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Systematic staging design applied to the fixed-bed reactor series for methanol and one-step methanol/dimethyl ether synthesis

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HIGHLIGHTS

- Systematic staging design is applied to methanol and methanol/DME synthesis.
- New configurations for the synthesis reactor network are proposed and assessed.
- Comparison with the industrial best practice is provided.
- Energy-process optimization is performed to improve the overall yield of the process.

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ABSTRACT

This work investigates possible design advances in the series of fixed-bed reactors for methanol and dimethyl ether synthesis. Specifically, the systematic staging design proposed by Hillestad [1] is applied to the water-cooled and gas-cooled series of reactors of Lurgi's technology. The procedure leads to new design and operating conditions with respect to the current best industrial practice, with relevant benefits in terms of process yield, energy saving, and net income. The overall mathematical model for the process simulation and optimization is reported in the work together with dedicated sensitivity analysis studies.

1. Introduction

Since the introduction of the high pressure methanol synthesis in the 1920s, several technologies have been introduced or are currently in development [2]; however the most important improvement is the introduction of the low pressure methanol synthesis in the 1960s, in fact several of the current technologies, like those available from Lurgi [3], Haldor Topsøe [4] and Davy Process Technologies [5], are based in such development. Nowadays, methanol is still produced from syngas (CO and H_2 mixture) obtained by means of steam reforming operations of natural gas [6], most of the aforementioned technologies employ a single water-cooled shell and tube boiler reactor (WaC) and therefore a great attention has been given to the study of such reactor by researchers. For instance, Shahrokhi and Baghmisheh [7] investigated the dynamic behavior and proposed a control strategy of the WaC portion of the reactor. Chen and co-workers [8] studied the WaC reactor and the related boiling system to optimize the yield in methanol synthesis. They obtained a methanol yield improvement estimated in about 7%. Similarly, our prior works investigated the steady-state optimal configuration of the WaC reactor [9], its dynamic behavior subject to possible syngas composition and inlet flow variations [10], the simultaneous control of the methanol production and hot-spot temperature position along the axial coordinate [11] and the monitoring strategy of the hot spot for methanol yield improvement [12]. On the other hand, another usual technology for the production of methanol consist of a couple of reactors: (1) a gas-cooled shell and tube reactor (GaC) and (2) the solely WaC reactor; the implementation of the GaC reactor implies a series of technical advantages in process intensification that will be discussed later. The WaC reactor is considered the key section of the overall system and, as indicated earlier, there is plenty of works on

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such reactor but the GaC portion is usually rejected. A typical WaC/GaC length ratio of 7/3 is normally used in industry; such ratio is near to the optimal design of the WaC reactor since the target is the optimization of methanol yield. Nonetheless, there are two aspects that should be accounted to improve the total revenue that does not generally imply any additional costs which are: (1) the optimization of the overall WaC/GaC reactor series: rather than optimizing only the sole WaC reactor, it is possible to exploit the integrated model of the WaC/GaC series to perform an overall design optimization to maximize the methanol yield; (2) the integration of energy production as medium pressure steam within the optimization procedure [13] according to the general energy policies also adopted in other closest fields [14]. The main objective of the current work is focused in the previous two elements; therefore, following the systematic staging design methodology by Hillestad [1] comprising the whole reactor system (i.e. both the WaC and GaC reactor) and considering the economic terms involved in both production yield and energy-process integration, a review of the optimal reactor configuration is presented for the production of methanol and also for the simultaneous production of methanol and dimethyl ether. Consequently, in Section 2 the methanol synthesis and the dimethyl ether processes are described followed by a description of the pseudo-homogeneous model in Section 3. In Section 4 the systematic staging design strategy is reviewed and finally in Section 5 the optimization strategy is described together with the numeric results and economic considerations.

