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An Efficient Approach to Robust Simulation of Claus Processes in Coking Plants

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Abstract

Claus Combustion is a significant process unit in coking plants. Its main purpose is the destruction of gaseous contaminants such as H_2S combined with the recovery of sulphur. However, since the feed flow contains much more components, it implies a complex gas reaction process, which can be divided into two parts, the furnace and the waste heat boiler, where additionally the condensation of sulphur takes place. All partial reactions occur with very different velocities and thus a complex kinetic model, involving all reactions is required. This leads to a stiff system for simulation tasks, which causes lacks of robustness concerning convergence properties. On the other hand, simulation robustness is absolutely necessary, since this process is linked to other process units in the entire coking plant. In this work, novel numerical approaches are proposed in order to assure convergence and robustness allowing flexibility for any changes of boundary conditions. For the furnace, modelled as CSTR, mainly the self-generation of initial values and the prevention of singularities in the jacobian matrices leads to robustness concerning convergence. For the waste heat reboiler, modelled as a PFR, discretisation by orthogonal collocation along the tubes including a step size control guarantees convergence. Since condensation of certain components may occur, flexibility for model switching is integrated in the step size control algorithm.

Keywords

Claus Combustion, Convergence properties, Plug flow Reactor

1. Introduction

Processes in coking plants produce plenty of waste gases, which need to be destroyed or separated. Claus combustion is a very important process unit in the entire process. It is commonly used in order to recover sulphur while destroying contaminants formed in upstream processes, particularly H_2S. However, particularly in coking plants, many other contaminant gas components feed the Claus plant as well, such as H_2S, H_2O, NH_3, CO_2 , HCN and several other carbon hydroxides. This leads to a complex system of chain reactions and parallel reactions in the process gas plant.

The Claus is usually divided into two steps, the thermal and the catalytic step [1]. While the catalytic step can be sufficiently described by the Gibbs reactor model, a more accurate kinetic model is required for the thermal step [2]. The thermal step can be divided into two units, the furnace and the waste heat reboiler. For both units different reactor model types are suitable, the CSTR for the former unit and the plug flow reactor (PFR) for the latter one.

The optimal operation conditions and also the outflow compositions are very sensitive to the expected Claus feed. Furthermore, the large number of components including intermediate products and reactions leads to a large-scale equation system, which needs to be solved simultaneously. Particularly the computation of an adiabatic process makes simulation to a challenging task, since the heat of all reactions needs to be considered for obtaining the right temperature. Additionally, the great differences of the single reaction rates and concentrations of the components at the solution points often lead to a stiff system which causes high convergence problems. This fact makes the simulation tool worthless to be linked to other processes in the coking plants or superior optimization tools.

In this work, different numerical approaches are proposed in order to account for robustness concerning convergence properties. For the CSTR model, it should be noted first that convergence properties at stiff and complex reaction systems strongly depend on the correct choice of initial values. A further problem represents the singularity of the jacobian matrix in the iteration steps. The appropriate initial values are mostly unknown, when feed condition changes. Thus, a method of automatically self-generating initial values has been developed which avoids the exhausting search by hand. Based on the use of the

logarithmic values of the variables instead of the variables themselves, singularity can be prevented by adding dummy values to the main diagonal of the jacobian matrix when all values of any line or column are close to zero. In order to consider both adiabatic and isothermal combustion the solver is combined with the bisectional method, a linear interpolation approach.

For simulation of the waste heat boiler, the heat exchange with a counter current water steam as cooling utility, what causes the supression of the undesired reaction kinetics, needs to be considered. However, at certain conditions and at certain locations, this may lead or not to condensation of components with relatively high boiling temperature. Thus, for those cases of hybrid processes the simulation tool must be flexible enough for optionally switching between different physical models following predefined switching criteria. For the implementation, the apparatus length is discretised by the five point orthogonal collocation method, which is applied in combination with a novel approach for adaptive step-size control. For the dynamic simulation, the collocation method in finite elements is also used in order to discretise the time.

All those numerical modifications implement a robust simulation allowing flexibility in changing feed composition, residence time and also the setting of catalysts.

2. Modeling of the Process

As mentioned above, the Claus furnace and the waste heat boiler are described by the CSTR and the PFR, respectively. For both cases, the kinetic model is considered for the mass balances:

$$\frac{dN_A}{dt} = \dot{N}_{A,in} - \dot{N}_{A,out} + V \cdot \left[\sum_{j=1}^{nrx} N_{Aj} \cdot \nu_j \cdot \exp\left(-E_j / RT\right) \cdot \prod_{k=1}^{n_j} (C_k)^{a_{kj}} \right] \qquad (1)$$

For the furnace, distinction has to be made between an isothermal reactor with a controlled temperature and an adiabatic one. For the latter case, the additional use of the energy balance is required:

$$\frac{dH_R}{dt} = H^{Feed} - H^{OUT} + Q \qquad (2)$$

For the waste heat boiler, the tubes are assumed to be split off into thin slices, working as many CSTR units in a row. Assuming one slice to be infinitely thin,

the derivative by length needs to be used additionally to describe the transfer of mass and heat, which leads to a partial differential equation.

$$C(T(x)) \cdot \frac{dc_i}{dt} = \frac{\partial \dot{n}_i}{\partial x} + r_i \cdot A_{Tube} \tag{3}$$

It should be noted that the reaction along the tube and the heat transfer to the water steam occurs simultaneously. Due to the permanent cooling along the tube condensation of components with the highest boiling temperature may (or may not) occur, and thus we could get a hybrid process, where switching between the following three models is required:

a) gas cooling only
b) partial condensation of a certain component at constant boiling temperature
c) total condensation and cooling below the boiling temperature

