

TRANSIENT SIMULATION OF REGENERATION OF METHANOL-TO-GASOLINE CATALYST IN FIXED BED REACTORS

Martin Dan Palis Soerensen*
Haldor Topsoe
Nymoellevej 55, 2800 Kongens Lyngby, Denmark

Abstract

The regeneration of coked methanol-to-gasoline (MTG) catalyst applied in the commercial TIGAS process (Topsoe Improved Gasoline Synthesis) was studied by kinetic investigations on the coke-burn rate from TPO analysis of coked catalyst from a pilot plant reactor. A transient reactor model including the reaction kinetics is derived and used to reproduce the in-situ regenerations conducted in the pilot plant. The effect of the initial axial coke deposition profile is subsequently investigated by means of modeling. It was found that hot spot temperatures far exceeding the adiabatic value can occur in the initial step in the regeneration procedure due to a fast travelling reaction front.

Keywords

Catalyst regeneration, methanol-to-gasoline (MTG), pilot reactors, dynamic simulation, moving reaction zone, non-linear parameter estimation, applied mathematics.

Introduction

In the commercial methanol-to-gasoline process, the catalyst deactivates due to deposition of different types of coke, primarily large aromatic compounds blocking the diffusion pathways in the zeolite pore network (Aramburo et al., 2013). Coke deactivation requires frequent catalyst regeneration. In this regeneration process, the coke is burned away in a stream containing a small amount of oxygen. The reaction between the oxygen in the gas phase and the hydrocarbons in the solid phase gives rise to a considerable heat production, which manifests as moving hot waves as the reaction zone progresses downwards along the reactor axial coordinate. The magnitude of the temperature waves (hot spot) depends on the ratio between the velocity of the reaction front, and the velocity of the temperature front, and can well exceed the adiabatic value calculated from a steady-state approach. The hot waves are of concern, since too high temperature may cause damage either to the reactor or the catalyst itself. Therefore, accurate prediction of the hot spots

formed during regeneration is of great importance. Westerterp, Fontein, and van Beckum (1988) put focus on describing the importance of velocity of the reaction front relative to the temperature front, and how the ratio of these velocities can affect the hot spot temperature. Byrne, Hughes, and Santamaria-Ramiro (1985) investigate the effect of the initial coke profile on the resulting hot waves travelling in the catalyst bed. The work compares the effect of uniform, serial, and parallel coke profiles, respectively, by numerical calculations.

In the present work an industrial relevant coke-burn model for a coked zeolite catalyst is established, using spent catalyst samples from pilot operation as well as process data obtained from regenerations conducted in the pilot plant. These pilot data provides a robust foundation for development of a transient reactor model, which subsequently can provide accurate predictions, and be

* To whom all correspondence should be addressed

used to both investigate and optimize the regeneration procedure in commercial applications.

Experimental

The experimental data is provided from the TIGAS pilot located at Haldor Topsoe headquarters in Lyngby, Denmark. The pilot is capable of simulating the full methanol-to-gasoline synthesis loop, and is specifically designed to replicate industrial performance, ensuring industrial mass flux in the reactor, void distribution, and adiabatic reactor operation, which is accomplished by using automated heat compensation in a dedicated pseudo-adiabatic reactor oven, (Rostrup-Nielsen and Christiansen, 1986). Regenerations are performed in-situ either by establishing a once-through nitrogen flow, or alternatively a recycle loop, the latter applied in industrial application. A small amount of oxygen is introduced into the main stream in a controlled manner to burn off the deposited coke. The temperature profile in the reactor is measured using a Rosemount K-type thermocouple (327.15 K to 1373.15 K) with 18 measurements along the spatial coordinate of the reactor length covering inlet to outlet. All flow rates are measured using coriolis flow meters from Brooks instruments. The oxygen consumption is monitored using an on-line X-STREAM device measuring the oxygen concentration at both reactor inlet and outlet. The composition of the reactor inlet and outlet is further analyzed by means gas chromatography. The GC analysis utilizes a flame ionization detector (FID) and thermal conductivity detector (TCD). The reactor tube is 2000 mm long and has an inner diameter of 75 mm, and is filled with pellets of a gasoline synthesis catalyst. The catalyst is an aluminosilicate zeolite belonging to the pentasil family of zeolites.

After a typical MTG operation, the spent (coked) catalyst was unloaded in fractions of 200 grams and from these fractions, small samples were taken and submitted analysis covering total carbon determination as well as temperature programmed oxidation (TPO). The remaining spent catalyst was then reloaded and regenerated.

Modeling and numerical solution

Kinetic parameters for the oxygen consumption rate are estimated from the TPO results. Furthermore, a transient heterogeneous reactor model consisting of five coupled nonlinear partial differential equations is derived and used to reproduce the regeneration procedure (development of the hot spots) carried out in the pilot plant. The system of differential equations are solved by discretizing the spatial coordinate using an orthogonal collocation method, thus reducing the PDE system into a system of ordinary differential and algebraic equation (DAE) system, which is solved using an implicit Runge-Kutta scheme with high numerical stability. The

measured feed rate, oxygen concentration, and inlet temperature, as well as the measured coke profile from the spent samples, are used as input when solving the resulting initial value problem. The numerical methodology applied is rigorously described by Soerensen (2014).

Results and Conclusion

Carbon analysis of the unloaded catalyst samples reveals that the coke is mainly deposited at the entrance of the reactor, resulting in an overall parallel coke deposition profile. TPO analysis of the spent samples indicate that there are two main types of coke; one with high H/C ratio with high reactivity, and one with low H/C ratio with considerable lower reactivity. It was also found that the amount of the highly reactive coke is much lower than the less reactive coke. The TPO data is applied for fitting a first order pellet kinetic model. The kinetic model is validated by reproducing high quality data from pilot plant operation applying a transient heterogeneous reactor model.

Transient modeling of an industrial adiabatic reactor system reveals that in case of the coke with high reactivity, the oxygen concentration must be chosen with care not to risk temperature waves which evidently can grow well above the steady-state adiabatic temperature. In a commercial application, the first step in the regeneration, which is conducted at lower temperatures, should therefore also be carried out with relatively low oxygen concentration.

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