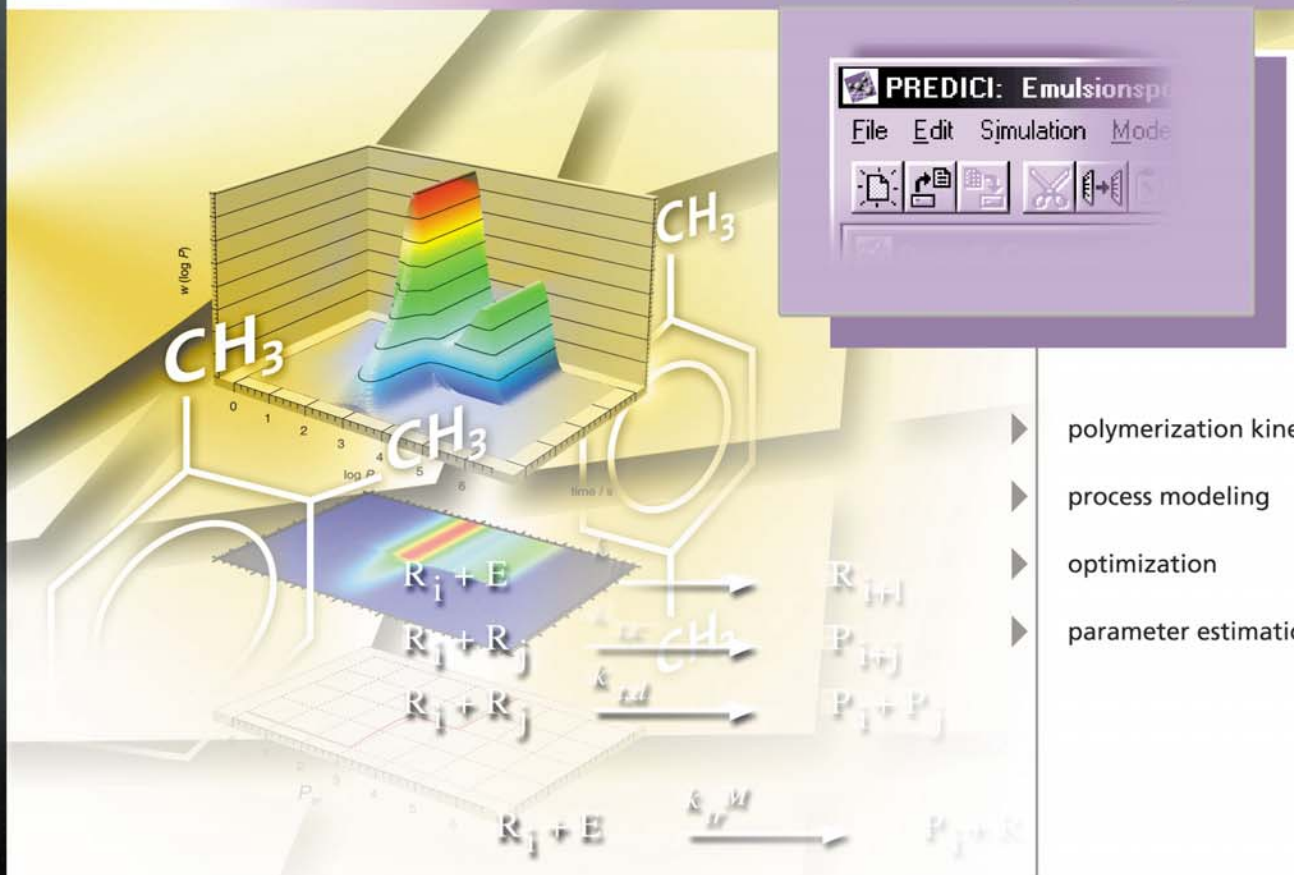
Computing in Technology

PREDICI

Dynamic Reactor Modeling

simulation program



- polymerization kinetics
- process modeling
- optimization
- parameter estimation

solutions for chemical engineering

CiT
Dr. M. Wulkow Computing in Technology GmbH

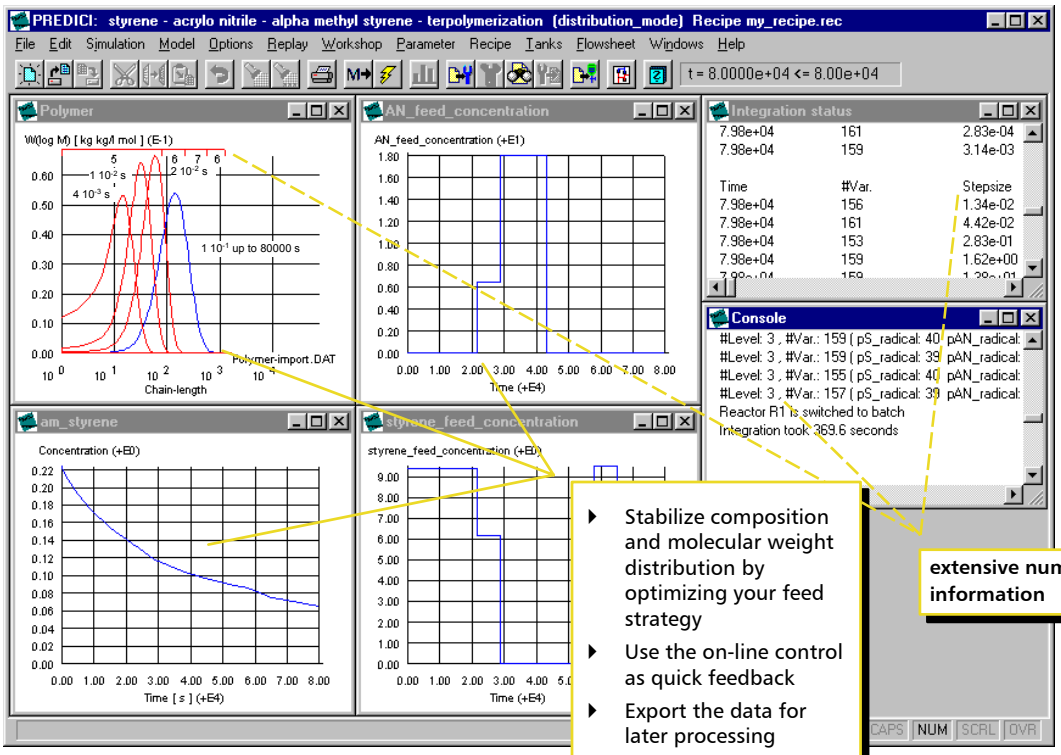
PREDICI

simulation program

Simulation

- unique numerical algorithms
- automatic pre-processing
- rigorous computation of MWDs
- on-line information
- direct interaction
- open data formats
- off-line capabilities

