THERMAL STABILITY ANALYSIS UNDER DYNAMIC CONDITIONS:

A REAL CASE STUDY

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Introduction

Safety is a high-priority topic for the chemical industry to minimize the frequency and severity of accidents. The processes that may undergo reaction thermal runaways are at the heart of these risks. The comprehensive study of such highly reactive systems is necessary to achieve their safe and productive operation as well as for safe new designs.

The objective of this study is to develop a general method to determine the thermal runaway boundaries for refining and petrochemical processes which may potentially undergo reaction thermal runaways. The method is divided in two parts:

1- A stationary analysis based on the Van Heerden criterion[1]. The criterion imposes that $dQ_{gen}/dT < dQ_{exc}/dT$ where dQ_{gen}/dT is the slope of the heat generated by the reactions and dQ_{exc}/dT is the slope of the heat extracted from the system.

2- A dynamic analysis which consists in performing small perturbations around stationary conditions of the whole set of variables involved in the material and thermal balance equations. The linearization of the perturbation model allows determining runaway boundaries by analyzing the eigenvalues of the resulting linear system.

It is well known from the literature that the stationary analysis criterion must be satisfied, however this is not sufficient to ensure reactor stability. Only the dynamic analysis will provide an accurate answer concerning the safe operation of the reactor. Some authors in the literature[2-3] have applied the dynamic analysis on simple reactors such as batch, semi-batch and CSTR. Other works[4-5] deal with more complex systems such as the determination of hot spots in packed-bed reactors. The objective of this study is to perform the dynamic thermal stability analysis of a complex refining process. The hydrotreatment (HDT) of an industrial Light Cycle Oil (LCO) gasoil in a fixed bed reactor is used as a case study. Experiments were carried out at industrial operating conditions in a representative pilot plant. Furthermore, an experiment to attain thermal runaway conditions was also performed. A complete dynamic model of the three-phase system was developed and fitted on experimental data. The dynamic simulation model was used to assess the thermal runaway analysis. The results of the stability analysis were compared with the simulations and the experimental runaway data to check the validity of runaway boundaries obtained from criteria developed from the dynamic analysis.

Dynamic reactor modeling of LCO hydrotreatment

The hydrotreatment of LCO was carried out in an up-flow co-current gas-liquid fixed-bed reactor. The feedstock was characterized according to six chemical families distributed in three boiling point cuts. The kinetic model is based on the reaction scheme described in Fig. 1 where 17 lumps are used to describe the LCO.

Fig. 1. Reaction scheme for LCO HDT and lumping by boiling points.

TRI + 2H$_2$ → DI	(reaction 1)
DI + 2H$_2$ → MONO	(reaction 2)
MONO + 3H$_2$ → SAT	(reaction 3)
SULF + 5H$_2$ → MONO + H$_2$S	(reaction 4)
OLEF + H$_2$ → SAT	(reaction 5)

BP cut ↓	H$_2$	H$_2$S	OLEF	SAT	MONO	DI	TRI	SULF
Pl-200°C	X	X	X	X	X			X
200-300°C			X	X	X	X		X
300°C+			X	X	X	X	X	X

Gas-liquid equilibrium was calculated using the Grayson-Streed method. The gas phase is considered to be in plug-flow. An axial dispersion model was used for the liquid phase. Mass

and thermal balances were time-dependent and calculated as indicated by Eqs. (1) and (2) respectively.

$$\frac{\partial\left(\varepsilon_g \cdot C_i^g + \varepsilon_l \cdot C_i^l\right)}{\partial t} = D_{ax} \cdot \varepsilon_l \cdot \frac{\partial^2 C_i^l}{\partial z^2} - u_l \cdot \varepsilon_l \cdot \frac{\partial C_i^l}{\partial z} - \varepsilon_g \cdot \frac{\partial\left(u_g \cdot C_i^g\right)}{\partial z} + \sum_j \mu_{ij} \cdot r_j \cdot \varepsilon_s \cdot \rho_s \tag{1}$$

$$\left(\varepsilon_g \cdot Cp_g \cdot \rho_g + \varepsilon_l \cdot Cp_l \cdot \rho_l + \varepsilon_s \cdot Cp_s \cdot \rho_s\right)\frac{\partial T}{\partial t} = \lambda_{eff} \cdot \varepsilon_l \cdot \frac{\partial^2 T}{\partial z^2} - \left(\varepsilon_g \cdot Cp_g \cdot \rho_g \cdot u_g + \varepsilon_l \cdot Cp_l \cdot \rho_l \cdot u_l\right)\frac{\partial T}{\partial z} + \tag{2}$$

$$\sum_j r_j \cdot \left(-\Delta H_{r_j}\right)\varepsilon_s \cdot \rho_s - \frac{4 \cdot U}{D} \cdot \left(T - T_c\right)$$

Fig. 2 shows simulation results of the a) parity plot of measured vs. predicted contents of aromatic families and b) the dynamic temperature profiles in the catalytic bed. These results validate the dynamic reactor model used for the thermal stability analysis.

