ANALYSIS OF OPERATIONAL VARIABLES ON THE PERFORMANCE OF A FIXED-BED FORMALDEHYDE SILVER-CATALYZED REACTOR USING A HYBRID SIMULATOR BASED ON ARTIFICIAL NEURAL NETWORKS

PAPES FILHO AC\textsuperscript{1} and MACIEL FILHO R\textsuperscript{1}

\textsuperscript{1}Universidade Estadual de Campinas - UNICAMP, Faculdade de Engenharia Química
E-mail para contato: acpapes@terra.com.br

ABSTRACT – A hybrid simulator for formaldehyde silver-catalyzed reactor was developed in this work, using Artificial Neural Network (ANN) trained with industrial and experimental data. The work reports the simulator application based on actual industrial data for analyzing the influence of operational variables (bed temperature, feed molar ratio methanol-to-oxygen, feed molar ratio water-to-methanol and residence time) on the reactor performance (conversion and selectivity). The trends obtained were compared to experimental data, validating the simulator and providing an important tool for the formaldehyde silver process operation. It is worthwhile mentioning that models and simulators available in literature are not applicable to actual industrial conditions.

1. INTRODUCTION

Formaldehyde is a key chemical intermediate for a variety of engineering products used by construction, metallurgy and automotive sectors. The worldwide production was expected to exceed 52 million metric tonnes per year of formalin 37% solution basis in 2017, having China as the main producing country. The Formox and the Silver processes, the main commercially available routes.

The Silver-catalyzed process is the classical route since the beginning of the twentieth century, where methanol-rich methanol-air-stream mixture is passed through a simple silver catalyst bed at 600 – 700 °C, at near atmospheric pressure. Formalin, an aqueous solution of formaldehyde, is obtained and commercialized as final product (Millar and Collins, 2017). Two parallel reactions account for the formaldehyde formation from methanol on silver catalyst: methanol oxidation (Equation 1) and methanol dehydrogenation (Equation 2). The formaldehyde generated reacts with oxygen on the silver catalyst, forming carbon dioxide (Equation 3) and it may also decompose on gas phase to carbon monoxide at high temperatures (Equation 4). Reactions 3 and 4 reduce the selectivity towards the desired product.

\begin{align}
\text{CH}_3\text{OH} + \frac{1}{2} \text{O}_2 & \rightarrow \text{HCHO} + \text{H}_2\text{O} \quad \Delta H = -159 \text{ kJ/mol} \\
\text{CH}_3\text{OH} & \not\Rightarrow \text{HCHO} + \text{H}_2 \quad \Delta H = + 84 \text{ kJ/mol} \\
\text{H}_2\text{CO} + \text{O}_2 & \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \Delta H = -514 \text{ kJ/mol} \\
\text{H}_2\text{CO} & \rightarrow \text{CO} + \text{H}_2 \quad \Delta H = + 7 \text{ kJ/mol}
\end{align}
Despite much work has been done worldwide to study the Silver process, there is no full mechanistic and kinetics understanding of methanol oxidation on silver surfaces under industrial conditions. Papes Filho and Maciel Filho (2010) developed a kinetic model for the methanol oxidation to formaldehyde using an Artificial Neural Network (ANN), with improved performance over the deterministic models available in literature (Andreasen et al., 2005).

2. SIMULATION METHOD FOR FORMALDEHYDE REACTOR

In this work, a hybrid reactor simulator was constructed, containing a deterministic model for the fixed-bed reactor, based on differential mass balance equation derived from the application of pseudo-homogeneous, bidimensional, plug-flow model for tubular reactor at steady-state operation. The outputs from the simulator are methanol conversion, selectivity towards formaldehyde, carbon monoxide and carbon dioxide. Formaldehyde yield, methanol specific consumption (tonnes of MeOH consumed per tonne of formalin 37% produced) and the outlet stream composition may also be provided by the simulator. The results were compared with experimental work reported on literature, as well as actual industrial data. The rate of each reaction (R-HCHO, R-CO$_2$ and R-CO) used by the reactor simulator presented here was calculated by a neural network with three layers, whose training is described by Papes Filho and Maciel Filho (2010). The three mass balance differential equations (for formaldehyde, carbon dioxide and carbon monoxide) were solved simultaneously, using the Crank-Nicholson numeric algorithm. Boundary conditions for the model solution procedure are: radial symmetry, homogeneous profile at reactor inlet and no mass transfer through the reactor walls. The catalyst bed operates isothermally.