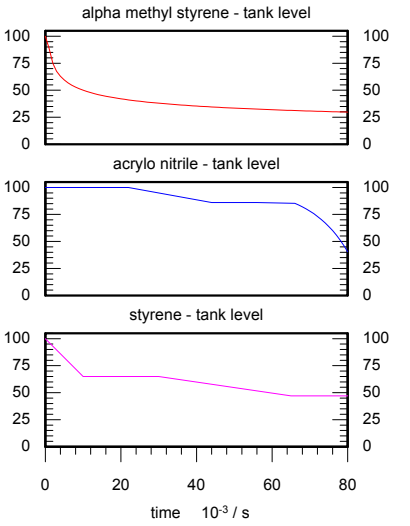
PREDICI is a sophisticated tool for modeling polymerization reactions setting benchmarks since 1992. High-end mathematical techniques are combined with a state-of-the-art user-interface. Within this framework the terminology of reactor, coefficient or species denomination is completely free to the user. All data may be plotted to graphical output windows during simulation. The output may be updated after each individual integration time-step. Furthermore, during simulation information about the actual chemical and numerical problem status is provided. The simulated data may be edited or modified during a run. The full run or parts of a simulation can be recorded for later examination.

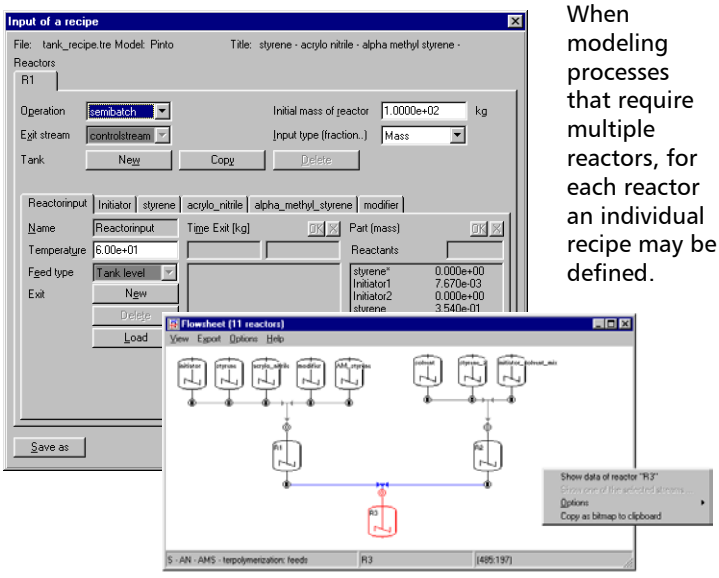


Control

- recipe concept
- flow visualization
- batch, feed-batch, CSTR, TUBE, complex operation modes

The definition of recipes allows an efficient control of feed streams and pre-set reaction mixtures. Flow recipes depict the operation procedure of continuously operated processes while tank recipes correspond to strategies of batch and feed-batch operation. Mass versus time profiles of individual components may be imported directly as ASCII data from your balance.

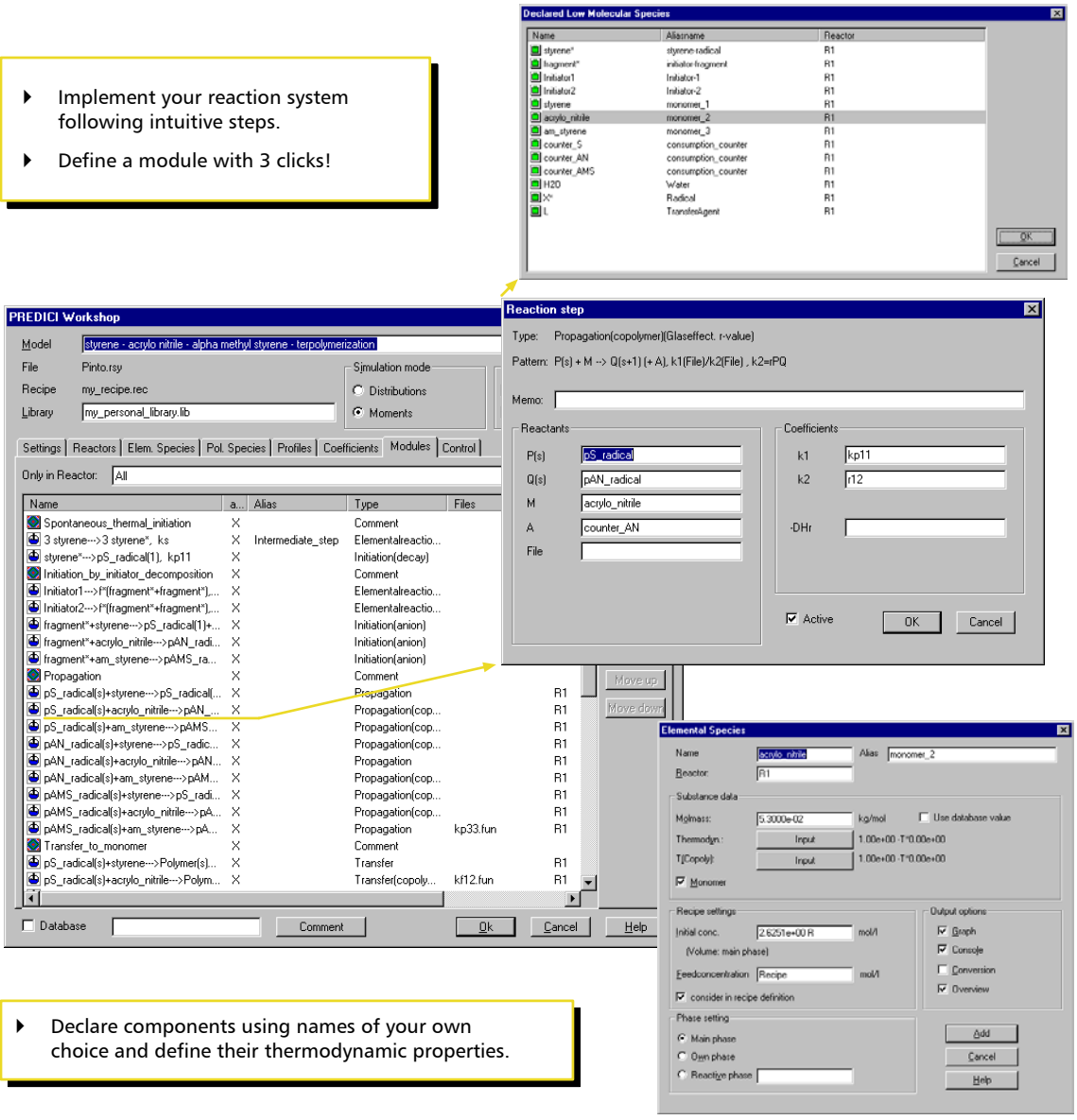




When modeling processes that require multiple reactors, for each reactor an individual recipe may be defined.