Fig. 2. Reactor model results: a) Aromatics contents, b) Temperature trends .
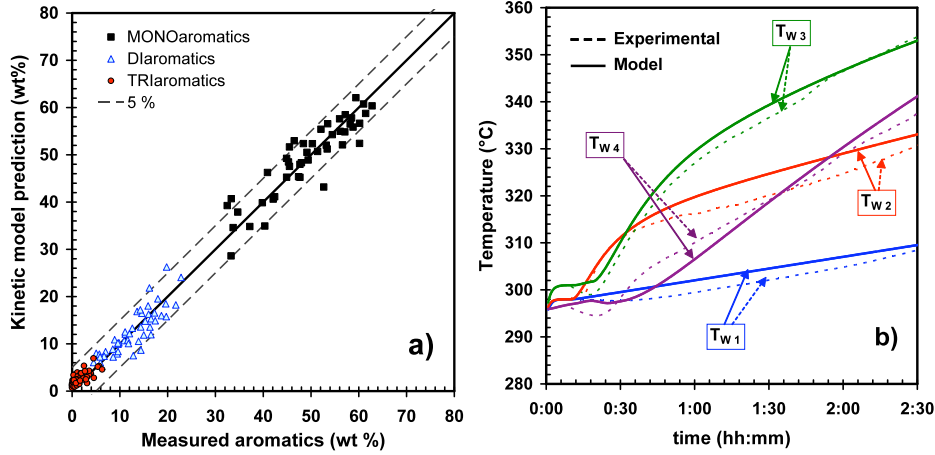
Thermal stability analysis

This mathematical model was used to realize the thermal stability analysis of the dynamic system using a perturbation method. The effect of the variation of the heat transfer coefficient on the thermal stability is presented. The spectral analysis of the eigenvalues indicating the stable/unstable behavior of the reactive system was compared with dynamic simulations. An excellent agreement was found between the simulations and the stability analysis. The case of oscillating behavior is also described. The frequencies of oscillation determined by the stability analysis are compared to the frequencies calculated by Fourier transform applied to the simulated signal. The reactor behavior and the oscillations features are accurately predicted with this stability analysis method.

Figure 3: Eigenvalue spectrum for U=150 W/m^2/K. a) All the eigenvalues, b) Zoom of values close to zero, c) Dynamic simulation, d) Fourier Transform of simulation.
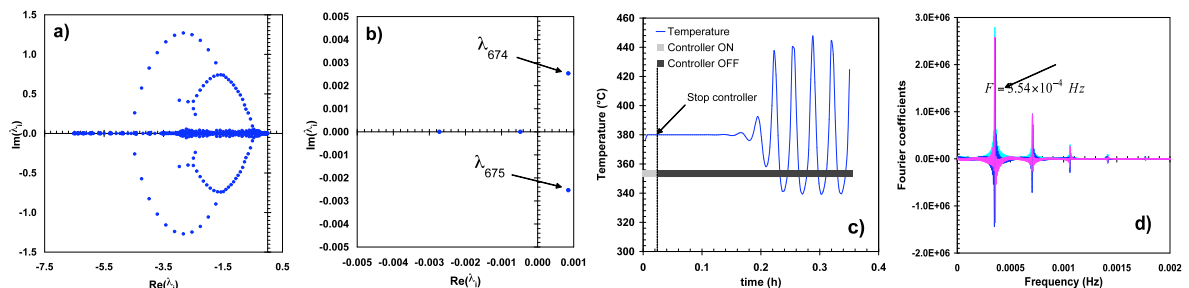
As observed in Fig. 3b, the period of the oscillation can be determined from the imaginary part of the eigenvalues having a positive real part.

$$T = \frac{2 \cdot \pi}{Im\left(\lambda_i\right)} = \frac{2 \cdot \pi}{2.53 \times 10^{-3}} = 42 \text{ min}$$

This period should correspond to one characteristic frequency obtained from the Fourier transform of the temperature signal (Fig. 3d). The characteristic frequency resulting from the Fourier transform analysis corresponds to a period of 47 min. The small difference is due to the accuracy of the linearization when oscillations are far from the stationary point.

Conclusions

The thermal stability analysis of the LCO hydrotreatment was realized with a perturbation method. The criterion of stability imposes that after the solution of the perturbation system, all the resultant eigenvalues must have a negative real part, otherwise the reactor will be unstable. As illustrated with an unstable behavior, the stability analysis presented in this work is a reliable method to establish if the reactor is stable or not.

References

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