Equation Based SPYRO® Model and Optimiser for the Modelling of the Steam Cracking Process

Marco W.M. van Goethem[a*], Florian I. Kleinendorst[a], Nils van Velzen[b], Mario Dente[c], Eliseo Ranzi[c]

[a] TECHNIP BENELUX BV., Pyrotec Division, P.O. Box 86, 2700 AB Zoetermeer, The Netherlands.
[b] VORtech Computing, P.O. Box 260, 2600 AG Delft, The Netherlands.
[c] Politecnico di Milano, Dipartimento di Chimica Industriale e Ingegneria Chimica "G. Natta", Piazza Leonardo da Vinci 23, 20133 Milano, Italy.

Abstract

This paper reports the equation-based SPYRO® model, including its optimisation features. A flexible equation-based SPYRO® model and solver for the simulation of the steam cracking process was the basis for the creation of a program with optimisation capabilities. This is now feasible because of the nowadays available computer power. The optimiser uses a reduced Hessian SQP algorithm of which the quadratic sub-problems are solved by an interior point method. The increase in flexibility is highlighted by means of presenting three case studies. First an example of a design optimisation is shown with the objective of determining optimal tube diameters. In the second case the optimal tuning variables are obtained of the SPYRO® model to describe a novel cracking reactor. The third case demonstrates that the equation-based model can also be used for the fine-tuning of the kinetic parameters of the model. It is concluded that a flexible equation-based SPYRO® program for optimisation and simulation of the steam cracking process has been created.

Introduction

SPYRO® is Technip's proprietary simulation program for the steam cracking process. The program has been functionally extended and improved over the years (Ranzi et al., 1983; Dente et al., 1993). It is a well-established tool for yield prediction, feedstock selection, run length determination, optimal furnace operation and one of the key instruments for the design and revamp of cracking coils for Technip.

The technology of the SPYRO® model is in its kinetic scheme, which has progressed over the years (Dente & Ranzi, 1999). The latest kinetic scheme contains about 6,600 reactions involving 240 components. Compared to the current commercial version it provides a more detailed description in the heavy feedstock range of components (Dente et al., 2001). Therefore the heavy liquid feedstock characterisation has also been extended. The latest scheme is currently being validated and will be released in a future version of SPYRO®.

The enormous increase in computing power has made it possible to develop equation-based SPYRO®, for the purpose of increasing model flexibility. The equation-based ($f(y, x) = 0$) approach has some inherent benefits over sequential SPYRO® ($y = f(x)$):

- The definition of boundary conditions at any position of the coil is possible and easy to specify.
- The SPYRO® model can be added as an equality constraint to an optimisation problem. This enables to perform calculations that were impossible with sequential SPYRO®, like tuning one or more model parameters, design optimisation and tuning of the kinetic parameters.
- A clear separation between the models, solver and data enhances the maintainability of the program.
- It can easily be integrated with a third party model, solver and visualisation tool.

At the ESCAPE-10 conference the simulation version of equation-based SPYRO® was presented (Van Goethem et al., 2000). The simulation version embodies a flexible system of building blocks to define the

* Corresponding author. Tel: +31 - (0) 79 3293631, Fax:+ 31 - (0) 79 3293573, E-mail adress: mvangoethem@technip-coflexip.com.

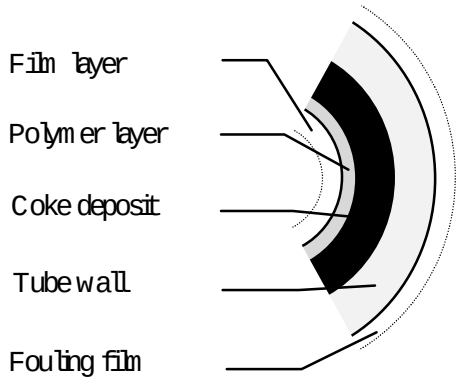
cracking coil and a robust equation solver to solve steady state problems. The simulation results of equation-based SPYRO® were validated with the results of sequential SPYRO®.
This paper presents the optimisation extension of the program. First an overview of the SPYRO® model and the chosen algorithms for optimisation are presented. Thereafter the capability and the flexibility of the optimisation extension is illustrated with three case studies.