The design of a model is supported by a comfortable workshop. Five templates provide the facility for defining individual sub-components that are necessary to picture a process. They make use of a graphical user interface (GUI) as known from any other Windows application, here demonstrated for the definition of an elementary reaction step. General system specific data may be imported from databases.

- Implement your reaction system following intuitive steps.
- Define a module with 3 clicks!



- Declare components using names of your own choice and define their thermodynamic properties.

Reactors: An arbitrary number of reactors can be defined, each having individual characteristics such as: temperature(-profiles), pressure, volume, heat-balance, operation mode (batch, feed-batch, continuous flow, CSTR or tubular). A powerful phase concept enables the treatment of multiple phases for precipitation, suspensions and emulsions.

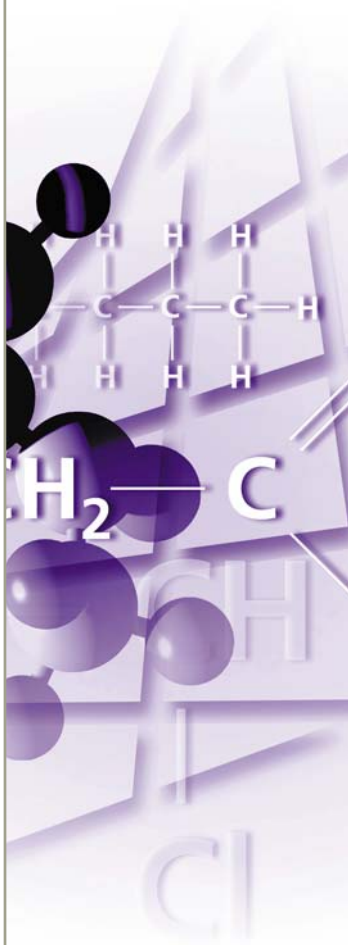
Coefficients: Rate coefficients and constants within a model may be defined as being temperature and pressure dependent following an Arrhenius term and being coupled to a certain reactor.

Reactants: Monomeric and polymeric species may be defined considering their thermodynamic properties, initial values of concentrations and distribution or feed-strategies.

Reaction steps: User defined combinations of elementary reaction patterns provide the potential for implementing almost any type of polymerization (free-radical, Ziegler-Natta, anionic, controlled, RAFT, ATR, poly-condensation, degradation, ...). They may be used in any combination and repetitively; additionally, there is no limitation with respect to their overall number.

Interface

- easy-to-use GUI
- flat dialog structure
- intuitive
- efficient



PREDICI

simulation program

Advanced Features

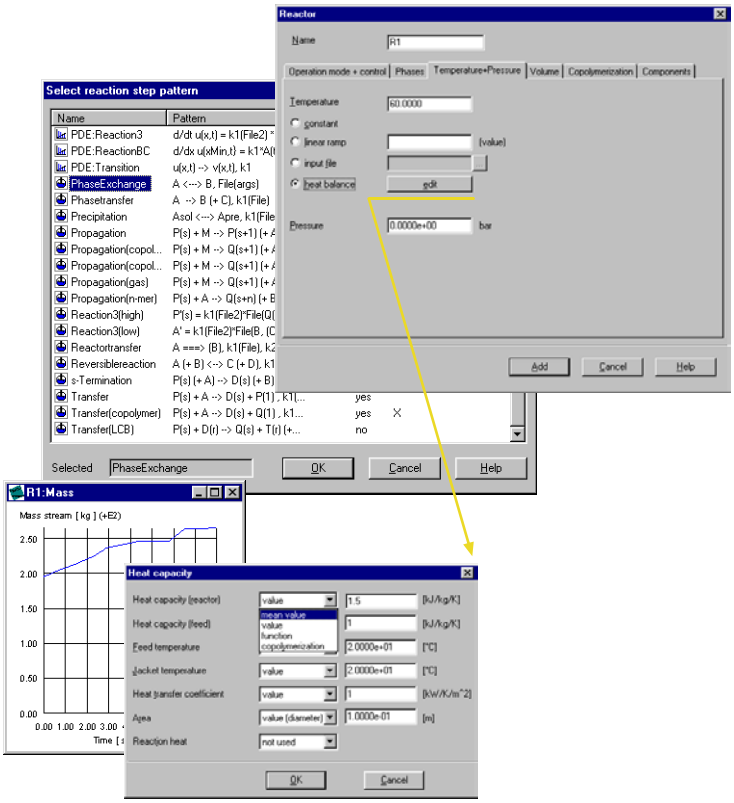
- interpreter
- library
- heat transfer
- thermodynamics
- multiple phase concepts

A flexible reactor concept provides stand-alone reactors or cascades. For each reactor the heat-balance and multiple phases may be defined. Special modules allow species exchange in-between the phases. Partial differential equations (PDE-modules) facilitate the implementation of spatial profiles, particle distributions or reactions in heterogeneous reaction mixtures.

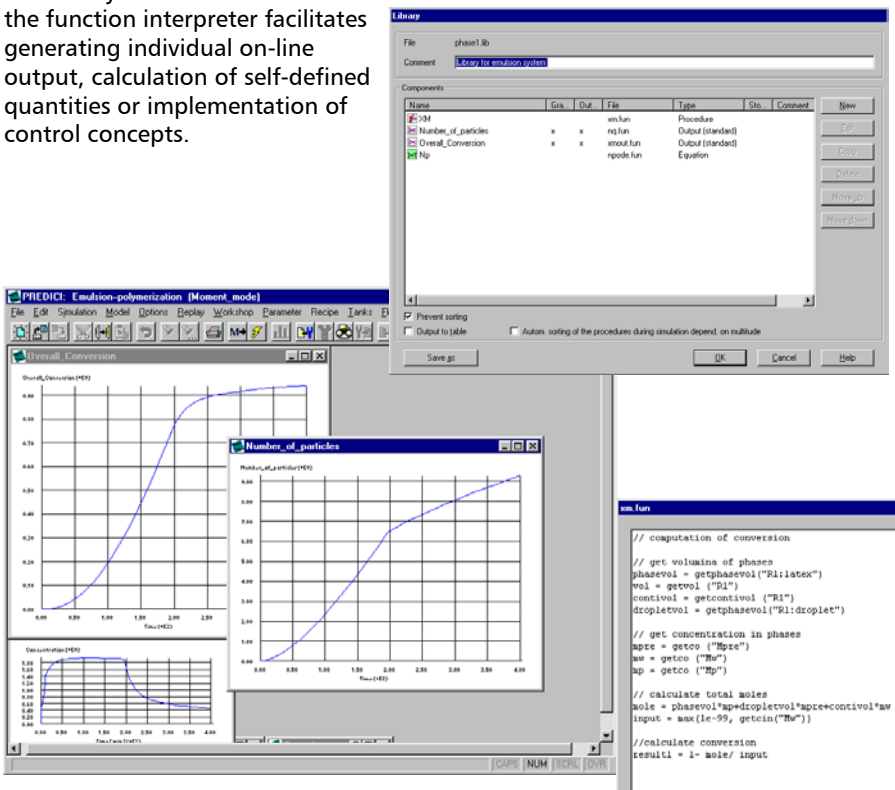
Using the integrated function interpreter arbitrary functionalities may be implemented for heat-balance, phase-exchange, particle-formation, -agglomeration or -degradation.