For Claus processes, it is pure sulphur, which may condense in the tubes. At the entrance of the tube, the gas coming from the upstream furnace is modeled according to a). The model will be switched to b) or c) when the boiling temperature of sulphur is reached *and* the heat flux density of heat exchange is higher than the one released by the sum of still occurring reactions:

$$T \le T^S_{S2,S4,S8} \; ; -\frac{\partial \overline{h}}{\partial x} \le \left(T - T_{Steam}\right) \cdot k \cdot U_{Tube} \tag{4}$$

The change to c) will occur, when no sulphur exists in the gas phase anymore *and* the sum of latent heat of newly produced sulphur and the reaction enthalpy is lower than the flux for heat exchange. The differential formulation of this switching condition can be written as:

$$n_{S2,S4,S8} \approx 0 \; ; \frac{\partial \overline{h}}{\partial x} + \frac{\partial \dot{n}_i}{\partial x} \cdot \Delta h^{LV}_{S2,S4,S8} \le \left(T - T_{Steam}\right) \cdot k \cdot U_{Tube} \tag{5}$$

3. Numerical methods

For the PFR model, the discretisation of the derivative by length is required at any rate. For dynamic processes, the derivatives by time need to be discretised additionally. Due to the strongly nonlinear and non-monotonic behavior of the process, the five-point collocation method is appropriate for efficient simulation [3]. For steady state processes in the furnace, we face the problem of the correct choice of initial values. Thus, a robust approach has been developed, which is described in *3.1*. For the implementation of the PFR model the five

point orthogonal collocation is used. However, for assuring convergence, particularly when the necessity of model switching could occur, a step size control algorithm needs to be combined to the solver, as briefly discussed in *3.2.*

3.1. Claus furnace

For steady state computation of CSTR at given feed conditions, convergence can be only assured at appropriate initial values, which are usually unknown as the solution point itself. To overcome this problem, we propose in this work a novel approach to self-generation of reliable initial values.

At a very low residence time, the outflow composition is close to the known input one and, thus, the input composition can be used as the initial one for the outflow. Under controlled increase of the residence time, the resulting values of the previous simulation run can be used as initial values for the current one, until the original residence time is reached. In order to simulate an adiabatic process, the reaction temperature at the steady state can be computed by the bisectional method, which generally assures linear convergence. In Fig. 1 the output flow of H_2S from the claus furnace is shown as well as the degradation of NH_3 and HCN.

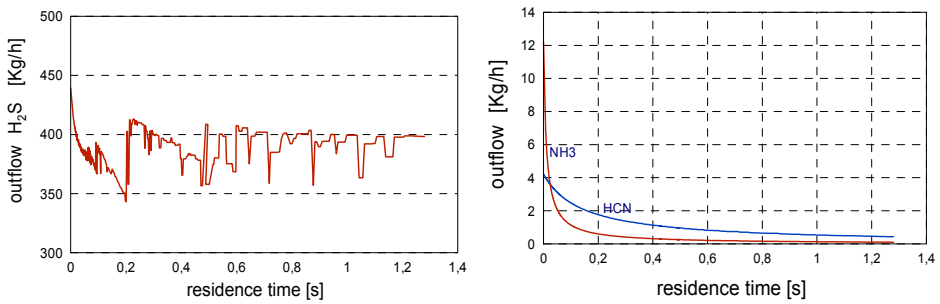

Fig. 1: Claus furmace: outflow of H_2S and degradation of NH_3 and HCN.

3.2. Waste heat boiler

As mentioned above, the discretisation of the derivative by length is required, but for dynamic cases, the two-dimensional collocation method is required, as illustrated in Fig. 2.

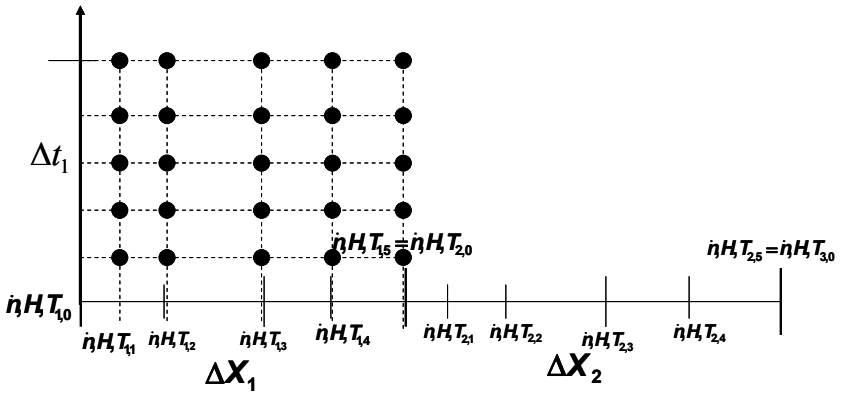

Fig. 2: two-dimensional orthogonal collocation

The step size control is based on reduction of the step size in case of non-convergence and doubling the step size in case of fast convergence.

4. Conclusions

New numerical approaches have been created in order to assure convergence for complex gas reaction processes such as Claus combustion. For steady state CSTR models self-generation of initial values has been created to overcome convergence problems. For dynamic problems and for PFR models the orthogonal five-point collocation method guarantees efficient computation when it is combined with model switching criteria, which are necessary because of possible condensation of certain components. Currently, those simulation approaches are extended to CFD modelling and additionally linked to optimisation tools.

References

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