Model Description

The heart of the model is the kinetic scheme consisting of a component library and defined reactions with their associated kinetic parameters. The kinetic parameters in the SPYRO® model are implemented as variables for possible future fine tuning.
The component library contains hydrocarbons from methane to heavy components in the range of vacuum gasoils. These are divided in different classes, like paraffins, olefins, naphthenes, aromatics, etc. Lumped components are used to reduce the computational effort while preserving enough detail for proper yield prediction.
The reaction scheme contains more than 6,600 reactions involving 214 hydrocarbon molecules and 27 radicals. Lumping of reactions is used to control the size of the reaction scheme. For example the H-abstraction of n-octane produces four radical isomers, which instantaneously decompose to smaller radicals and molecules (Ranzi et al., 2001). These reactions are lumped into one overall reaction in the reaction scheme.
The reaction rates are calculated with the use of both the simple and the modified Arrhenius equation.
The SPYRO® model consists of 259 (partial) differential and 74 algebraic equations. The time dependent nature of the model is caused by the growth of coke on the inner tube wall. A mechanistic model describes the coking process (Ranzi et al., 1985). The model contains three coking mechanisms to calculate the coking rate: polymeric growth based on a catalytic mechanism, addition of unsaturated radicals and molecules, and trapping of heavy components into the polymeric matrix. The change in coke morphology is also accounted for.
The cracking process is considered in pseudo steady state; hence the deposit of the coke on the tube wall at a time step is neglected. Therefore the steady state plug flow reactor model can be applied to describe the cracking coil. The continuity equations for the components, the energy balance and the mechanical energy balance are described by ODE's conforming to this model type. An elaboration on some of the equations is given below.
A detailed layer build-up (Figure 1) is used to relate the outside tube skin temperature to the process gas temperature. Several non-linear algebraic equations describe this relation.
In the SPYRO® model there are various non-linear equations to account for radial and circumferential effects. These equations are not solved numerically, but approximated solutions are used. Amongst others in radial direction the cracking in the film layer is considered. In the circumferential direction the maximum outside tube skin temperature and the circumferential average coking rate are determined. These effects are caused by the arrangement of the tubes in the radiant box.
The SPYRO® model is divided into sub-models for two major reasons (Van Goethem et al., 2001).

- It makes it possible to handle the model discontinuities properly. Examples of discontinuities locations are: the coil entrance, exit, tube bends, adiabatic zones and those locations where flows are split and where parallel tubes are combined.
- It enables the modeller to describe the different process parts with more or less detail as desired.

The SPYRO® model contains spatial and time derivatives. The spatial derivatives are inherently stiff, caused by radical mass balances. This stiffness is tackled by applying the method of orthogonal collocation on finite elements (Villadsen & Michelsen, 1978). The time derivatives are approximated with an implicit Euler scheme. At each integration step a set of non-linear equations (about 15,000) is solved. Analytical Jacobian matrices are used for robustness and calculation speed, Figure 2 shows a typical Jacobian matrix.



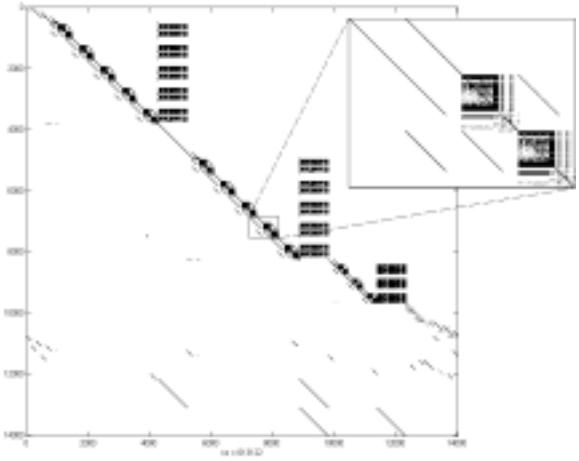


Figure 1: Sketch of the coke layer build-up.

