

OPTIMIZATION OF THE PRODUCT SPECTRUM FOR 1-PENTENE CRACKING ON ZSM-5 USING SINGLE-EVENT METHODOLOGY: TWO-ZONE REACTOR AND RECYCLE REACTOR

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Abstract

In this work, kinetic parameters obtained by the single-event methodology are used to maximize propene yields from 1-pentene cracking on ZSM-5. In a regular plug flow reactor, high amounts of propene can only be achieved in combination with high ethene yields. Furthermore, the product streams usually contain significant amounts of higher olefins. Thus, two different reactor setups are shown here which lead to higher propene to ethene ratios. The first concept divides the reactor into two zones with different temperatures. The earlier low temperature zone favors dimerization so that cracking in the subsequent high temperature zone leads to more propene than ethene. The second concept is a recycle reactor where all olefins from butene on are separated from the product stream and led back to the reactor inlet. This setup allows selective conversion of higher to lower olefins with propene being the main product.

Keywords

Single-events, Kinetic model, Reactor optimization

Introduction

Lower olefins are widely used in the polymer industry due to their broad range of applications. Their usual production routes via steam cracking or FCC suffer under high energy input, low flexibility in feedstock and limited possibilities of influencing the products (Rahimi and Karimzadeh, 2011). Since the demand for propene is growing faster than that for ethene, the production of olefins on demand would be advantageous (Mokrani and Scurrall, 2009). In this context, catalytic cracking of olefins gains in importance.

The reaction networks of such cracking processes are very complex. Nevertheless, a fundamental, microkinetic

model has to account for every single reaction to ensure broad validity. Thus, an effective reduction of kinetic parameters is necessary which is done here by making use of the single-event methodology. This procedure allows extrapolation out of the experimentally covered range so that the obtained parameters can be applied for process optimization and reactor design.

Kinetic Model for 1-Pentene Cracking

The essential idea of the single-event concept is subdividing the rate coefficient into two parts. The first

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part accounts for structural differences between reactant and transition state whereas the second part considers the different types of carbenium ions being involved (Thybaut and Marin, 2013). In an earlier work, kinetic parameters for 1-pentene cracking on ZSM-5 have been estimated using this methodology (von Aretin et al., 2015). For this purpose, data from 165 different experiments with 23 conditions being varied was used. The estimated parameters show small confidence intervals and lead to high parity between model and experiment.

Reaction Pathways on ZSM-5

The product distribution of 1-pentene cracking is highly influenced by reaction temperature. Trends observed in literature (Abbot and Wojciechowski, 1985) can be confirmed by evaluating the kinetic model: Dimerization to higher olefins with subsequent cracking of these species is the dominant pathway at lower reaction temperatures. Much more propene than ethene is obtained because cracking to ethene has to proceed via an energetically less favored primary carbenium ion. On the other hand, monomolecular cracking of pentenes is the central mechanism as temperature rises. It leads to equal amounts of ethene and propene since these are the only possible products when cracking C5-species.

Two-Zone Reactor

A reactor with two evenly distributed zones is introduced. Optimal temperatures for both zones are determined in order to increase both conversion and propene to ethene ratio. It shows that a low temperature zone with 580 K followed by a high temperature zone with 760 K is the best compromise. The resulting molar flows of the different species along the reactor length can be seen in Figure 1 (ratio of molar flow F to initial molar flow of 1-pentene F^0 over catalyst mass W divided by F^0).

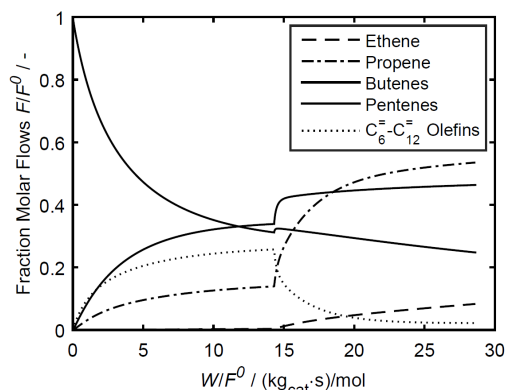


Figure 1. Two-zone reactor with 580 K in the first and 760 K in the second zone

The characteristics of the first zone are high pentene consumption and considerable production of higher olefins because of the high dimerization rate with almost no ethene formation. The second zone shows high cracking rates of larger olefins to especially propene and butenes and with only low ethene production. Although propene and ethene yields are decoupled in this setup, the product stream of a two-zone reactor still contains a significant amount of olefins higher than propene.

Recycle Reactor

The recycle reactor is another concept to increase propene to ethene ratio, especially when higher olefins in the product stream are not desired. In this setup, a separator is installed downstream to the reactor where all olefins higher than propene are split off and led back to the reactor inlet. Thus, the inlet stream consists of a mixture of 1-pentene and other olefins. The kinetic model used can handle this scenario because of the fundamental character of the estimated kinetic parameters. Evaluations at different temperatures show that the optimum operating point is a compromise between high propene to ethene ratio (low temperature) and low recycle ratio (high temperature). The best results are obtained at 680 K.

Conclusions

Single-event kinetics allow reactor design as it is shown here for 1-pentene cracking on ZSM-5. Two suitable concepts are introduced which both lead to higher propene production compared to ethene. In future work, detailed process optimization can assess efficiency of the concepts, especially of the separation unit included in the recycle reactor.

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