The Prediction of Cold Spots in Reverse Water Gas Shift Reactors

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Highlights

- A sensitivity-based methodology for reverse water gas shift reactors is presented.
- Different outcomes for reversible and irreversible reactions are elucidated.
- Presentation of a single-point procedure propedeutic for a complete stability diagram.

1. Introduction

To date, most investigations on the loss of control in a chemical reactor have focused on evaluating exothermic reactions because of the safety-oriented target. However, deviations from the desired conditions or failure of auxiliary systems can also lead to detrimental effects in terms of process performances in the case of endothermic reactions. Among the others, the reverse water gas shift reaction (rWGS) is gaining particular interest because of its relevance in CO_2 utilisation and within the value chain of methanol production. Currently, several research activities are mainly devoted to catalyst optimisation, with lower effort on the optimisation strategies of reactor design. From the perspective of increasing the sustainability of industrial processes and activities, implementing optimisation and design strategies are also paramount. A possible theory that can be involved in the sensitivity analysis [1]. The primary outcomes obtainable through this theory are reactors' stability and performance diagrams, suitable for identifying optimised and safe conditions. Under these perspectives, the present work aims to elucidate a helpful methodology to involve the sensitivity analysis for endothermic reactions. The methodology will be applied to a reaction unit carrying out a rWGS reaction to elucidate the proposed concepts, based on the operative conditions currently indicated in the literature as suitable for this process.

2. Methods

A multi-tubular fixed-bed catalytic reactor was assumed in this work. The kinetic data of the rWGS reaction performed over a commercial Ni-Al_2O_3 catalyst was taken from the literature [2]. Thermodynamic properties, transport coefficients, and the required correlations were obtained from dedicated manuals [3] [4]. The system has been modelled considering an inlet temperature equal to 930°C, an operating pressure equal to 1bar, a single tube diameter equal to 1inch and length equal to 6m, an inlet molar fraction of CO_2 and H_2 respectively equal to 0.4 and 0.6, and an inlet molar flow rate per single tube equal to 0.1kmol/h. Each reactor tube has been modelled considering only axial gradients. The catalyst's efficiency factor has been involved in considering radial gradients inside the pellets. A stability diagram reporting on the y-axis an index of reactivity (i.e., the Damköhler number Da) and on the x-axis the heat of reaction index (i.e., the dimensionless heat of reaction B) was obtained. The transition boundaries between different regimes are reported in the stability diagrams. In the operation diagram, it will be possible to graphically understand the trend of yield and selectivity obtained in correspondence with each transition border. To determine the transition between regimes, the governing relations formed by mass, heat balance and sensitivity equations were solved iteratively. For clarity, in Eq. 1 the expression of the nomalized sensitivity is reported, being Θ the dimensionless temperature of the reacting fluid.

$$S(\Theta; B) = \frac{B}{\Theta}\frac{\partial \Theta}{\partial B} \quad (1)$$

3. Results and discussion

Three main operation regimes can be defined in endothermic processes: the pseudo-adiabatic operation (PAO), the first (CSO_1) and the second cold spot operation (CSO_2). In the PAO region, no minimum temperature profile can be observed in the reactor. In the CSO_1 region, a minimum in the temperature profile can be found inside the reactor, but the yield has yet to reach its maximum. Meanwhile, in the CSO_2 region, both a minimum and a maximum can be recorded in the temperature and yield profiles. For brevity, the value of B, Da, yield, and selectivity of CO at each transition boundary between working regimes will be reported together The stability and operation diagrams can be determined by applying the proposed methodology for a series of values of B, determining the related yield and selectivity at each transition boundary.

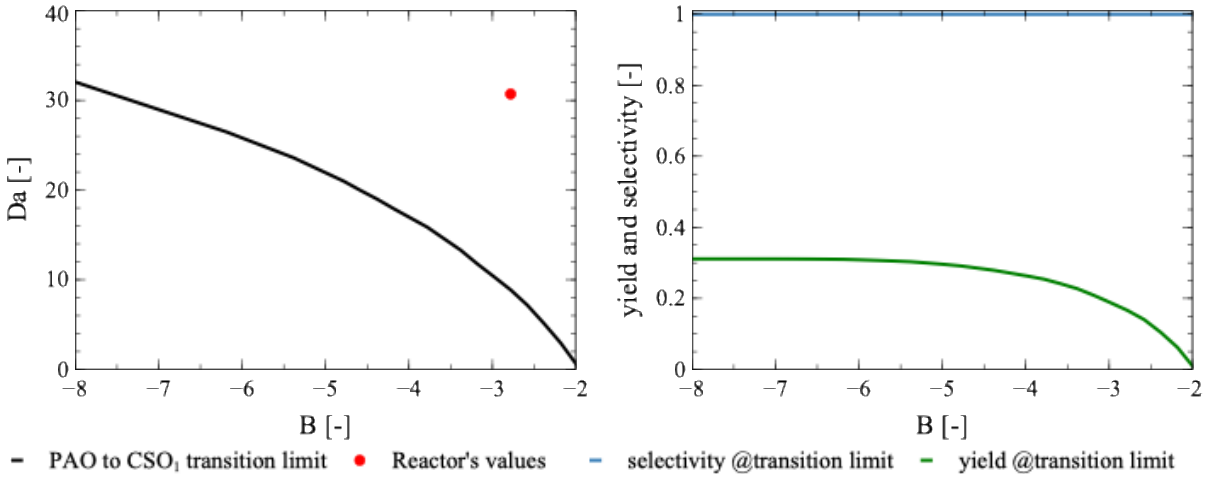

Figure 1. Stability and operation diagrams are on the left and right sides of the figure, respectively.

Something remarkable is that in an equilibrium reaction like the rWGS, the CSO_2 region is practically impossible. Indeed, the system will asymptotically tend to the equilibrium conversion and yield values, reachable only for infinite residence time value. Regarding selectivity, it assumes a value practically equal to a unit since the temperature inside the reactor is always over the limit at which a side reaction responsible for coke formation is present. Eventually, the obtained results agree with what is reported in the current literature, always avoiding catalyst deactivation and sintering. At operating point, the selectivity, yield and conversion are equal to 1.000, 0.423 and 42.3%, respectively.

4. Conclusions

Endothermic processes of industrial interest can be optimised or designed using a sensitivity approach, a methodology traditionally developed for exothermic reactions. As elucidated in the present work, an iterative solving procedure and a complete stability and operation diagram can be produced. For irreversible endothermic reactions, three operating regimes could be established (PAO, CSO_1 and CSO_2), whereas for reversible responses, only two areas of interest could be practically reached (PAO and CSO_1).

References

[1] A. Varma, M. Morbidelli, and H. Wu, *Parametric Sensitivity in Chemical Systems*, 1st ed. Cambridge University Press, 1999.

[2] A. Wolf, A. Jess, and C. Kern, "Syngas Production via Reverse Water-Gas Shift Reaction over a Ni-Al2O3 Catalyst: Catalyst Stability, Reaction Kinetics, and Modeling," *Chem Eng Technol*, vol. 39, no. 6, pp. 1040–1048, Jun. 2016, doi: 10.1002/ceat.201500548.

[3] D. W. Green and M. Z. Southard, *Perry's Chemical Engineers' Handbook*, 9th ed. McGraw-Hill Education, 2019.

[4] G. F. Froment, K. B. Bischoff, and J. De Wilde, *Chemical Reactor Analysis and Design*, 3rd ed. John Wiley & Sons, Inc., 2011.

Keywords

Sensitivity analysis; endothermic processes; design; optimisation.