Figure 2: Jacobian sparsity pattern of cracking coil.

Optimisation algorithm

The equation-based SPYRO® model of the steam cracking process can also be used to solve different types of optimisation problems. The modeller must write an optimisation input file for this purpose. The following optimisation building blocks can be defined in the input file:

- boundary values which are set in the simulation model can be deactivated,
- definitions of:
  - variables,
  - equality constraints,
  - simple bounds on variables,
  - free variables.

The input file is processed and analytical derivatives of the new equality constraints are computed. The resulting non-linear programming (NLP) problem for the typical equation-based SPYRO® model has the following properties:

- a large number of unknowns ($n \approx 15{,}000$),
- a small number of free variables (difference between the number of equality constraints and n), less than 10 for most problems,
- a very small number of simple bounds on variables.

A Sequential Quadratic Programming (SQP) algorithm (Han, 1977) was developed at Technip that is capable of solving this kind of optimisation problems efficiently.

The framework of the developed algorithm is based on the SQP algorithm 'donlp2' (Spellucci, 1994) that is designed for solving small dense NLP's. For an estimation of the Lagrange multipliers (λ) and search direction (d^k) two Quadratic Problems (QP) are solved at each iteration (k). Most other SQP algorithms solve only one QP for the estimation of both. The approach of 'donlp2' gives a better selection of weight factors for the penalty function. The penalty function is used to determine the damping factor (α_k). This factor is used to compute the new approximation of the solution $x^{k+1} = x^k + \alpha_k d^k$. The fundamental difference between our algorithm and 'donlp2' is the use of complete QP sub-problems, i.e. all inequality constraints are included in each quadratic sub-problem.

The property of small degree of freedom is used to reduce the size of the QP sub-problems. The large QP problem that is generated by the SQP algorithm is projected on the null-space of the linearised equality constraints. The resulting QP problem is of the size of the number of free variables and can be solved at low computational cost.

The coefficient matrix of the QP sub-problem is a positive definite approximation of the Hessian of the Lagrangian. In general this is a full n x n matrix that is too large to handle. Reduced Hessian SQP-methods (rSQP) (Biegler et al., 1997) approximate a projection of the Hessian on the null-space of the

linearised equality constraints. This approach did not work for the equation-based SPYRO® model because for this model no proper first reduced Hessian could be constructed. Instead of an approximation of the projected Hessian a limited memory approximation (Byrd et al., 1994) of the Hessian of the large QP-problem is used. By using this limited memory approximation the product between the Hessian approximation and a vector is computed efficiently, without constructing the Hessian explicitly.
Modified Newton with the free variables fixed is applied as a second order correction to reduce the residuals of the equality constraints. The computational time is hereby significantly reduced.
Different methods have been tested to solve the quadratic sub-problems efficiently. Different Interior Point (IP) methods and direct methods are tested to solve the Quadratic sub-problems. An IP QP-method is chosen, because the algorithm is less complex compared with direct methods and therefore easier to maintain. Another unexpected advantage is that in case of an infeasible QP-problem the not converged approximation, which is generated by the IP-method proves to be a good choice to use by the SQP method. This is in contrast with direct methods, which needs to generate an appropriate search direction in those cases.

Case Studies

The equation-based SPYRO® optimisation version can be used in several fields, as the following case studies will show. In each case study the full SPYRO® model is added as an equality constraint to the optimisation problem, while additional constraints and the target function are specified with the aid of the optimisation input file.