2. Methanol and dimethyl ether synthesis process

As mentioned above, the methanol synthesis process is usually based on two fixed-bed tubular reactors [15], although several other configurations have been proposed [16]. According to the final production target, methanol synthesis can be coupled with the dimethyl ether synthesis which is usually obtained in a two-step process; in this, the first reactor system is employed for the synthesis of methanol which is followed by a second reactor system for the production of dimethyl ether from methanol. Coupling both systems in a one-step process allows to employ a single reactor system with a bifunctional catalyst for the simultaneous production of both methanol and dimethyl ether en a process called direct dimethyl ether synthesis; , this is of key-relevance especially when the syngas originates from renewable sources (e.g., biomass) as discussed elsewhere [17]. Following the process flow direction of Fig. 1, the syngas is fed to the shell side of the gas-cooled reactor (Stream 1), where it is pre-heated by the hot process stream flowing in the fixed-bed tube bundle, this is advantageous in terms of process intensification as the usually large inlet pre-heater is replaced by a smaller unit and reducing in the same way the consumption of process utilities. The pre-heated syngas is then fed to the catalytic bed for methanol conversion and specifically to the tube side of the WaC reactor (Stream 2). Please note that different technologies may have the catalyst in the shell side (e.g., Davy Process technology), but they are not considered for the sake of simplicity and conciseness. The syngas fed to the fixed-bed of the catalytic tube bundle is partially converted into methanol along the first reactor. The methanol synthesis is particularly exothermic and the shell side is filled of boiling water (Stream 8) to preserve the desired operating conditions of the WaC reactor. The intrinsic intensified nature of modern methanol process allows to combine the methanol conversion to the medium pressure steam generation (Stream 9). As discussed in previous works [9], the phenomena occurring in the first portion of the reactor (first 1–2 m along the reactor) is kinetically limited, while in the later part the chemical equilibrium plays a major role limiting the reaction. In this first part a point with maximum temperature is developed called temperature hot-spot. The importance of the hot-spot is critical in order to improve no only the process efficiency but also to preserve the catalyst activity and process safety [18] and some special techniques are required to monitor it [11]. Continuing with the process flow, the outflow of the WaC reactor is fed to the tube side of the GaC reactor (Stream 3) where the methanol synthesis continues. GaC temperature profile is controlled exchanging with the fresh inlet syngas to be pre-heated in countercurrent in the shell side (Stream 1). The GaC reactor outflow (Stream 4) is then sent to the downstream process where the methanol is recovered (Stream 7) and the unreacted syngas is recycled back (Stream 5) except a purge system to remove by-products, and accumulations of incondensable gas (Stream 6).

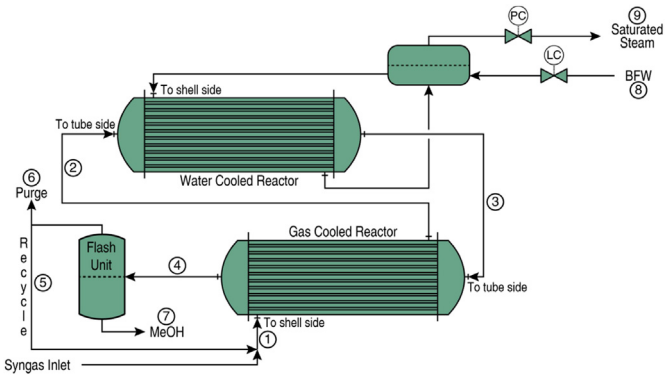

Fig. 1. Methanol synthesis loop with water/gas-cooled (WaC/GaC) reactors.

2.1. Methanol synthesis

Methanol (MeOH) is produced from syngas from three main reactions:

$$CO + 2H_2 \leftrightarrow CH_3OH \quad \Delta H_{298\ K} = -90.55 kJ/mol \tag{1}$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H_{298\ K} = 41.12 kJ/mol \tag{2}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H_{298\ K} = -49.43 kJ/mol \tag{3}$$

These reactions are not independent and any one of them can be expressed as a linear combination of the others as indicated elsewhere. Rather than using the chemical species, as in the typical mathematical modeling of chemical reactors, the chemical elements C, H, and O must be considered to reduce the size of the resulting numerical system [10]. Exothermic reactions (1) and (3) are favored at low temperature despite the reaction rate; moreover, it is necessary to operate at high pressure (for instance 80 bar) to improve the equilibrium conversion exploiting the reduction in the number of moles. Typically, the synthesis of methanol is conducted over commercial $CuO/ZnO/Al_2O_3$ which has an estimated life of 3–4 years. Since catalyst deactivation occurs at temperatures above the 550 K, the operating range of temperature is 484 K–540 K. Typical feed molar composition is: $CO = 0.046$; $CO_2 = 0.094$; $H_2 = 0.659$; $H_2O = 0.0004$; $CH_3OH = 0.005$; $N_2 = 0.093$; $CH_4 = 0.1026$ [15].

2.2. Direct dimethyl ether synthesis

Dimethyl ether (DME) is a promising efficient alternative fuel for diesel engines as it possesses a high cetane number, produces a smoke-free combustion due to its high oxygen content and has a