3. RESULTS AND DISCUSSION

The ANN was trained using industrial process data, according to the procedure described by Papes Filho and Maciel Filho (2010). Results are shown on Figure 1, indicating the simulated conversions and selectivity against actual measured data. The correlation factors and analysis of variance indicated good correlation, validating the ANN training. In this paper, the simulator was tested with different conditions near the industrial set-point, in order to illustrate the influence of bed temperature, feed molar ratio methanol-oxygen, feed molar ratio water-methanol and residence time on the conversion and selectivity. Results were validated by comparing the trends to lab experimental work reported on literature (Papes Filho and Maciel Filho, 2010).

3.1. Reference condition

Base conditions for the simulations presented here are: bed temperature of 630 °C, pressure of 1.2 atm, air flowrate at 6060 kg/h, methanol flowrate at 3681 kg/h, water flowrate at 364 kg/h, reactor diameter of 1.5 m, bed length of 20 mm and catalyst size of 0.6 mm. At the conditions above, the molar ratio methanol to oxygen is 2.6 and the molar ratio water to methanol is 0.18. The simulated methanol conversion is 94.0%, with a formaldehyde selectivity of 86.8% and carbon dioxide selectivity of 13.2%. Formaldehyde yield is 81.6% and carbon dioxide yield is 12.4 %. Carbon monoxide selectivity and yield are very low. Exit composition contains 39.2% nitrogen, 11.4% hydrogen, 3.4% carbon dioxide and 0.01% carbon monoxide, besides formaldehyde and water. The simulator was run for a series of operational conditions, varying one parameter at a time in order to generate the profiles for conversion and selectivity over the studied variables range.
3.2. Influence of reactor operational parameters

Bed temperature: Normal operating temperatures seen in industrial processes are in the range of 600 – 700 °C, depending on the particular conditions of the plants. In the studied case, simulated methanol conversion increases monotonically with increasing temperature, approaching 100% when temperature approaches 700 °C. Conversions close to 90% are obtained at 600 °C and close to 95% at 650 °C. The maximum formaldehyde selectivity (86.9 %) is found on the range 630 – 660 °C, which is recommended as the optimum range for reactor operation. These results from the simulations have good agreement with industrial and experimental work from literature, as could be observed on Figure 2.

Methanol-oxygen molar ratio: The simulator was run on the molar ratio range of 2.0 to 3.4, keeping the other variables at the industrial set-point conditions presented above. At molar ratio of 2.26, the simulated conversion is 97.4% and the formaldehyde selectivity is 82.0%, while at molar ratio of 3.05, the conversion is 83.7% and the selectivity is 86.9%. Small changes on simulated selectivity were seen above molar ratio of 3.0. These trends are explained by the reaction mechanism, where the higher the oxygen availability, the higher the rate of formaldehyde combustion. Based on the simulations, if the formaldehyde plant is equipped with methanol distillation tower, the molar ratio methanol-oxygen closer to 3.0 should be pursued.

Water-methanol molar ratio: Simulations here were performed on the molar ratio range of 0.07 to 0.44, maintaining the other variables at their set-points stated above. At molar ratio of 0.15, the simulated conversion is 94.2% and the formaldehyde selectivity is 86.6%, while at molar ratio of 0.4, the conversion is 92.2% and the selectivity is 88.8%.

There is a lack of quantitative information on literature concerning the influence of water on the formaldehyde reaction at industrial conditions. Here resides one significant contribution of this work, indicating details of this relationship. Simulations show a clear indication that the inclusion of water to the reactor feed increases the selectivity towards the desired product, consistent to industrial and literature reports (Sukunya and Kittisupakorn, 2014). Simulations also show that methanol conversion decreases while increasing molar ratio. Based on the simulations, if the formaldehyde plant is equipped with methanol distillation tower, higher molar ratio water-methanol should be pursued.
Residence time: All studies agree that longer residence time increases the methanol conversion, but also the carbon dioxide and carbon monoxide selectivity, consequently decreasing the formaldehyde selectivity (Qian et al., 2003; Waterhouse et al., 2004). In the base simulation performed in this work, the residence time was 6.2 ms. Simulated trends are in accordance with experimental data from Qian et al. (2003). Using residence time of 5 ms, methanol conversion was 93.8% and formaldehyde selectivity was 88.2%. Using residence time of 9 ms, methanol conversion was 98.2% and formaldehyde selectivity was 83.5%. Based on the simulations, if the formaldehyde plant is equipped with methanol distillation tower, lowest residence time should be pursued.

4. CONCLUSION

A hybrid simulator for formaldehyde silver-catalyzed reactor was developed in this work and used to study the influence of operational parameters on reactor performance, based on actual industrial data, showing good results in conditions not covered by simulators reported in literature.

5. REFERENCES