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Design, control and comparison of fixed-bed methanation reactor systems for the production of substitute natural gas

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ABSTRACT

The design and control of processes for the methanation of synthesis gas to produce substitute natural gas (SNG) using fixed-bed reactors is investigated. Three different strategies for controlling the reactor temperature rise are considered: recycle of a portion of the reactor effluent, introduction of additional water into the reactor feed, and non-adiabatic reactor operation with catalyst dilution. The results show that the process with a non-adiabatic reactor has the lowest cost and produces the greatest amount of high-pressure steam. However the efficacy of catalyst dilution for preventing reaction run-away has not been tested experimentally. Among the remaining options, partial recycle of reactor effluent is preferred because it can produce a greater amount of high-pressure steam than the process with additional water. Control studies indicate that all processes can be controlled and can tolerate production rate changes, however none can tolerate a large change in the feed composition due to inherent stoichiometric limitations.

1. Introduction

Production of synthetic (or substitute) natural gas (SNG) from coal or biomass *via* syngas has attracted interest for application in locations where a reliable local supply of natural gas in unavailable. Biomass is a renewable resource, and coal is more easily transported and stored than gas, ensuring a reliable gas supply in the event of temporary transportation disruptions. When SNG is produced from coal, carbon capture and storage (CCS) can capture a significant amount of the carbon content in the coal, reducing greenhouse gas emissions.

The final step in the production of SNG is the methanation reaction, in which synthesis gas (primarily carbon monoxide and hydrogen) is converted into methane with water produced as a byproduct. The reaction is highly exothermic, which presents several technical challenges: (1) In order to be economically competitive, the heat of reaction cannot be wasted but must be recovered in the production of high-pressure steam, which can be used to generate electricity. Therefore heat integration and recovery is a critical consideration. (2) The reaction equilibrium is favored by a lower temperature. Therefore, almost all process designs operate with several reactors in series with interstage cooling, thereby allowing reactors later in the reaction train to operate at lower temperature. (3) The adiabatic temperature rise in the first reactor far exceeds what can be tolerated by available catalysts, therefore some method must be employed to prevent the reactor temperature from exceeding this constraint. Several reviews of technologies for production of SNG from coal and biomass have been published [1–5].

The most widely discussed design for a methanation process is the TREMP (Topsoe Recycle Energy-efficient Methanation Process) sold by the Haldor Topsøe Company of Lyngby Denmark [6,7]. This process was also the basis for a case study of a coal gasification process performed by the US DOE National Energy Technical Laboratory (NETL) [8]. In this process, a fraction of the effluent from the first reactor is compressed and recycled back to the reactor inlet. The forward reaction is suppressed by diluting the fresh feed with the reactor effluent, which contains product species methane and water. The drawback of this approach is that an expensive gas compressor is required for the recycle loop.

A second alternative is to introduce excess low-pressure steam into the reactant feed. Because water is a product, this will shift the reaction equilibrium in the opposite direction and prevent the reactor from over-heating. In this case, a recycle compressor is not required, however the excess water must be removed at a later stage which may increase costs and reduce the amount of heat that can be recovered. This approach was the basis for the RMprocess [9] and the ICI/Koppers process [10].

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A third alternative is to incorporate cooling within the reactor itself. This can potentially eliminate the need for a recycle compressor or excess water, however it is challenging to incorporate adequate area for heat transfer given that the reaction takes place in the gas phase (and so the heat transfer coefficient is low) and it is potentially risky since the reactor may overheat if the cooling fails. This process was proposed by Linde [1].

Although the basic idea of these design alternatives has been known for some time, we are not aware of a report in the open literature in which the economics and controllability of these design alternatives are investigated. That is the purpose of this work. The remainder of this manuscript is organized as follows: In Section 2, general information about modeling is presented. Section 3 presents the design results for the three process alternatives. Section 4 presents results of the dynamics and control. Finally Section 5 presents conclusions.

