

MODELLING AND ANALYSIS OF THE LURGI-TYPE METHANOL-TO-PROPYLENE REACTOR

Xun Huang, Wen-De Xiao*

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University,
Shanghai 200240, China

Abstract

A multi-stage fixed-bed reactor model was developed for the design and optimization of methanol to propylene (MTP) process based on two-phase heterogeneous reactor model and mass balance of the recycled olefins. Simulation shows that an overall propylene selectivity of 61.89% with a space velocity of $0.71 \text{ g}_{\text{MeOH}}/\text{g}_{\text{cat}}/\text{hr}$ can be obtained under typical reaction conditions for a 6-stage reactor, which agrees fairly with the commercial results of a 500 kT/y unit with an anticipation of 65% propylene yield. It was revealed that prolongation of the reaction residence time was the main cause for the low propylene selectivity.

Introduction

The fixed-bed Methanol to Propylene (MTP) reactor technology was developed by Lurgi Company and has been industrialized in China in 2011 with an annual capacity of about 500kT/y propylene. However, the propylene selectivity turned out to be less than 60%, failed to meet the anticipated requirement of 65%, and the total selectivity including ethylene and propylene is much lower than fluidized-bed technology (>80%).

The present work theoretically studied the performances of the MTP reactor by means of an adiabatic heterogeneous model (Guo *et al.*, 2012) accounting for interfacial and intra-particle gradients as well as the mass balance of recycle olefins. The cause to low propylene selectivity was analyzed through case study and measures for improvement was proposed.

Model description

With the recycle of unwanted olefins, the MTP process is essentially a co-reaction of methanol and olefins, as shown in Figure 1. Our previous work (Huang *et al.*, 2016a; Huang *et al.*, 2016b) has established a kinetic model for this process based on the methylation-cracking mechanism (We *et al.*, 2011), which shows excellent agreement with the experimental data.

The MTP reactor is illustrated in Figure 1. Each of the packed stage can be described by a conventional one-dimensional adiabatic heterogeneous model and the mixture process between stages can be calculated via heat and mass conservation equations. The space time and the inlet methanol fraction of each stage were determined by the specific methanol conversion and temperature rise. The mass balance of recycle olefins is achieved in an iteration loop.

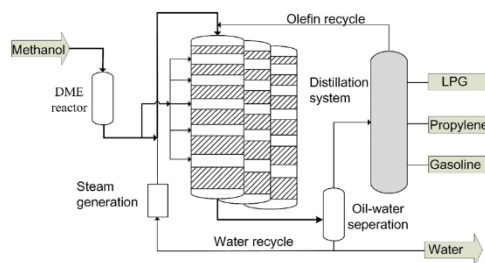


Figure 1. Flow chart of MTP process

The above procedure was coded in Matlab program and the nonlinear system of ordinary differential equations including bulk and solid phase of each stage was solved

* To whom all the correspondence should be addressed

efficiently by Comsol Multiphysics through finite element method.

Results and Discussion

Table 1 listed the most concerned design parameters of each stage with 99.5% methanol conversion, 25 °C temperature rise, 3.6 mm catalyst diameter and 2.5 atm feed pressure. With the increase of stage number, the space velocity of individual stage decreases from 1.106 to 0.626 $\text{g}_{\text{MeOH}}/\text{g}_{\text{cat}}/\text{hr}$. The total space velocity and methanol conversion is 0.71 $\text{g}_{\text{MeOH}}/\text{g}_{\text{cat}}/\text{hr}$ and 99.9%, respectively.

