluent heat exchanger (FEHE). The stability of the reactor loop and the reactor alone is compared through the system transfer functions, and further demonstrated by the responses of reactor variables when the inlet temperature and CO concentration are perturbed separately or simultaneously. In addition, the essential behavior, including fast concentration response, slow temperature response, wrong way behavior and limit cycle behavior, is also revealed for the study of counteraction and synergy effects through the concentration and temperature variations. The main purpose of our work is not to predict the industrial case with great numerical accuracy, but rather to yield qualitative and further insight into possible phenomena, which could contribute to the system identification and optimal control for the methanation process of COG.

2. Modeling

2.1. Basic assumptions

Except for hydrogen, carbon monoxide and carbon dioxide, there is also some methane and a little nitrogen in COG [19]. The following independent reactions are involved in the methanation system of COG

$$CO + 3H_2 \Longleftrightarrow CH_4 + H_2O \quad (1)$$

$$CO_2 + 4H_2 \Longleftrightarrow CH_4 + 2H_2O. \quad (2)$$

Fig. 1 shows the methanation system, which consists of three adiabatic fixed bed reactors with interstage cooling. The diameter of the reactor is 1 m, and the lengths of the three beds are 2.8, 1.9 and 2.5 m. Besides, a feed-effluent heat exchanger is added for surplus heat utilization, and its heat exchange area is 11.51 m^2.

To develop the dynamic model, we make a few assumptions.

(1) In the COG methanation system, methanation of CO_2 may be restrained in the presence of CO [20,21], so methanation of CO mainly takes place in the first stage and continues in the middle stage, and methanation of CO_2 mainly occurs in the last stage. The CO_2 concentration is relatively low (about 2%) and the reaction heat of CO_2 methanation is less than that of CO methanation, so only the CO methanation in the first stage is considered.

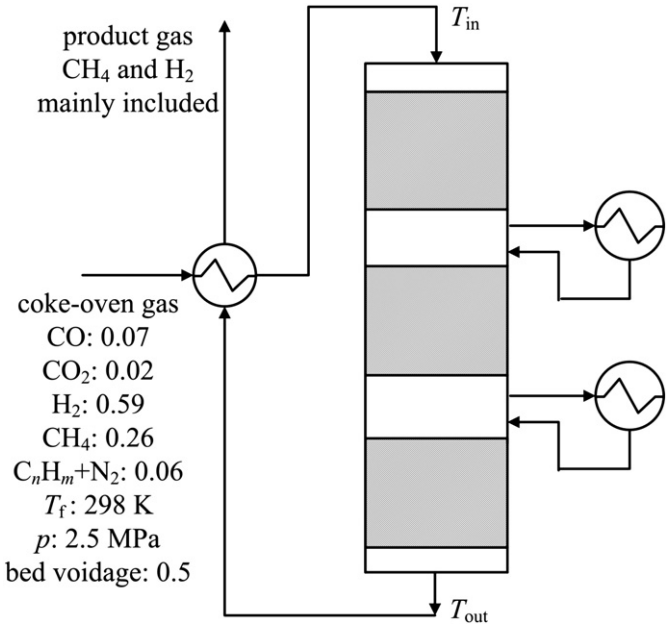

Fig. 1. Reactor system of COG methanation.

(2) The axial dispersion and radial gradients in the reactor are negligible, the gas mixture moves with a uniform velocity in the reactor and Ni/Al_2O_3 catalyst is uniformly distributed. Catalyst specifications are listed in Table 1.

(3) The methanation reaction of CO is controlled by the rates of intrinsic kinetics and external diffusion, which can be described as

$$-r = \frac{k}{p_{H_2}^{2.5}}\left(\frac{p_{CO}p_{H_2}^3}{k} - p_{CH_4}p_{H_2O}\right) \Big/ \left(1 + K_{CO}p_{CO} + K_{H_2}p_{H_2} + K_{CH_4}p_{CH_4} + K_{H_2O}p_{H_2O}/p_{H_2}\right) \quad (3)$$

$$k = k_0 \exp(-E/RT) \quad (4)$$

$$-r_{CO} = \eta_e(-r) \quad (5)$$

$$\eta_e = \frac{1}{1 + Da} \quad (6)$$

$$Da = (1-\varepsilon)\rho_s k_0 / k_g a \quad (7)$$

where η_e is the effectiveness factor, Da is the Damkohler number expressing the ratio of reaction rate to mass transfer rate, K is the adsorption coefficient, and k_0 and k_g represent the reaction rate constant and mass transfer coefficient, respectively. The intrinsic kinetic parameters are taken from Xu and Froment [22]. k_g is evaluated as follows [23]

$$Sh = k_g d_p / D_g \quad (8)$$

Here Sh is the Sherwood number and is written as

$$Sh = 2 + 0.654 Re^{1/2} Sc^{1/3} \quad (9)$$

with

$$Re = v\rho_g d_p / \mu \quad (10)$$

$$Sc = \mu / \rho_g D_g \quad (11)$$

where $D_g = 8.34 \times 10^{-6} T^{1.75}/p$ is the diffusion coefficient of CO.

2.2. Nonlinear dynamic model

Based on the mass and heat balances, the dynamic performance of the reactor can be described by two partial differential equations

$$\frac{\partial C_{CO}}{\partial t} = -v\frac{\partial C_{CO}}{\partial z} - (-r_{CO}) \quad (12)$$

$$\left[\varepsilon\rho_g C_{pg} + (1-\varepsilon)\rho_s C_{ps}\right]\frac{\partial T}{\partial t} = -v\rho_g C_{pg}\frac{\partial T}{\partial z} + (-\Delta H)(-r_{CO}) \quad (13)$$

where v is the gas velocity, ε is the voidage of catalyst bed, C_{pg} and C_{ps} represent the specific heat of gas mixture and catalyst particles, respectively, and ΔH is the reaction heat of CO methanation.

Table 1
Physical parameters of Ni/Al_2O_3 catalyst in the methanation reactor

Catalysts density ρ_s/kg·m^{-3}	Particle diameter d_p/m	Specific area a/m^2·m^{-3}	Specific heat C_{ps}/J·kg^{-1}·K^{-1}
2732	0.005	516	880