For special demands ordinary differential equations (ODE-modules) provide direct access and control e.g. to species, species distributions or balance variables.

Feed and exit streams may be controlled either directly, using the recipe or ODEs to conserve reactor volume.



The library in combination with the function interpreter facilitates generating individual on-line output, calculation of self-defined quantities or implementation of control concepts.

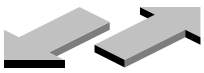


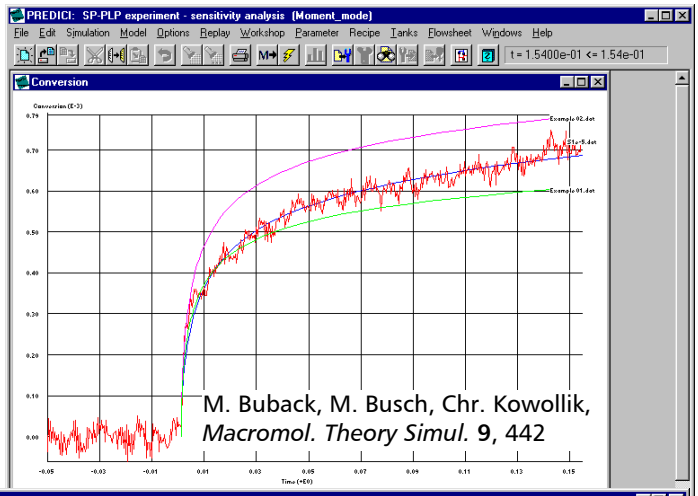
The syntax is intuitive and comparable to usual programming language. Subroutines may be used for structural implementation avoiding unnecessary and error-prone redoubling of code.

The OLE automation server facilitates parameter screening and sensitivity studies, controlled e.g. by Visual Basic or any alternative OLE client. Large data quantities may be processed following automated schemes.

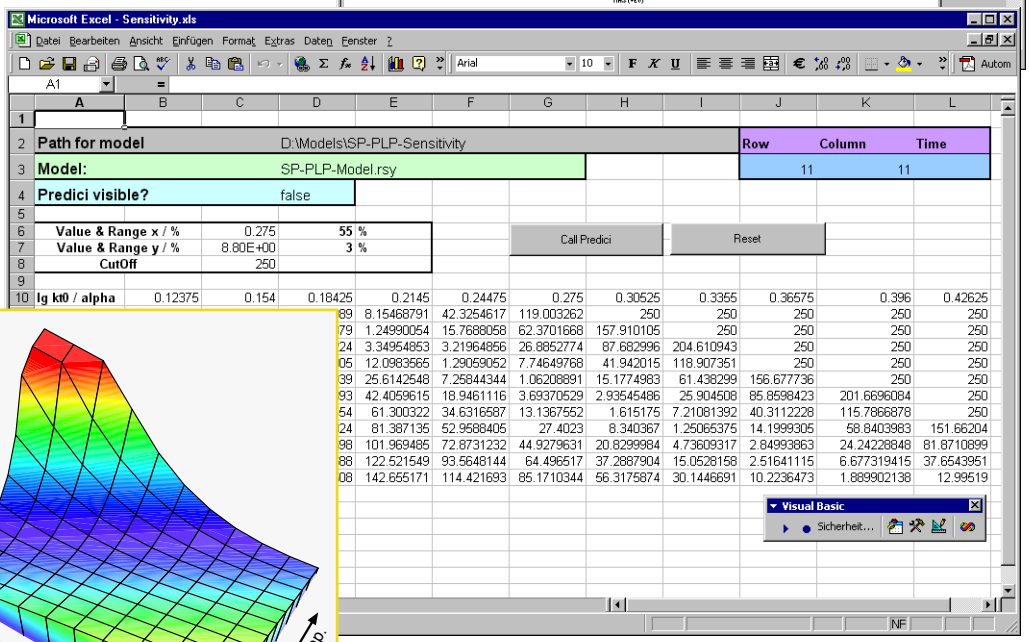
Example given here:

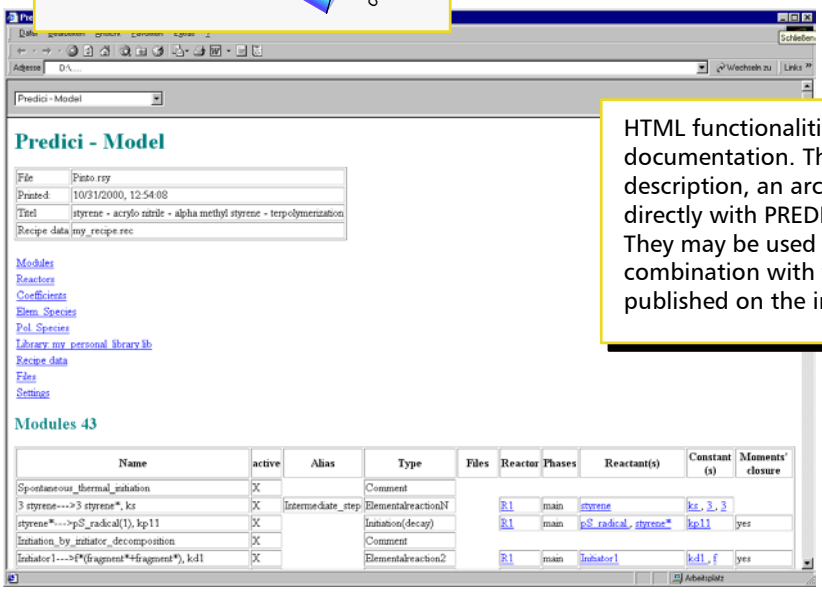
Analyzing the correlation of two model parameters and monitoring the sensitivity of the experimental sensor in single-pulse laser experiments when using kinetic models with chain-length dependent termination rate coefficients.





