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Full Length Article

Numerical investigation on methanation kinetic and flow behavior in full-loop fluidized bed reactor

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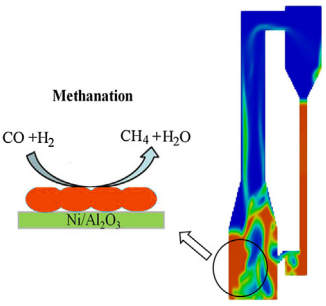
GRAPHICAL ABSTRACT



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ABSTRACT

Methane production using syngas is a feasible way for overcoming the shortage of natural gas supply and a clean utilization of coal. The full-loop circulating fluidized bed will be a good choice to improve the methane production and extend the catalyst lifetime. This work is the first attempt to adopt the full-loop reactor for producing methane, and also the ready for industrial application. Methanation process is investigated numerically in full-loop fluidized bed over Ni/Al_2O_3 catalyst. The influences of operation parameter on reactants conversion and CH_4 yield are evaluated. Meanwhile, the performance of water gas shift reaction is taken into consideration during reactions to improve the conversion rate. The fluidization behavior and reaction characteristic are analyzed for better understanding the methanation process.

1. Introduction

As is well-known, natural gas is a safe, efficient, environmentally friendly energy carrier with high calorific value. It attracts increasing attention due to rise of price, depletion of nature gas resource and greenhouse effect caused by released CO_2. On the other hand, modern society requires coal cleaning combustion and upgrade for sustainable development, especially in coal rich area [1]. It is an effective method to convert coal into synthetic natural gas (SNG) by gasification, gas cleaning, methanation and fuel upgrading, which will realize the coal cleaning utilization, transportation of energy and supplement for natural gas [2]. The production of SNG by CO methanation using syngas goes back to more than 100 years and has attracted sufficient attention for low emissions. The CO methanation has also been extended to the storage of electrical energy produced from renewable source based on the power to gas concept [3]. The excess electricity from plant is used to electrolyze steam and carbon dioxide into syngas, which is converted into SNG by methanation reactor and injected into the natural gas network. When high electricity consumption peaks appear, the stored SNG is used to produce the electricity [4]. Moreover, methanation is also used for reducing the CO mass fraction in the hydrogen-rich reformed gas for fuel cell applications [5] to avoid

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Nomenclature

c	Specific heat [J/(kg K)]
C_d	drag coefficient [–]
d	diameter [m]
g	gravitational acceleration [$m^2\ s^{-2}$]
h	heat transfer coefficient [w/(m K)]
J	diffusion flux [–]
k	thermal conductivity [W/(mk)]
p	pressure [Pa]
Pr	Prandtl number [–]
r	Reaction rate [mol/s kg_{cat}]
R	Source term [–]
Re	Reynolds number [–]
t	time [s]
T	temperature [K]
u	velocity [m/s]
Y	mass fraction gas species [–]

Greek letters

α	volume fraction [–]
β	drag coefficient [–]
μ	Shear viscosity [Pas]
λ	bulk viscosity [Pas]
ρ	density [kg/m^3]
θ	granular temperature [m^2/s^2]
κ	conductivity of granular temperature [S/m]
γ	dissipation rate from collision [–]
τ	stress tensor [Pa]

poisoning catalyst deactivation. Sufficient investigations are essential for understanding and extending the application of methanation. The main reactions are described as following:

CO methanation reaction:

$$CO + 3H_2 \overset{catalyst}{\longleftrightarrow} CH_4 + H_2O \quad \Delta H_{298K} = -206.28\ kJ/mol \tag{R1}$$

Water-gas shift reaction:

$$CO + H_2O \overset{catalyst}{\longleftrightarrow} CO_2 + H_2 \quad \Delta H_{298K} = -41.16\ kJ/mol \tag{R2}$$

CO_2 methanation reaction:

$$CO_2 + 4H_2 \overset{catalyst}{\longleftrightarrow} CH_4 + 2H_2O \quad \Delta H_{298K} = -165.0\ kJ/mol \tag{R3}$$

