



Preserving Safety and Improving Yield Performances in Methanol Processes

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The industrial best practice for methanol synthesis is the use of a fixed-bed tubular reactor. The exothermic nature of methanol synthesis, the possibility to activate the methanation reaction (intensely exothermic) and the discrete nature of temperature acquisition throughout the reactor claim for novel technological solutions for process control and optimization. Specifically, the aim of this work is to monitor the hot-spot temperature and to manipulate it to improve the yield of methanol.

1. Introduction

Even though many improvements have been made since its first industrial technology, in 1923, and a series of new production technologies are being developed (Lange, 2001; Olah et al., 2009; Basri et al., 2009; Gomez-Castro et al., 2010; Mayra and Leiviska, 2009; Sie et al., 2009), methanol is still largely produced, with very low conversions, from natural gas, specially via synthesis gas (or syngas, CO and H₂ mixture). The latter is produced by means of steam reforming operations. Moreover, the methanol process is usually characterized by high potentiality, relatively high pressure, and some side reactions that must be controlled to prevent any operational risk.

In this context, it is difficult to maintain the performances of methanol conversion, while the safety of the operations must be fulfilled; this further contributes to the yield in methanol less than 7 %. For example, the well-established directives are to operate the methanol synthesis reactor in the range 500-540 K (Lommerts et al., 2000; Graaf et al., 1986; Graaf et al., 1988). Lower temperatures correspond to poor catalyst activity, whereas higher temperatures activate the so-called methanation reaction:



Even if the methanation reaction, which is provided by the copper coating, takes place at more than 570 K, the safety threshold of operation is estimated around 540 K. It accounts for the fact that the overall reaction process from syngas to methanol is exothermic and, therefore, the reaction environment moves towards higher temperatures. In addition, being the system kinetically controlled for the first part of the reactor and thermodynamically controlled for the remaining part, the temperature profile of the methanol reactor is characterized by a maximum so called hot-spot (Manenti et al., 2011a; Manenti et al., 2011b). Nevertheless, the temperature is measured by a multi-thermocouple,

which is intrinsically discrete (i.e. the temperature is acquired every meter), and the hot-spot cannot be measured being it not corresponding with the thermocouple position.

This work illustrates a method for the process safety improvement by maintaining the yield performances of methanol production and vice versa.

The application of a numerically performing detailed dynamic model for the methanol synthesis fixed bed reactor, allows to predict the hot-spot temperature and its position along the coil, thus, to control the process as well as to improve the performances when the operating conditions are favourable.

2. Identification and measurement of hot-spot temperature

The hot-spot is the highest value of temperature inside the tube bundle of the methanol synthesis reactor. Moreover, it is the boundary between the kinetic and thermodynamic limitations along the axial coordinate. It is usually positioned in the range of 0.5 m and 2.5 m from the reactor inlet, according to the operating conditions, the catalyst efficiency and the current plant production.

As qualitatively and quantitatively showed elsewhere (Manenti et al., 2011a), the hot-spot can migrate quickly along the axial coordinate, in accordance with the system dynamics. Also, gradual migrations are expected with the catalysts deactivation, but this point is less relevant for the scope of the paper, since this behaviour can be brought back to a more general hot-spot migration (paragraph 4).

Since the multi-thermocouple placed within the tube bundle is discrete, however dense, the hot spot can result far from the two adjacent measures of temperature and, in the worst case, it can be in the middle of the “blind area” (no-measure area) as shown in Figure 1. Thus, certain violations of the safety operating conditions can remain undetected.

