Automatic kinetic model generation: a combination of the rule-based and rate-based termination criteria

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TERMINATION CRITERIA

1. The algorithms of two types of termination criteria, rule-based and rate-based, are implemented in the automatic kinetic model generation software Genysis.
2. The number of species and reactions in the final kinetic model are evaluated for both termination criteria by varying constraints and tolerances for a heptane pyrolysis example.
3. Three algorithms are combined to have an optimal kinetic model size.

RULE BASED

Application of constraints based on users knowledge of present characteristic structural features in species
1. Constraints on reaction families
2. Constraints on product species

Example 1: The size of product species

Pro
Controlled by the user

Cons
Includes species independent of kinetics
Model valid for wide range of conditions

Example 2: The size of abstracting and adding species

Pros
Controlled by the user
Includes species independent of kinetics
Model valid for wide range of conditions

CONS
User’s knowledge required
Lots of redundant species included

Example 3: The number of double bonds

Rate of fly with CHEMKIN

Larger tolerance => smaller networks => smaller edge => shorter simulation time
Optimal \( \varepsilon \) depends on the system, model performance for different \( \varepsilon \) needs to be evaluated

"Optimal" conditions:
- max 2 double bonds, max 8 heavy atoms, abstracting or adding species max 3 heavy atoms
- Size of the species and reactions in the core varies little when applying constraints. Most of the time, the size of the edge and simulation time reduce when the constraints are more stringent.
- If constraints are applied, the number of species and reactions in the core remain the same with varying \( \varepsilon \).
- The size of the edge for \( \varepsilon = 0.001 \) reduces from 1644 to 88 species and the simulation time goes from 2856 s to 151 s.
- Applying constraints to rate-based algorithm reduces simulation time and edge size significantly, while a similar microkinetic model is obtained in the end.

REFERENCES


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CONCLUSION

• The size of the model developed with the rule-based criterion increases fast. Long simulations times and memory issues are present for too large reactants. The model performs well for all conditions.
• Simulation times for the rate-based criterion are already high for only small kinetic models. The core depends on the availability of good kinetic data. The model performs well for the selected reaction conditions.
• The choice of the termination criterion depends on the user’s knowledge, the availability of good kinetic and thermodynamic data and the purpose of the final kinetic model.
• Combining rule and rate based termination enables the automatic generation of small kinetic models with good model performance in reasonable simulation time.