Case study 1
Recoiling projects are often executed at Technip. Recoiling means the replacement of old radiant coils with newly engineered coils in the existing radiant box. In these projects the box measurements, operating conditions (e.g. the feed flow and cracking severity) and the type of feedstock are known beforehand. Suppose the common GK5 coil (Technip technology, a split U-coil with two parallel inlet tubes and a single outlet tube) is selected. The length of the tubes is set by the height of the radiant box. Only the diameters of the inlet and outlet (respectively d_{inlet}, d_{outlet}) tubes of the GK5-coil can be varied. Inequality constraints are set on both diameters. Other inequality constraints on process variables (X_p) are present, e.g. on the maximum tube metal temperature. The objective is to find the optimal diameters such that the selectivity of ethylene is maximised. This problem can be rephrased to the optimisation problem (1). The variables for the in and outlet diameters are set free in the SPYRO® model.

$$\max \; C_2H_{4\,Effluent}$$
$$\text{subject to} \begin{cases} SPYRO\,model = 0 \\ d_{inlet,min} \le d_{inlet} \le d_{inlet,max} \\ d_{outlet,min} \le d_{outlet} \le d_{outlet,max} \\ X_{p,min} \le X_p \le X_{p,max} \end{cases} \qquad (1)$$

Solving problem (1) results in an unconstrained optimum. In similar problems the optimal diameters to maximise the selectivity of ethylene plus propylene, ethylene plus propylene plus butadiene, ethylene plus propylene plus butadiene plus BTX (Benzene Toluene Xylene) are determined. Table 1 presents the ratios of the optimal diameters for the different problems. The difference between the cases is explained by the preference to ethylene over propylene in the optimal ethylene selectivity case.

Table 1: Ratios of the outlet and inlet tube of a GK5-coil at maximum productions

Maximum selectivity of	C_2H_4	C_2H_4 & C_3H_6	C_2H_4 & C_3H_6 & C_4H_6	C_2H_4 & C_3H_6 & C_4H_6 & BTX
d_{outlet}/ d_{inlet}	2.71	1.92	1.93	1.94

Case study 2

During the research phase, novel cracking reactor designs need to be assessed for their potential. This case shows an interesting reactor design for a specific feed with a special cracking severity range. The reactor geometry is very novel, therefore a proper model is not available for this reactor. In order to make a proper assessment the measured data obtained from this pilot plant has to be validated with SPYRO®. The SPYRO® model contains several tuning parameters to enable a closer match with the actual measured data. Apart from the measured effluent composition, also a process temperature profile in the pilot reactor is available.

The optimisation capabilities of equation-based SPYRO® are used to fit the effluent composition of N_{comp} main components by changing the N_{tune} tuning variables (X_{tune}) within a range of 10 % deviation. A maximally 10% deviation is chosen to prevent unphysical solutions. The variances (σ) on the N_{temp} temperature measurements (T_m) were used to adapt the temperature profile. The optimisation problem is formulated by problem (2). The temperatures and tuning variables are set free in the SPYRO® model. The total number of free variables is 16 and the number of equality constraints about 14,000.

$$\min \sum_{i=1}^{N_{comp}} \left(x_{wt,measured,i} - x_{wt,SPYRO,i} \right)^2$$

$$\text{subject to} \begin{cases} SPYRO\,model = 0 & \\ T_{m,j} - \sigma \le T_{SPYRO,j} \le T_{m,j} + \sigma & j = 1 .. N_{temp} \\ 0.9 \le X_{tune,k} \le 1.1 & k = 1.. N_{tune} \end{cases} \tag{2}$$

A constrained optimum is found for problem (2). The relative deviations of the estimated effluent main components are within 3 % of the measurements. With the optimised values for the tuning variables and temperature profile, a proper assessment of the potentials of this novel reactor design can be made.

Case study 3

In the kinetic scheme many cross-linked kinetic parameters are present. Therefore tuning the kinetic parameters is a very delicate matter. To tune a part of the kinetic scheme one should have a thorough understanding of it and have access to a large amount of reliable data. The next case is purely illustrative because there is not enough information in the measurements for the determination of the large number of decision variables. The performance of the reduced Hessian optimisation algorithm is shown for large QP sub-problem.