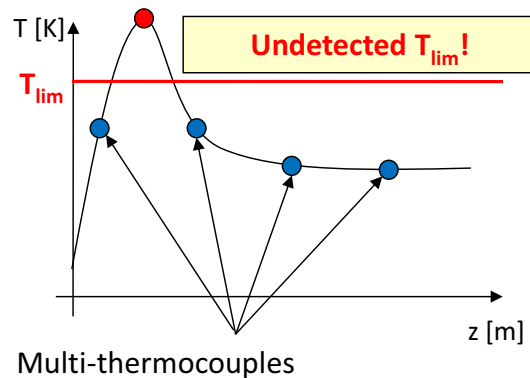


Figure 1: Example of undetected hot spot

In fact, it is necessary to assure in the process that the reactor never enters the pressure-temperature region where the methanation reaction takes place. To provide the safe condition and also to keep the potentialities of the methanol plant, it would be useful to characterize the dynamic behaviour of methanol synthesis reactor so as to monitor on-line and with high accuracy the hot-spot temperature and its position.

Accordingly, the calculated temperature profile must be overlapped to the measures acquired by the multi-thermocouple. This can be obtained by using a dynamic model of the reactor.

3. Hot-spot monitoring

3.1 Existing technologies

There are several technologies for methanol production. Lurgi and Aldor-Topsoe technologies are characterized by the tube side packed with catalyst. Davy Process Technology patents are characterized by the shell side packed by catalyst. There are also other technologies, such as the Casale Group plates-reactor or the Air Products slurry bubble reactor. We selected the former technology, with the tube side packed by catalyst, since it is the most diffused in the recent plants.

3.2 Mathematical model

Methanol synthesis reactors are particularly difficult to model as they involve at least four significant dimensions through which the system might evolve: the axial direction of the reactor; the radial direction of the reactor tubes; the catalytic particle radius; and the time. However, when the research focuses on the implementation of hot-spot monitoring tools, the mathematical model is satisfactory if its axial behaviour and the time evolution are well-simulated. Nevertheless, as already highlighted elsewhere (Manenti et al., 2011a), it is important to consider that, although the methanol yield is particularly low, there is a significant deviation in the numerical results if the molar decrease across the reactor is neglected. Therefore, the simplified (no side reactions are considered in this preliminary work) reaction mechanism is:



Two independent balances for methanol and water by means of mass fractions can characterize the process:

– Methanol:

$$\varepsilon_b \rho_{gas} \frac{\partial \omega_{\text{CH}_3\text{OH}}}{\partial t} = -\frac{M}{A_{int}} \frac{\partial \omega_{\text{CH}_3\text{OH}}}{\partial z} + D \rho_g \frac{\partial^2 \omega_{\text{CH}_3\text{OH}}}{\partial z^2} + MW_{\text{CH}_3\text{OH}} r_{\text{CH}_3\text{OH}} \quad (5)$$

– Water:

$$\varepsilon_b \rho_{gas} \frac{\partial \omega_{\text{H}_2\text{O}}}{\partial t} = -\frac{M}{A_{int}} \frac{\partial \omega_{\text{H}_2\text{O}}}{\partial z} + D \rho_g \frac{\partial^2 \omega_{\text{H}_2\text{O}}}{\partial z^2} + MW_{\text{H}_2\text{O}} r_{\text{H}_2\text{O}} \quad (6)$$

The energy balance reads as follows:

$$\left[\varepsilon_b \rho_{gas} c_{p_{mix}} + (1 - \varepsilon_b) \rho_{cat} c_{p_{cat}} \right] \frac{\partial T_n}{\partial t} = k \frac{T_{n+1} - 2T_n + T_{n-1}}{(\Delta z)^2} + \frac{M}{A_{int}} c_{p_{mix}} \frac{T_n - T_{n-1}}{\Delta z} + \pi \frac{U}{A_{int}} (T_{shell} - T_n) + \left[r_{\text{CH}_3\text{OH}} (-\Delta H_{r_1}) + r_{\text{H}_2\text{O}} (-\Delta H_{r_2}) \right] \quad (7)$$