M. Buback, M. Busch, Chr. Kowollik, *Macromol. Theory Simul.* **9**, 442





HTML functionalities simplify documentation. The files include the model description, an archive that may be run directly with PREDICI and simulation results. They may be used either stand-alone, in combination with text processors or published on the inter- or intranet.

Connectibility

- open data formats for import / export
- batch automation
- OLE capability
- web-functionality

PREDICI

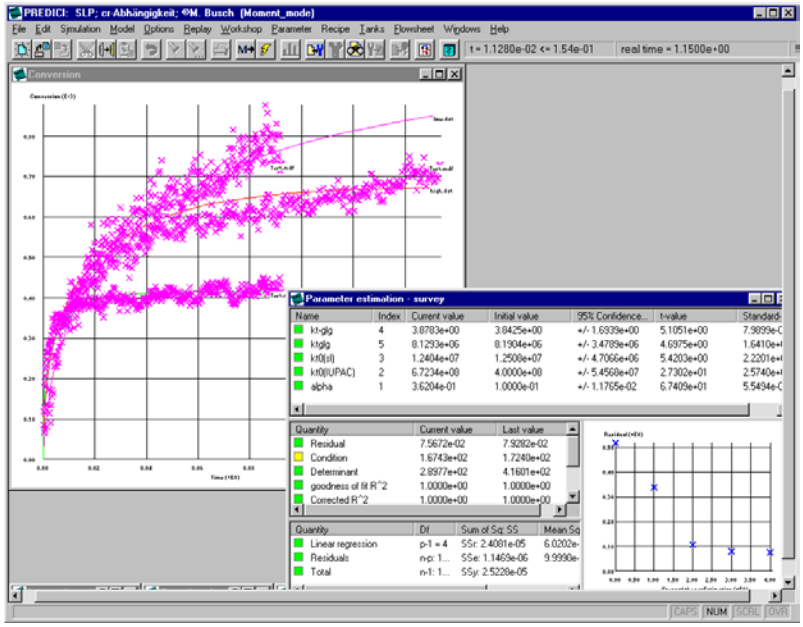
simulation program

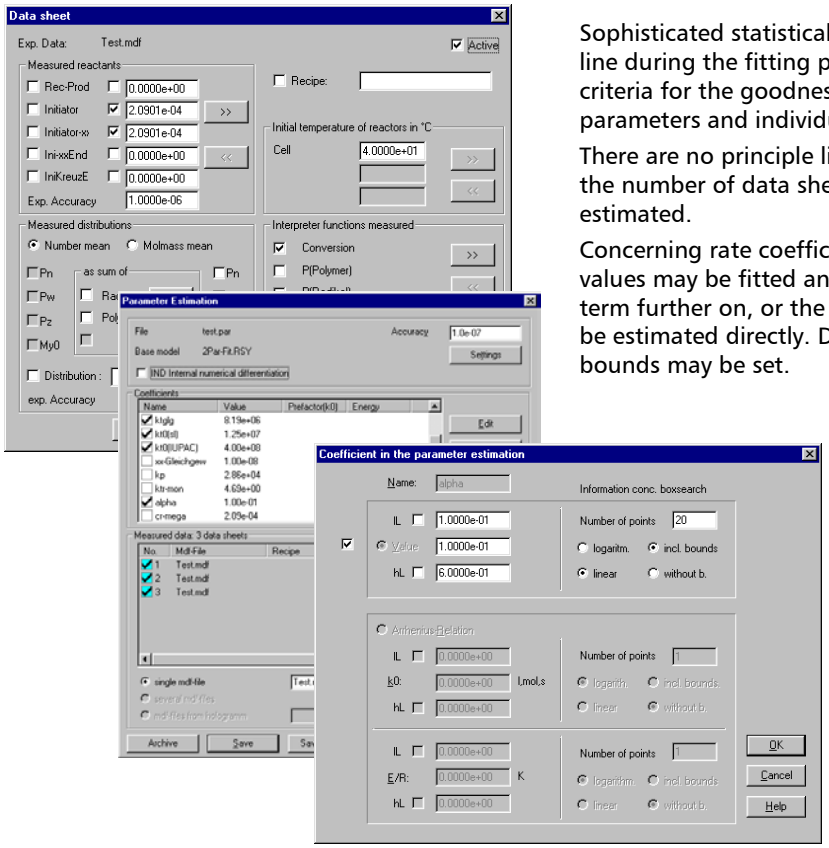
Parameter Estimation

- rate parameter
- Arrhenius estimation
- model parameter
- statistical information
- no sheet or data limitations
- value scaling
- value weighting
- free penalty functions

Rate coefficients and any other model parameters can be fitted by the parameter estimation tool. As sensors any species and system variable may act. Also quantities that are defined by the user via the function interpreter can be used.

An unlimited number of data sheets can be processed, each corresponding to an individual experiment having its own recipe, operation mode, temperature and feed profile.





Sophisticated statistical information is displayed on-line during the fitting procedure. Results providing criteria for the goodness of fit, correlation of parameters and individual sensitivity are available.

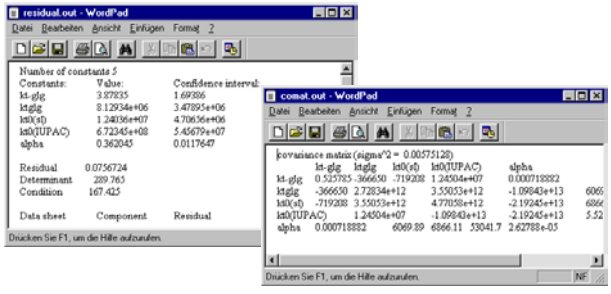
There are no principle limitations with respect to the number of data sheets or parameters to be estimated.

Concerning rate coefficients, either their absolute values may be fitted and evaluated as Arrhenius term further on, or the Arrhenius parameters may be estimated directly. During estimation limiting bounds may be set.

Quick sensitivity tests can be performed without changing the general setup of the estimation arrangement via activating or deactivating individual constants or data sheets.