For a specific case, a naphtha feedstock cracking case with experimental effluent data available, the optimiser is used to tune kinetic parameters. The kinetic parameters for a specific group of reactions N_{reac} are set free within a range of 10% deviation and the equation-based SPYRO® model is added as a constraint. The sum of squares of the differences between measurements and simulation results for N_{comp} effluent components is minimised. The optimisation problem consisted of 256 free variables, 512 inequality constraints and 13,000 equality constraints.

$$\min \sum_{i=1}^{N_{comp}} \left(x_{wt,SPYRO,i} - x_{wt,measured,i} \right)^2$$

$$subject\,to \begin{cases} SPYRO\,model = 0 & \\ 0.9 \le A_{tune,k} \le 1.1 & k = 1..N_{reac} \\ 0.9 \le E_{tune,k} \le 1.1 & k = 1..N_{reac} \end{cases} \tag{3}$$

The optimiser solves problem (3) successfully. For this naphtha feedstock case, the sum of squares is reduced to one fifteenth of the initial value calculated for the above-described kinetic scheme. This demonstrates that the optimiser with equation-based SPYRO® is capable of fine tuning kinetic parameters.

Conclusions

The developed equation-based SPYRO® model is used for the simulation of the steam cracking process. The same model can be used as an equality constraint in optimisation problems.
An optimiser based on the reduced Hessian successive quadratic programming algorithm is implemented in the equation-based SPYRO® program. The optimiser is capable of solving different types of optimisation problem, which is illustrated by the three successfully solved cases.
It is shown that the objective is met: the creation of an equation-based flexible rigorous model for the simulation and optimisation of the steam cracking process.

References

Biegler L.T., Nocedal J., Schmid C., Ternet D. *Numerical experience with a reduced hessian Method for large scale constrained optimization*. Optimization Technology Center 1997.

Byrd R.H., Nocedal J. & Schnabel R.B. *Representation of quasi-Newton matrices and their use in limited memory methods.* Mathematical Programming 63 (1994) pp. 129-156.

Dente M. & Ranzi E. (1999). SPYRO® *2000*. European SPYRO® Users Conference 1999, Technip Benelux B.V./Division Pyrotec.

Dente M., Pierucci S., Ranzi E., Bussani G. & Valkenburg, P. (1993). *Mathematical Modeling of Steam Cracking Reactors*. Chemical and Process Engineering: Abstracts, Aidic, pp. 393-397.

Dente M., Ranzi E., Bozzano G., Faravelli T. & Valkenburg P.J.M., *Heavy Component Description in the kinetic Modeling of Hydrocarbon Pyrolysis*, Presented at: AIChE 2001 Spring National Meeting, Houston TX, April 22-26.

Han S.P. *A Globally Convergent Method for Nonlinear Programming*. Journal of Optimization Theory and Applications. Vol. 22, No. 3, (1977).

Ranzi E., Dente M., Goldaniga A., Bozzano G. & Faravelli T., *Lumping Procedures in Detailed kinetic modeling of Gasification, Pyrolysis, partial oxidation and Combustion of Hydrocarbon Mixtures*, Progress in Energy and Combustion Science 27 (2001), pp. 99-139.

Ranzi E., Dente M., Pierucci S. & Biardi G. (1983). *Initial product distributions from pyrolysis of normal and branched paraffins*. Ind. Eng. Chem. Fundam. 22, pp.132.

Ranzi E., Dente M., Pierucci S., Barendregt S. & Cronin P. (1985). *Coking simulation aids on stream time*. Oil and Gas Journal, September 2, pp. 49-55.

Spellucci P., *A SQP method for general nonlinear programs using only equality constrained subproblems.*(1994).

Van Goethem M.W.M., Kleinendorst F.I., Van Leeuwen C. & Van Velzen C., *Equation Based Spyro® Model and Solver for the Simulation of the Steam Cracking Process*, In: Pierucci S., European Symposium on Computer Aided Process Engineering – 10, Elsevier, 2000, pp. 589-594.

Van Goethem M.W.M., Kleinendorst F.I., Van Leeuwen C. & Van Velzen C., *Equation Based Spyro® Model and Solver for the Simulation of the Steam Cracking Process*, Computers and Chemical Engineering 25 (2001), pp. 905-911.

Villadsen J., & Michelsen M. L. (1978). *Solution of differential equation models by polynomial approximation*. International series in physical and chemical engineering science, Englewood Cliffs, NJ: Prentice-Hall.