PARAMETRIC SENSITIVITY OF A GASOIL HYDROTREATMENT REACTOR

Ricardo SARDELLA[1], Jean-Marc SCHWEITZER[2*], Hua WU[3], Clementina LOPEZ GARCIA[2], Massimo MORBIDELLI[3]

1 PDVSA-Intevep. 76343, Caracas 1070 A, Venezuela
2 Institut Français du Pétrole, IFP Lyon, P.O. Box 3, 69360, Solaize, France.
3 Institute for Chemical and Bioengineering. Swiss Federal Institute of Technology
Zurich. ETH. 8093 Zurich, Switzerland

Summary

Thermal stability analysis is imperative to ensure the safe operation of chemical reactors carrying out highly exothermic reactions. This work presents a thermal stability study based on stationary and dynamic criteria. A fixed bed gasoil hydrotreatment reactor working at industrial operating conditions was investigated. The stationary study is based on the van Heerden criterion and parametric sensitivity. The influence of the variation of the most important operating parameters was studied. Stability maps were traced and the parametrically sensitive regions were identified. Finally, a complementary dynamic stability criterion was applied to evaluate the dynamic stability close to the bifurcation points. This comprehensive stability study enables to determine the safe/unsafe operating regions of this reactor.

Keywords

Parametric sensitivity, hydrotreatment, thermal stability.

Introduction

Hydrotreatment is a catalytic process that aims to purify oil fractions at high hydrogen partial pressure to obtain improved quality products by eliminating heteroatoms and increasing their H/C ratio. Hydrotreatment accounts of more than one thousand units all around the world covering a capacity of about 44 millions of barrels per calendar day[1]. It is one of the most important processes in the oil refining industry. Gasoils are petroleum cuts issued from different operations and processes in the refining chain and must be hydrotreated to meet commercial diesel specifications. Gasoil hydrotreatment (HDT) reactions mainly consist on hydrogenation of aromatics, olefins and hydrodesulfurization reactions; all are exothermic. Hydrotreatment of gasoils that have a high aromatics content such as light cycle oils (in average 80 wt%) is generally carried out by dilution with other kinds of gasoils having a much lower aromatics content. This is a choice not only based on the poor light cycle oils (LCO) quality, but also based on safety concerns since hydrotreatment is extremely exothermic. Hence, this study aims at determining the safe operating regions of a LCO HDT reactor *via* a thermal stability analysis.

Different approaches to realize a thermal stability study are reported in literature. Van Heerden[2] studied exothermic reactions under stationary conditions. This author showed that a diagram representing the heat consumption and production enables to determine if the reactor temperature is maintained (stable) or a multiplicity of steady states occurrence (unstable). A stationary stability criterion is deduced establishing that the slope of heat generated by the reactions $\left(dQ_{gen}/dT\right)$ must be lower than the slope of the heat transferred $\left(dQ_{trans}/dT\right)$. Another approach for thermal stability analysis under steady-state conditions is the parametric sensitivity. Parametric sensitivity analysis consists to assess how the reactor temperature responds to changes of parameters controlling the reactive system[3-4]. The sensitivity S is calculated as $S(T;\phi_j)=dT/d\phi_j$, where the variable studied is temperature (T) and the model parameters are ϕ_j. Finally, a complementary dynamic stability criterion[5] can also be applied. Consisting on the perturbation of the reactor model, the stability condition states that after solution of the perturbed model, the real part of all the eigenvalues must be negative. This work presents a detailed parametric sensitivity analysis as well as the complementary approaches (van Heerden and dynamic analysis).

Results

A dynamic reactor model was developed to carry out the thermal stability study. The detailed description and validation of this model has been reported elsewhere[6]. The most relevant points are indicated here. The model

---

[*] j-marc.schweitzer@ifp.fr

represents the triphasic gas-liquid-solid system. A power law kinetic model was fitted with pilot plant experiments carried out with commercial catalyst, real LCO feeds in the industrial range of operating conditions. The most important HDT reactions from the thermal point of view are taken into account in the model.

The effect of variation of total pressure is presented in Fig. 1. The wall cooling temperature was kept constant all along the reactor and an internal temperature profile was obtained; only the average temperature is illustrated. Different steady-state operating curves are obtained at different total pressures. The shape of the curves changes when pressure is increased forming a “S” shape. For curves ranging from 140 to 170 bar, a multiplicity of steady states is obtained (3 T_{mean} for a unique value of wall cooling temperature). The unstable stationary behaviour is located between the bifurcation points marked by numbers (ex. #8 and #9 for 170 bar). This stability behaviour can be explained by the fact that hydrogen partial pressure will increase when total pressure increases. A higher content of H_2 will favour the kinetics, hence the heat generated by the exothermic system. At low total pressure (<120 bar) a stable behaviour is observed.