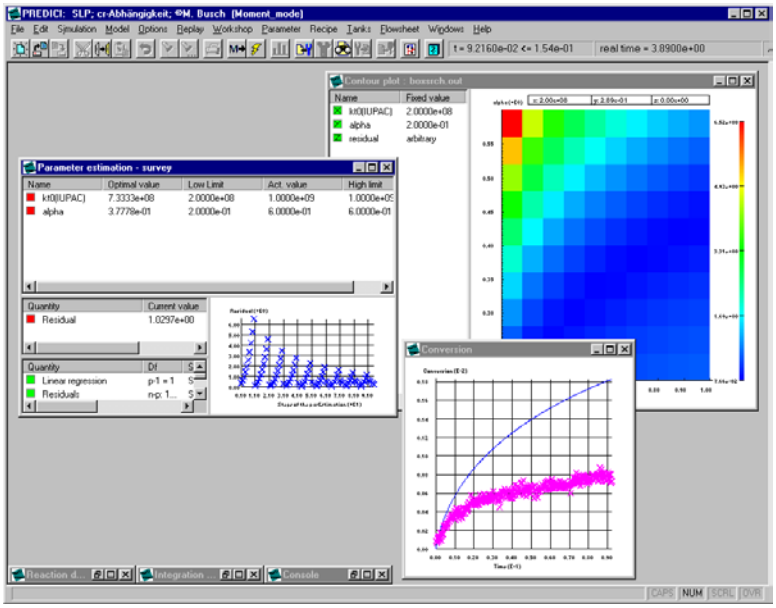
The full configuration incorporates the data collection, model and rate coefficients as well as scaling and weighting preferences together with penalty functions.

ASCII log-files provide a history of the fitting procedure for later inspection of the efficiency of the estimation process. All statistical information together with the course of parameter estimates are collected. Even detailed information about individual contributions of single compounds to the residual within each experiment is available.



Parameter Estimation

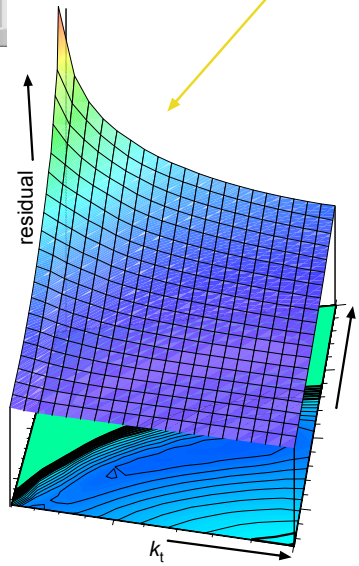
- box-search
- simulated annealing
- 3D-visualization
- Arrhenius plot



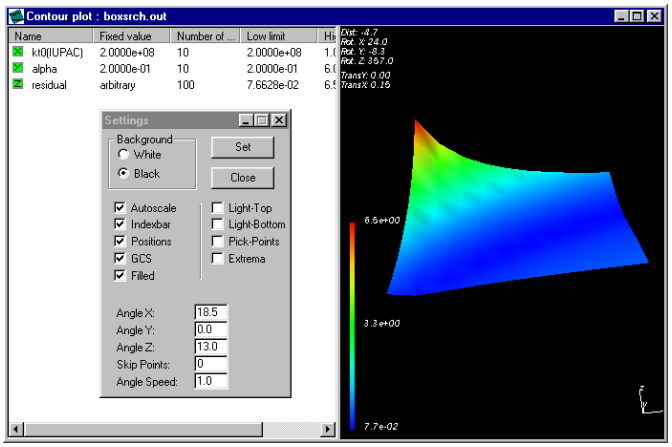
The box-search is the ideal tool for taking a first glance at a fitting problem and getting an idea about parameter sensitivities or correlations, leading to efficient initial values.

For the fitting of more than two parameters, the sensitivity of any of their combinations may be inspected using the internal contour plot function.

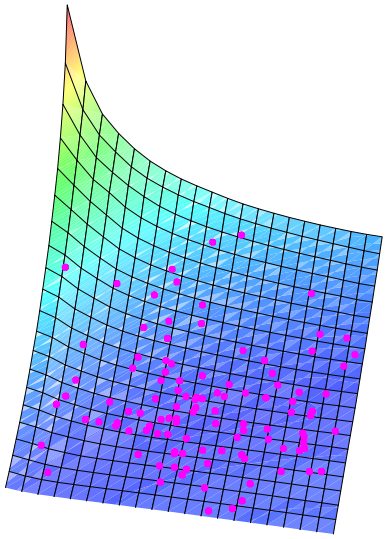
ASCII output files enable the processing and the visualization of data using other programs.



The integrated 3D OpenGL visualization helps to inspect sensitivity matrices and correlations of estimated parameters efficiently. The surface may be zoomed, shifted and rotated by any axis. It may be displayed as colored or shaded surface as well as transparent grid.



This feature is also available as stand-alone tool for the visualization of matrices.



In order to avoid laborious screening, a simulated annealing algorithm is implemented for a statistical search. The combination of gradient and random walk techniques assures finding identical solutions from varying initial conditions while concentrating computational efforts on the sensitivity area of interest.

The data are logged into ASCII files for later inspection and graphical representation by other sophisticated programs.

PREDICI

simulation program

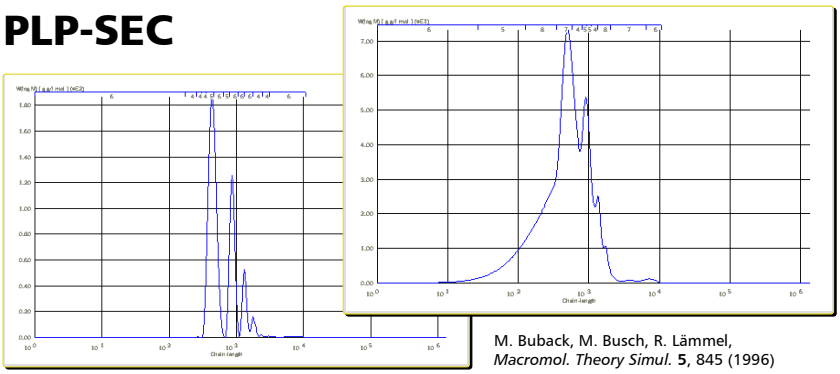
Examples

- kinetic experiments
- process description

Wide Ranged Applications - from Academia to Industry

From academic kinetic models such as used in pulsed-laser or single-pulse laser experiments over the description of catalytic or condensation processes up to the simulation of full industrial processes, e.g. the LDPE process, PREDICI provides its potential in modeling kinetics and polymer structural properties.

PLP-SEC

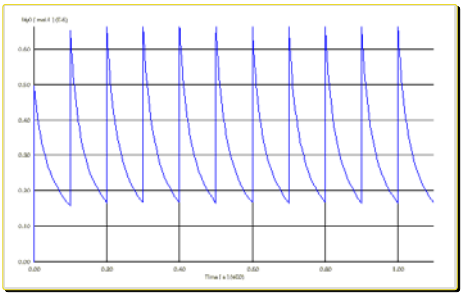


Include graphs into your documentation by simple copy and paste!