Table 1 Stage parameters under typical conditions

stage	$F_{i,0}/F_R$	$y_{\text{MeOH},0}(\%)$	$sv_i (\text{g}_{\text{MeOH}}/\text{g}_{\text{cat}}/\text{hr})$
1	1.083	7.68	1.106
2	1.179	5.47	0.768
3	1.263	5.17	0.712
4	1.348	4.99	0.673
5	1.437	4.86	0.644
6	1.531	4.84	0.626

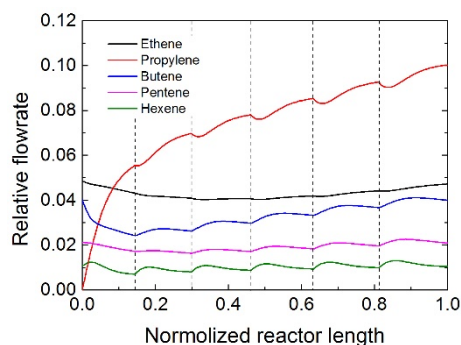


Figure 2 Flow rates distributions along the reactor.

Figure 2 shows that the individual flow rate of recycled olefin including ethylene, butylene, pentene and hexene are nearly the same between inlet and outlet of the reactor, which implies that most of methanol is indeed converted into propylene by recycling olefins other than propylene. Nevertheless, propylene selectivity decreases with the stage number, as illustrated in Figure 3. For the studied six-stage reactor, the overall propylene selectivity is 61.89%, which agrees fairly with the large-scale commercial achievement of 500 kT/y unit with an anticipation of 65% in propylene yield.

Catalyst size is found to have a significant influence on the reactor performance, as shown in Figure 4, which indicates that decreasing catalyst pellet size may benefit the MTP process with increasing the propylene selectivity. However, the pressure drop is also increased when using smaller catalyst pellet.

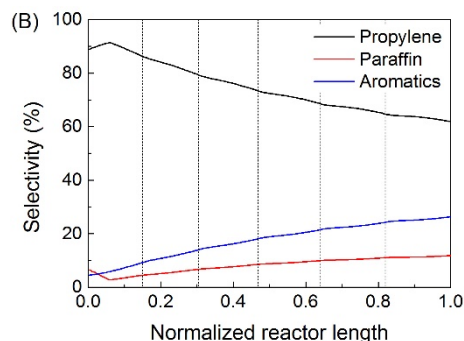


Figure 3 Conversion and selectivity along the reactor.

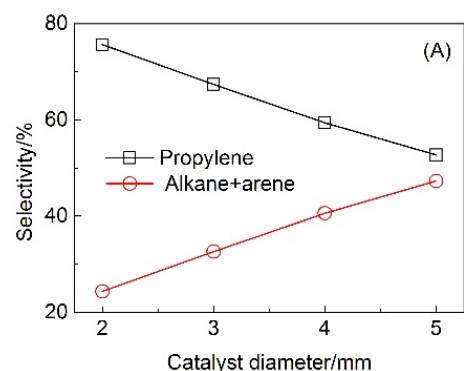


Figure 4 Effect of catalyst pellet diameter

Conclusion

In this work, a six-staged fixed-bed reactor for MTP reaction has been successfully modeled and the key results are close to the industrial process. The low yield of propylene in such a reactor is due to its large stage number and the severe restriction of inner diffusion inside the catalyst pellet. Improvement can be made by using monolith catalyst instead of pellet, which is an ongoing topic in our lab.

References

- Wu W, Guo W, Xiao W, Luo M. (2011) Dominant reaction pathway for methanol conversion to propene over high silicon H-ZSM-5. *Chem. Eng. Sci.*, 66(20), 4722-4732.
- Guo W, Xiao W, Luo M. (2012) Comparison among monolithic and randomly packed reactors for the methanol-to-propylene process. *Chem. Eng. J.*, 207-208, 734-745.
- Huang X, Aihemaitijiang D, Xiao WD. (2016). Reaction pathway and kinetics of C3-C7 olefin transformation over high-silicon HZSM-5 zeolite at 400-490°C. *Chem. Eng. J.*, 280,222-232.
- Huang X, Aihemaitijiang D, Xiao WD. (2016). Co-reaction of methanol and olefins on a high silicon HZSM-5 catalyst: a kinetic study. *Chem. Eng. J.* Accepted.