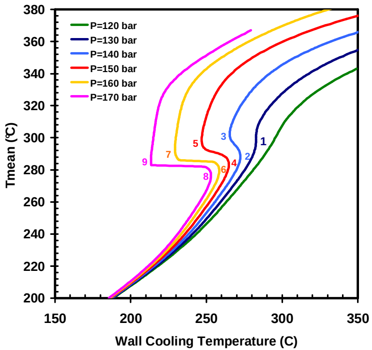

Fig. 1 Stationary stability curves as a function of the variation of total pressure.

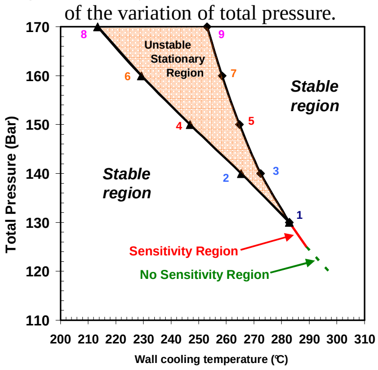

Fig. 2 Unstable/sensitive/stable operating region map as a function of total pressure.

Using this information a stability map was established (Fig. 2). The unstable stationary region as a function of the wall cooling temperature with increasing total pressure is illustrated. The stability boundaries correspond to the bifurcation points marked in Fig. 1. The sensitivity region was determined carrying out sensitivity calculations as a function of the increasing cooling temperature for different parameters at 130 bar (Fig. 3). This pressure was chosen since no clear bifurcation point was obtained. The normalized sensitivities have a maximum/minimum corresponding to the same cooling temperature; this value corresponds to the cooling temperature marked as point #1 in previous figures. This procedure was applied at different total pressures to trace the sensitivity/no sensitivity region. The last corresponds to safe reactor operation. The effect of the variation of Liquid Hourly Space Velocity (LHSV) was also investigated. Fig. 4 presents the stable/unstable map. The original shape of the bifurcation curves is explained by two different phenomena. For low LHSV the conversion is high but heat generated is limited by the low feed amount. The opposite effect is observed at high LHSV.

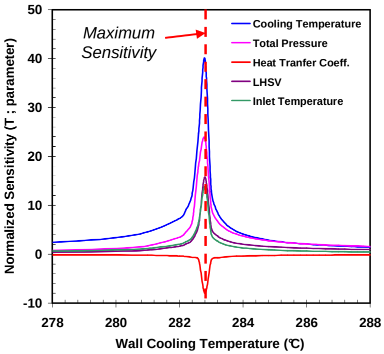

Fig. 3 Sensitivity curve at a total pressure of 130 bar as a function of cooling temp.

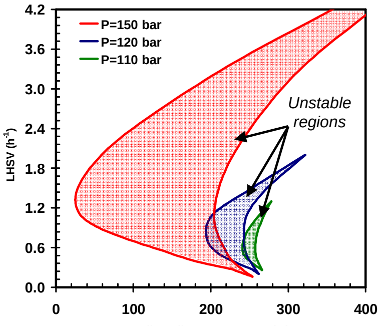

Fig. 4 Bifurcation points and stable/unstable regions as a function of LHSV.

Finally the dynamic criterion was applied to confirm the steady-state stability results. With this information it could be possible to determine that, for this case, both the dynamic and the stationary criteria cover the same stability regions. However, interesting additional information was obtained since the axial location of the hot spot was determined *via* the eigenvectors.

Conclusions

A comprehensive thermal stability study of a real triphasic HDT reactor was presented based on stationary and dynamic criteria. Stable/unstable maps were established for this complex system. Based on the parametric sensitivity approach it was possible to identify *a priori* the regions where process operation becomes unreliable. In further work, the stability analysis presented will be applied to an industrial scale reactive system.

References

(1) Koottungal, L. 2008 Worldwide Refining Survey. *Oil & Gas Journal*. **Dec. 2008**, *22*, 1.

(2) van Heerden, C. Autothermic Processes Properties and Reactor Design. *Industrial and Engineering Chemistry*. **1953**, *45*, 1242.

(3) Morbidelli, M.; Varma, A. A generalized criterion for parametric sensitivity: application to a pseudo-homogeneous tubular reactor with consecutive or parallel reactions. *Chemical Engineering Science*. **1989**, *44*, 1675.

(4) Varma, A.; Morbidelli, M.; Wu, H. Parametric Sensitivity in Chemical Systems. *Cambridge University Press*. **1999**.

(5) Perlmutter, D. D. Stability of chemical reactors. *Prentice-Hall Inc.*, **1972**, New Jersey.

(6) Schweitzer, J.M. et al. Thermal runaway analysis of a three-phase reactor for LCO hydrotreatment. *Chemical Engineering Science*. **2009**. In press.