M. Buback, M. Busch, R. Lämmel, *Macromol. Theory Simul.* **5**, 845 (1996)

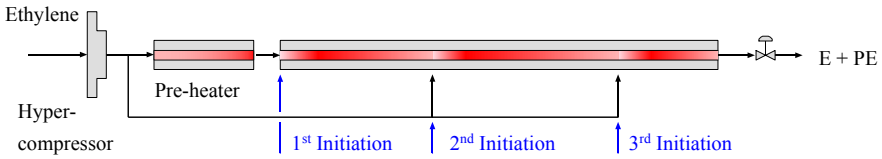
Modeling highly structured MWDs that result from PLP-SEC experiments puts special demands on adaptivity and error control of distribution species during numerical integration. These demands are met by the unique implementation of the h-p-method representing the state-of-the-art in self-adaptive treatment and error control for numerical integration. The algorithms are robust and provide problem oriented control mechanisms to optimize computational efficiency and results.

Discrete events can be introduced by external control of feed strategies, recipes and numerical integration.



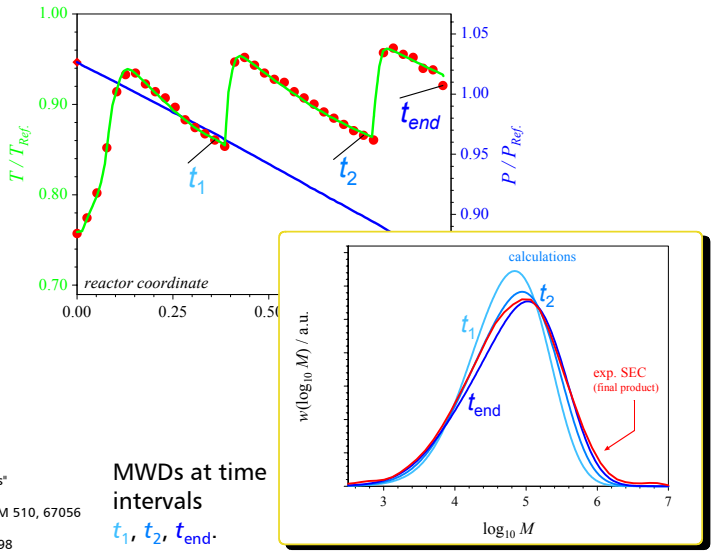
LDPE

basell Polyolefins



Basell and the Georg-August-University of Göttingen used PREDICI to simulate and improve the LUPO*TECH*® T Polyethylene Process.

The combination of LUPO*SIM*® T (which models the reaction engineering aspects of tubular LDPE reactors) with PREDICI allows the calculation of the dynamic evolution of MWD and branching structure during the course of synthesis along the reactor.



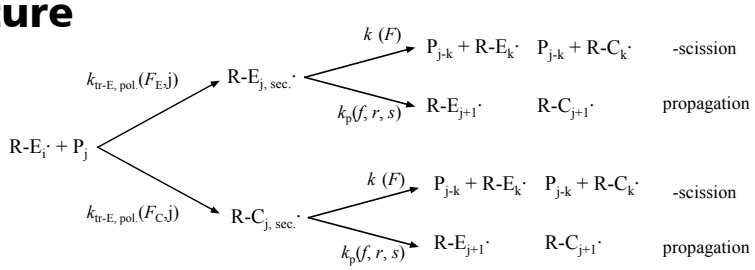
MWDs at time intervals t_1, t_2, t_{end}.

"Modeling of High Pressure Ethylene Polymerization in Tubular Reactors"
M. Buback, M. Busch
F.-O. Mähling, R. Klimesch (BASF AG, Kunststofflaboratorium, ZKP/NE, M 510, 67056 Ludwigshafen)
Macro98, World Polymer Congress, Gold Coast (Australia), 12.-17.7.1998

F.-O. Mähling, R. Klimesch, M. Schwibach, M. Buback, M. Busch, *Chem. Ing. Tech.* **71** (11), 1301 (1999)

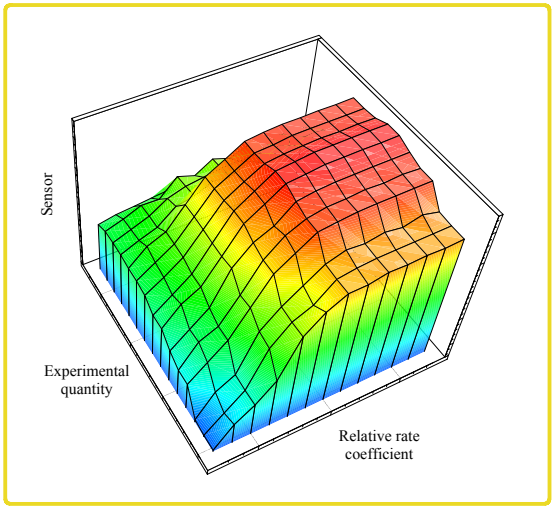
Copolymer Structure

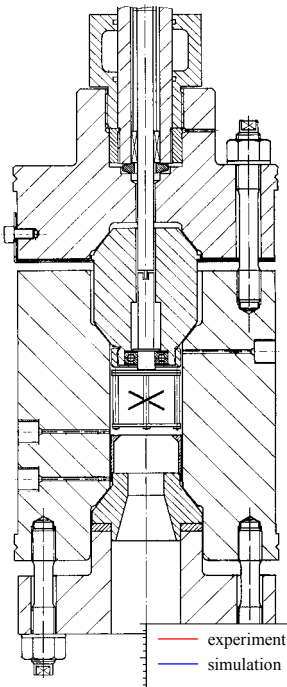
Copolymerization schemes require a large scale of elementary reaction steps considering several models for the calculation of the individual rate coefficients. Accounting for copolymer properties five distribution classes interact with each other by coupled kinetic processes.

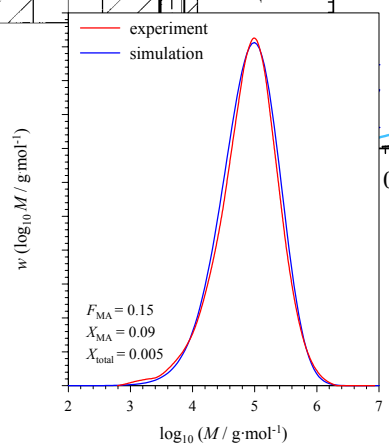


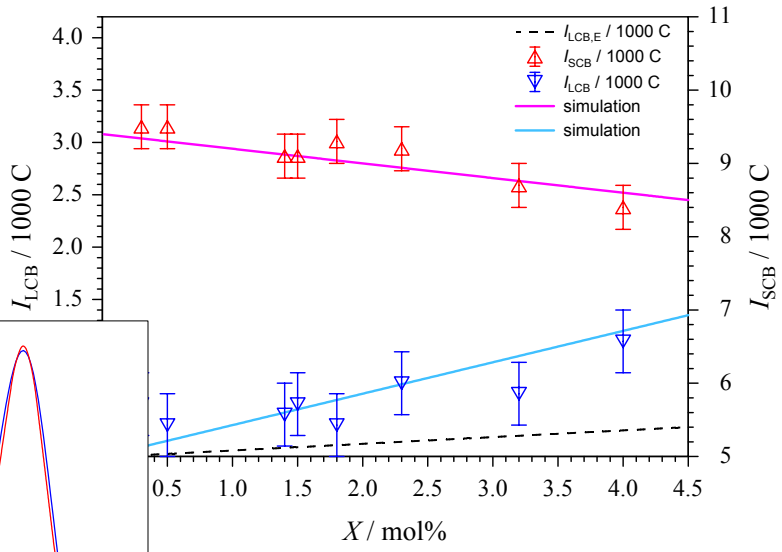
Experimental strategies for determining the required rate coefficients may be developed and tested using models by performing sensitivity studies.