For methanation of CO and CO_2, it is a fast reaction and nickel is usually chosen as catalyst considering the selectivity, activity and price [6,7]. CO methanation is an exothermic reaction using carbon monoxide and hydrogen as educts for the catalytic production of methane and water [8]. A rapid temperature rise can been found in the reactor near the educts inlet caused by the methanation reaction. Mechanism is thought to proceed via molecular and subsequent dissociation of carbon monoxide [9]. Adsorbed carbon reacts with hydrogen stepwise to methane. Another confirmed mechanism is that the oxygenated is considered as an intermediate [10]. The elementary mechanism, kinetics and thermodynamics have been studied since in 1902 and some findings are summarized in [11–13]. The reaction is characterized by a significant volume contraction of the reacting gases. High pressure favors the production, but high temperature limits the methane formation in thermodynamic equilibrium. Numerous efforts have been made to investigate methanation process. Liu et al. [14] studied the performance of fluidized bed methanation by experiment and found that raising the H_2/CO ration of syngas increased proportionally the CO conversion and CH_4 selectivity. Gao et al. [15] investigated the influence of operating conditions and found that a high methane production was obtained at high pressure and low temperature. A comparative study conducted by Liu et al. [16] showed the technical advantages of fluidized bed over fixed bed reactor. Liu and Hinrichsen's [17] work showed that the hydrodynamic and chemical boundary conditions influence the process and the performance of reactor. It is necessary to investigate the detail of reactor by numerical simulation, which has become a powerful tool used in various energy engineering, for better understanding the details [18]. In addition, the modeling of methanation reactor is beneficial for the optimization, design, scale-up and obtaining high efficiency of process [19]. Kopyscinski et al. [20] did the first attempt to model the methanation fluidized bed reactor for investigating the flow behavior and reactions. The main objective in the development of methanation reactor is to achieve efficient removal of reaction heat to minimize catalyst deactivation [21] due to thermal stress and to avoid a limitation in the methane yield caused by approaching the chemical equilibrium. However, until now, a few studies on fluidization bed reactor have been well done in the laboratory scales, and we have not found the full loop reactor operating at a fast fluidization state which is beneficial for removal reaction heat and promoting production. Moreover, the methanation reaction has been well known for decades, unfortunately very few studies have focused on a complete and systematic investigation on the effect of operating conditions and syngas composition.

A good understanding of the methanation characteristics will provide useful guidance for the development of this technology. In this work, a numerical model considering gas-solid flow behavior, heat transfer and methanation kinetics is adopted to simulate the syngas methanation reaction in full loop fluidized bed reactor. Methanation performance is evaluated by the CO and H_2 conversion, CH_4 production, reaction rates under different reactant components, solid flux and fluidization gas velocity. This is an attempt and ready for industrial application of methanation and for better understanding of detail of methanation.

2. Mathematical models

In full loop fluidized bed reactor, the continuity equations for gas and solid phase are given as following [22]:

$$\frac{\partial(\alpha_g\rho_g)}{\partial t} + \nabla\cdot(\alpha_g\rho_g\mathbf{u}_g) = R_g \tag{1}$$

$$\frac{\partial(\alpha_s\rho_s)}{\partial t} + \nabla\cdot(\alpha_s\rho_s\mathbf{u}_s) = R_s \tag{2}$$

where ρ, α, and $\mathbf{u}$ are density, volume fraction and velocity, respectively. The R_g and R_s represent the source terms due to the reaction.

The momentum conservation equations for gas and solid phase are given as [23]:

$$\frac{\partial(\alpha_g\rho_g\mathbf{u}_g)}{\partial t} + \nabla\cdot(\alpha_g\rho_g\mathbf{u}_g\mathbf{u}_g) = -\alpha_g\nabla p + \nabla\cdot(\alpha_g\tau_g) + \alpha_g\rho_g\mathbf{g} + \beta(\mathbf{u}_s-\mathbf{u}_g) \tag{3}$$

$$\frac{\partial(\alpha_s\rho_s\mathbf{u}_s)}{\partial t} + \nabla\cdot(\alpha_s\rho_s\mathbf{u}_s\mathbf{u}_s) = -\alpha_s\nabla p-\nabla p_s + \nabla\cdot(\alpha_s\tau_s) + \alpha_s\rho_s\mathbf{g} + \beta(\mathbf{u}_g-\mathbf{u}_s) \tag{4}$$

β is the momentum transfer coefficient between gas phase and solid phase, the detail and further discussion can be found in Refs. [24]. In current study, Gidaspow model [25] is adopted for calculating the momentum transfer coefficient: