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Automatic kinetic model generation:

a combination of the rule-based and rate-based termination criteria

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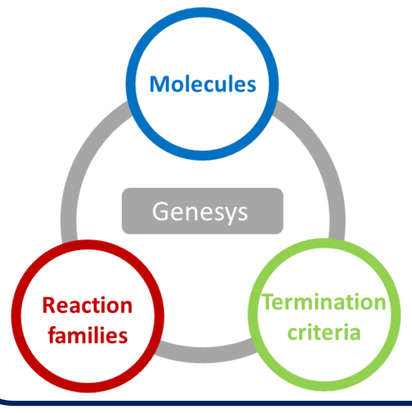
AUTOMATIC KINETIC MODEL GENERATION



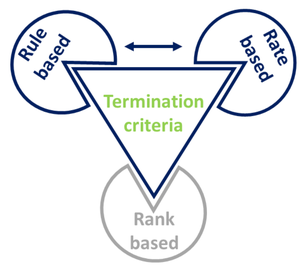
Construction of microkinetic models, that contain essential chemistry while maintaining a **manageable size**, with software like **Genesys** [1,2]

Model development by hand is tedious, error prone and often incomplete

Automatic generation of microkinetic models starts from a list of **reactants**, **reaction families** and **constraints** or **reactor conditions**

Unique representation of **molecules**, **reaction** recognition, fast thermodynamic property and kinetics assignment and control of the reaction network **size** are key properties of automatic kinetic model generation

TERMINATION CRITERIA



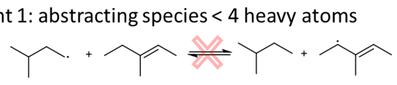
1. The algorithms of two types of termination criteria, **rule-based** and **rate-based**, are implemented in the automatic kinetic model generation software Genesys
2. The number of species and reactions in the final kinetic model are evaluated for both termination criteria by **varying constraints**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

Rule based » Constraints on species and reaction families **Rate based** » Rate of production Reactor conditions **Rank based** » Fixed maximum of reaction steps

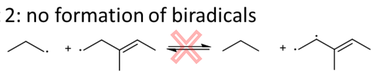
RULE BASED

Hydrogen abstraction

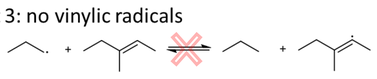
Constraint 1: abstracting species < 4 heavy atoms



Constraint 2: no formation of biradicals



Constraint 3: no vinylic radicals



Pros

Controlled by the user

Includes species independent of kinetics

Model valid for wide range of conditions

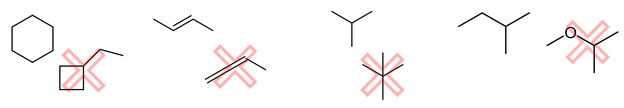
Cons

User's knowledge required

Lots of redundant species included

Application of constraints based on **users knowledge** of present characteristic structural features in species

1. Constraints on reaction families
2. Constraints on product species



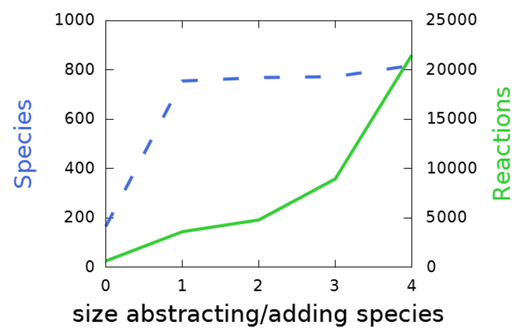
Example 1: The size of product species

Extra constraints: max 3 C=C, max 3 C in abstracting species, max 2 tertiary C, no quaternary C

# heavy species	Species	Reactions
7	720	8667
8	2596	15458
9	Memory issues	

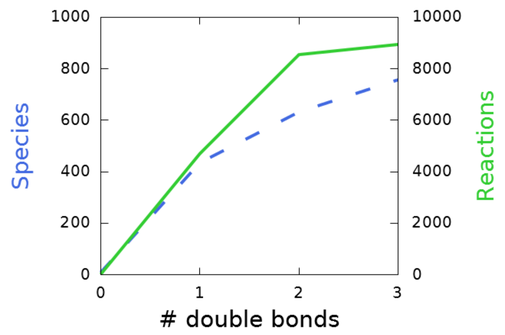
Rule based criterion not for too large species
Network size increases quickly

Example 2: The size of abstracting and adding species



Number of reactions increases fast
(max 7 heavy atoms)

Example 3: The number of double bonds

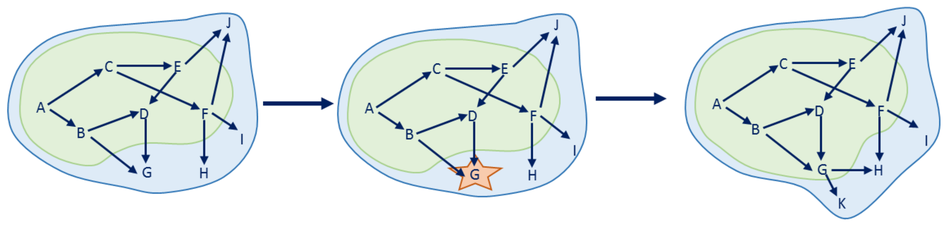


Stabilizes at max 3 double bonds
(No C=C=C allowed, max 7 heavy atoms)

RATE BASED

All possible reactions of species in the **core** are included in the **edge**. Species in the **edge** are included in the **core** based on their **rate of production** after reactor simulations.

$$R_i(t) \geq R_{\min}(t) = \varepsilon \left(\sum_j R_j^2(t) \right)^{1/2}$$



Pros

No user's knowledge

Only most important species

Cons

Good kinetics required

Kinetic model only applies for specified reactor conditions

Solving reactor equations takes time

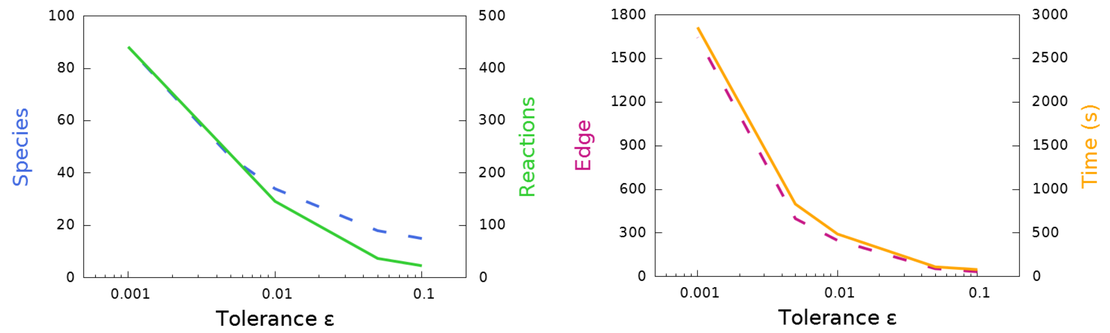
Reactor simulations done on-the-fly with CHEMKIN [3]

One set of conditions, possible reactors:

1. Plug flow reactor
2. Perfectly stirred reactor
3. Homogeneous batch reactor

Example: Plug flow reactor, $F_{m,0}$ = 6 g/s, p = 1 Mpa, T = 1100 K, L = 23.14 m, d = 0.01 m

Example: The influence of ε on the size of the core, on the size of the edge and on the simulation time

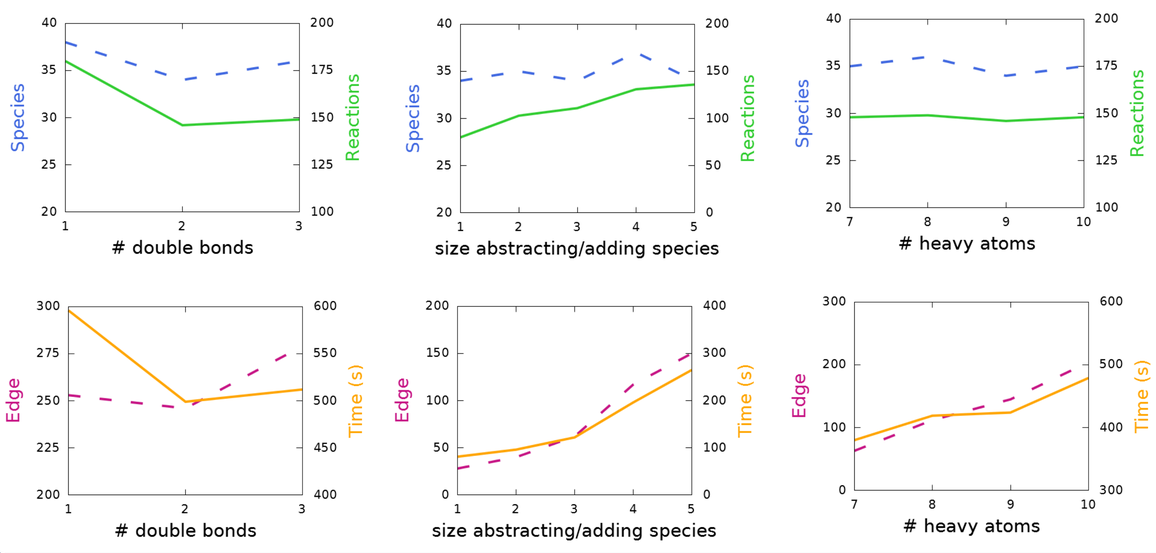


Larger tolerance ↔ smaller networks ↔ smaller edge ↔ shorter simulation time

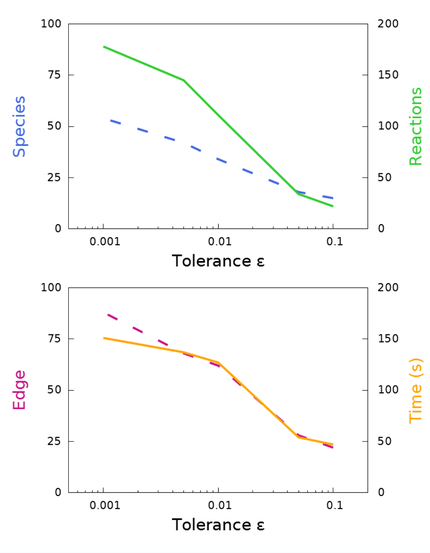
Optimal ε depends on the system, model performance for different ε needs to be evaluated

COMBINED TERMINATION CRITERIA

Apply constraints while performing rate-based simulations with ε=0.01.



Vary ε at "optimal" conditions



"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 ε. The size of the edge for ε = 0.001 reduces from 1644 to 88 species and the simulation time goes from 2856 s to 151 s.

Applying constrains to rate-based algorithm reduces simulations time and edge size significantly, while a similar microkinetic model is obtained in the end.

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 only for the selected reactor 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**.

REFERENCES

[1] Vandewiele, N. M., K. M. Van Geem, M. F. Reyniers, and G. B. Marin. 2012. Chemical Engineering Journal 207:526-538. doi: 10.1016/j.cej.2012.07.014.

[2] Van de Vijver, R., N. M. Vandewiele, P. L. Bhoorasingh, B. L. Slakman, F. S. Khanshan, H. H. Carstensen, M. F. Reyniers, G. B. Marin, R. H. West, and K. M. Van Geem. 2015. International Journal of Chemical Kinetics 47 (4):199-231. doi: 10.1002/kin.20902.

[3] CHEMKIN-PRO 15141. Reaction Design: San Diego.

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