Where:

$$r_{\text{CH}_3\text{OH}} = \rho_{cat} (1 - \varepsilon_b) \eta_1 (r_{\text{CO} \rightarrow \text{CH}_3\text{OH}} + r_{\text{WGS}}) \quad (8)$$

$$r_{\text{H}_2\text{O}} = \rho_{cat} (1 - \varepsilon_b) \eta_2 (r_{\text{CO}_2 \rightarrow \text{CH}_3\text{OH}} + r_{\text{WGS}}) \quad (9)$$

For more details on the methanol synthesis model and the parameters adopted for the simulation, the reader can refer to (Manenti et al., 2011b; Manenti et al., 2011a). The model is efficiently solved using

several numerical tools and the algorithms implemented in the BzzMath library (Buzzi-Ferraris, 2011; Buzzi-Ferraris and Manenti, 2010b; Buzzi-Ferraris and Manenti, 2010c; Buzzi-Ferraris and Manenti, 2010a; Buzzi-Ferraris and Manenti, 2012).

4. Results and discussion

As mentioned above, it is not possible to establish a priori the position and the extent of the hot spot temperature accurately. Hence, beyond the uncertainty due to the measurement accuracy of the multi-thermocouple, an additional level of uncertainty is added (see Figure 2): in fact, the unknown position of temperature hot-spot reduces our perception on the current operating conditions of the methanol synthesis reactor. It is worth noting that the possibility of insertion a denser multi-thermocouple for several technological and economical cannot be taken into consideration.

This unavoidably means that it should be necessary to operate with large margins below the operational limits to preserve the process safety (in other words, to prevent methanation reaction). Conversely, an accurate and reliable prediction of the hotspot value and position can significantly decrease the degree of uncertainty. As a consequence, the operating conditions of the methanol synthesis reactor can be changed so as to better exploit the process capacities, without entering any unsafe operational region. For example, looking at the numerical results illustrated in Figure 3, some considerations can be done.

Figure 3 is obtained by efficiently solving the resulting partial differential equations (PDE) system described in the paragraph 3. It shows the temporal and axial evolution of the methanol synthesis reactor subject to a step-disturbance on the inflow. It is important to highlight that, although the multi-thermocouple has a discretization of 0.5 m, the hotspot migration is undetected. In fact, the temperature measurement at 1 m from the inlet is the highest value before the disturbance and after as well. The problem is that the hot-spot position falls in the middle of the blind (not-measured) areas for both the situations and the system seems not to change even though a relevant disturbance is affecting it. Conversely, combining the multi-thermocouple measurement with the detailed PDE model, it is not only possible to quantify with high accuracy the hot-spot value, but also to monitor its migration and, therefore, to improve our consciousness on the current operating conditions. Based on this information, it is possible to higher the yield of the methanol in the synthesis reactor, without overcoming any process threshold for safety purposes.

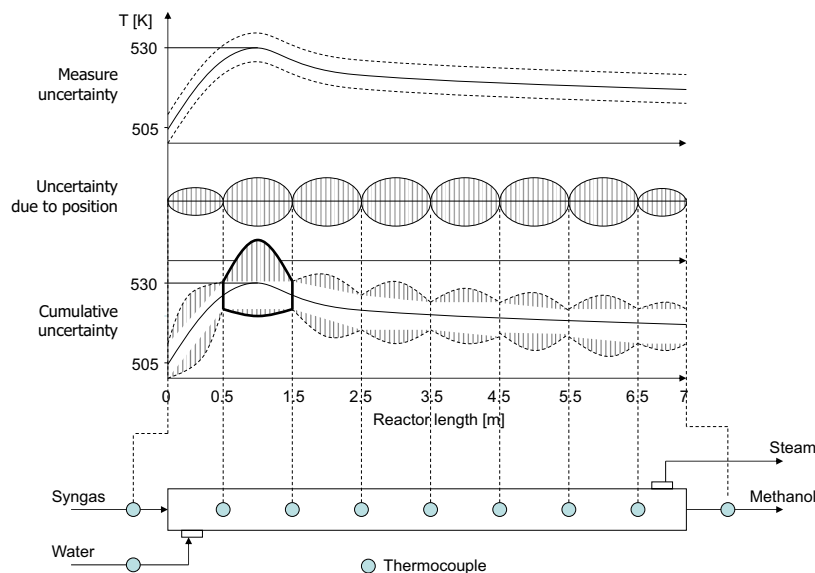


Figure 2: Qualitative combination of effects: the measure uncertainty is related to the measurement accuracy and undetected hot-spot position.