2. Process model

2.1. Reactions and kinetics

Three reactions are assumed to occur in the methanation reactors:

Reaction

$$CH_4 + H_2O \Leftrightarrow 3H_2 + CO \tag{1}$$

Reaction

$$CO + H_2O \Leftrightarrow H_2 + CO_2 \tag{2}$$

Reaction

$$CH_4 + 2H_2O \Leftrightarrow 4H_2 + CO_2 \tag{3}$$

The reaction kinetics are taken from Xu and Froment [11]:

$$r_1 = \frac{k_1}{P_{H_2}^{2.5}} \frac{\left(P_{CH_4}P_{H_2O} - P_{H_2}^3 P_{CO}/K_1\right)}{(DEN)^2} \tag{1}$$

$$r_2 = \frac{k_2}{P_{H_2}} \frac{(P_{CO}P_{H_2O} - P_{H_2}P_{CO_2}/K_2)}{(DEN)^2} \tag{2}$$

$$r_3 = \frac{k_1}{P_{H_2}^{3.5}} \frac{\left(P_{CH_4}P_{H_2O}^2 - P_{H_2}^4 P_{CO_2}/K_3\right)}{(DEN)^2} \tag{3}$$

where

$$DEN = 1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + \frac{K_{H_2O}P_{H_2O}}{P_{H_2}} \tag{4}$$

$$K_1 = \frac{1}{10266.76\exp(-26830/T + 30.11)} \quad 1/kPa^2 \tag{5}$$

$$K_2 = \exp\left(\frac{4400}{T} - 4.063\right) \tag{6}$$

$$K_3 = \frac{K_1}{K_2} \quad 1/kPa^2 \tag{7}$$

A $Ni/MgAl_2O_4$ catalyst is used for the kinetics. For Ni-based catalysts, a temperature below about 200–300 °C will cause the formation of nickel carbonyl, and a high temperature above 550–650 °C may cause carbon deposition ("whisker carbon"). Both the phenomena will deactivate the catalyst [6]. In addition, the reaction kinetics indicate that the methanation reaction is more active when the reaction temperature is above 350 °C. Therefore, the reactor is specified to be operated in the range of 350–600 °C (662–1112 °F).

2.2. Other modeling considerations

The Peng–Robinson equation of state was used for all thermodynamic calculations. The pressure drop was estimated using the Ergun equation:

$$f_p = \frac{150}{Gr_p} + 1.75 \tag{8}$$

where

$$f_p = \frac{\Delta P}{L}\frac{D_p}{\rho V_s^2}\left(\frac{\varepsilon}{1-\varepsilon}\right) \tag{9}$$

$$Gr_p = \frac{D_p V_s \rho}{(1-\varepsilon)\mu} \tag{10}$$

The bed voidage ε is taken to be 0.6 for hollow cylinders, the particle density ρ is taken to be 1.014 g/cm^3, and the particle diameter D_p is taken to be 0.008 m.

In this study, Aspen Plus was used for steady state design and Aspen Dynamics was used for the process dynamics and control study. Fixed-bed reactors in this work were modeled with an RPlug block in Aspen Plus. The equations used in the determination of capital and operating costs are given in the Appendix. The payback period was assumed to be 3 years for the TAC calculation.

3. Process design results

For the three design concepts described previously, processes were designed using heuristic methods [12,13]. Rigorous optimization of the process designs was not attempted because in almost all cases the optimal values of the design variables lie on constraints (especially the reactor temperature constraint). The SNG product purity specification is ≥96 mol% CH_4 and the production rate is set to 8400 lb mol/h.

3.1. Process with recycle

The flowsheet for the process with recycle is shown in Fig. 1, and adiabatic reactors are used in the process. The feed passes through two feed-effluent heat exchangers before entering the first fixed bed reactor. The effluent from the first fixed bed reactor passes through a heat exchanger which generates high-pressure steam. A fraction of the effluent is then compressed and recycled to suppress the reaction in the first reactor and prevent overheating. The remaining effluent is fed to the second reactor, and the effluent from reactor 2 is passed through heat exchangers 4 and 5, with exchanger 5 generating additional high-pressure steam. The gas then flows through the third reactor and then through heat exchangers 2, 6, 7 and 8 with exchanger 7 generating low-pressure steam. The gas is then fed to a flash unit where water of reaction is removed, and then through heat exchangers 6 and 4 before entering the final fixed-bed reactor. Finally the effluent from the final reactor is passed through heat exchangers 1 and 9 before a final flash unit and molecular sieve are employed to remove remaining reactor water and carbon dioxide respectively. It is assumed 98% of the carbon dioxide in the product stream can be removed by the molecular sieve. Finally the gas is compressed for transmission to the pipeline.

The reactor size is determined so that 99% of the reaction equilibrium is achieved in each reactor. The diameter of each reactor is listed in Table 1, and the aspect ratio of the reactor is chosen to be 2 to reduce the pressure drop along the reactor based