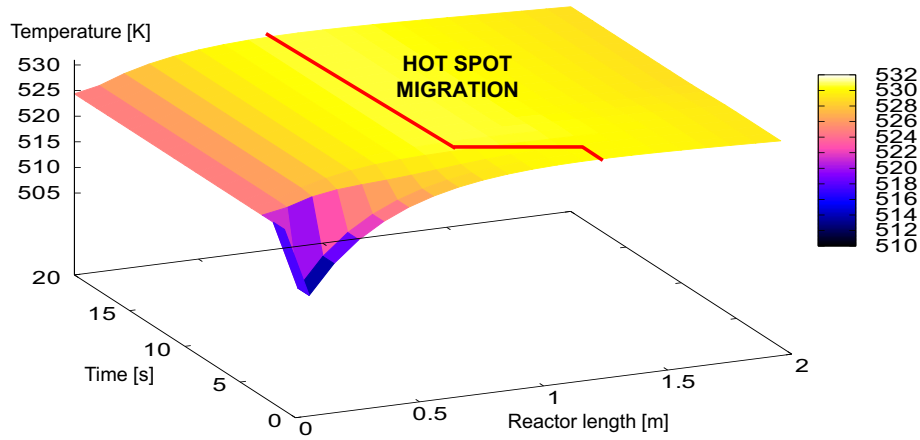


Figure 3: Temperature hot-spot migration due to a step-disturbance on the inflow. The first portion only (2 m) of the reactor length is plotted for the sake of clarity.

5. Conclusions

The hot-spot temperature in the fixed-bed tubular reactor for methanol synthesis is a key-information. The discrete nature of the multi-thermocouples placed along the axial coordinate of the reactor could provide an accurate measurement of neither the hot-spot value nor the hot-spot position. It is therefore useful to combine the measurements with a reasonably detailed model to detect and monitor the migrations of the hot-spot.

Nomenclature

A_{int}	Internal area of the tube	$[m^2]$	r_{WGS}	Reaction rate Water Gas Shift	$[\frac{mol}{s \cdot kg}]$
a	Specific surface area of the catalytic pellet	$[\frac{m^2}{m^3}]$	$r_{CO \rightarrow CH_3OH}$	Reaction rate of methanol from carbon monoxide	$[\frac{mol}{s \cdot kg}]$
$c_{p_{mix}}$	Specific heat of gas at constant pressure	$[\frac{J}{kg \cdot K}]$	$r_{CO_2 \rightarrow CH_3OH}$	Reaction rate of methanol from carbon dioxide	$[\frac{mol}{s \cdot kg}]$
M	Mass flowrate	$[\frac{kg}{s \cdot tube}]$	ϵ_b	Void fraction of catalytic bed	[-]
MW	Molar weight of Component	$[\frac{kg}{kmol}]$	ΔH_j^{react}	Enthalpy of j-th reaction	$[\frac{J}{mol}]$
T	Temperature of the gas phase	[K]	η_j	Efficiency of reaction j-th	[-]
T_{shell}	Temperature of the shell-side of reactor	[K]	ρ_{cat}	Density of the catalytic pellet	$[\frac{kg}{m^3}]$
U	Overall heat transfer coefficient	$[\frac{W}{m^2 \cdot K}]$	ρ_{gas}	Density of the gas phase	$[\frac{kg}{m^3}]$
Z	Axial coordinate	[m]	ω_i	Mass fraction of the component i in the gas phase	[-]

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