M. H. C. M. van Boxtel, M. Busch, *Macromol. Theory Simul.* **10**, 25 (2001)
M. Busch, *Macromol. Theory Simul.* **10**, 408 (2001)









A large scale of functionalities assist during development of model and analysis of data, as there are:

- the copolymerization assistant for design of basic models
- balance counter for analyzing composition and sequences
- implicit calculation of copolymer composition, weight and density

Examples

- sensitivity analysis
- experimental design

PREDICI

simulation program

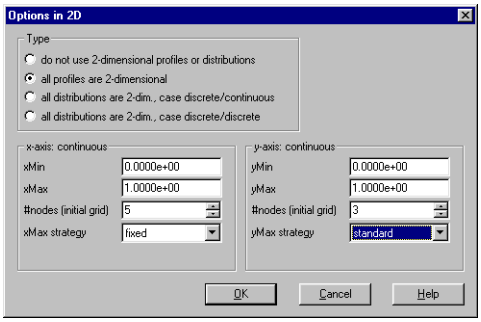
Partial differential equations

- spatial gradients
- species profiles
- dynamic computation
- 2D-problems

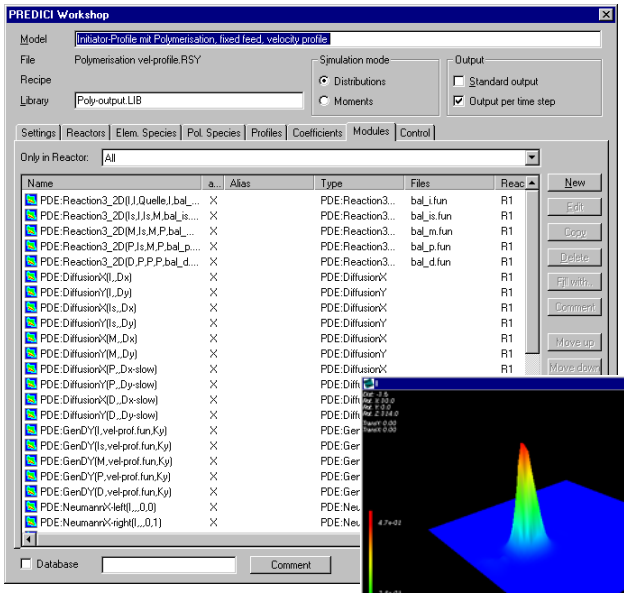
PREDICI is not only a very efficient tool for modeling polymerization systems, but includes a leading solver for systems of partial-differential equations.

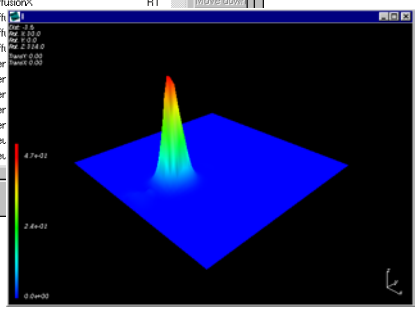
Numerous modules for a general description of convection, transport, diffusion, dispersion, boundary conditions, agglomeration and arbitrary kinetic reactions allow an easy transfer of kinetic schemes to distributed variables (e.g. axial or radial coordinates in a non-stationary tubular reactor, mixing problems, general PDE's). Parameters and coefficients of these processes can be formulated as spatial dependent.

The Galerkin h-p-algorithm works full self-adaptively, all discretizations are error-controlled. The drawbacks of other solvers (poor error control, missing adaptivity, large number of approximating variables, restriction to local operators, method-of-lines approach), are avoided and overcome in PREDICI. A series of challenging problems could be solved with this tool in a unique way. Even free boundary problems (e.g. single particle models) can easily be solved in PREDICI using these powerful features.



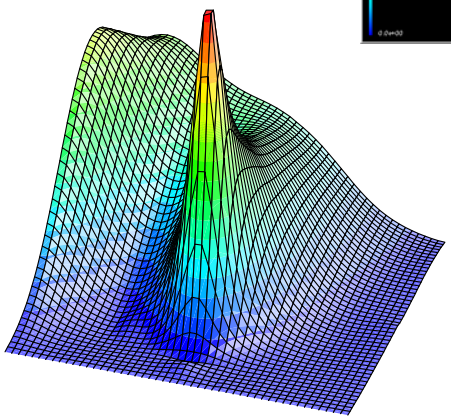
As a special extension features for treating 2D-problems are available. By this 2 continuous axis, 2 discrete or a combination of discrete and continuous axis can be introduced into simulation models.



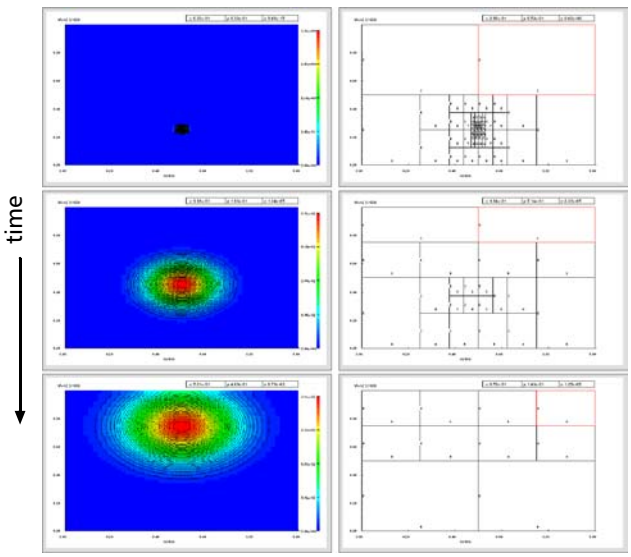


The example shows this for the dynamic 2D-computation of a tracer pulse. Note the unique free 2D-adaptivity of the grid!

The dynamic changes of concentration profiles are displayed on-line as 3D-openGL graph or contour plot.



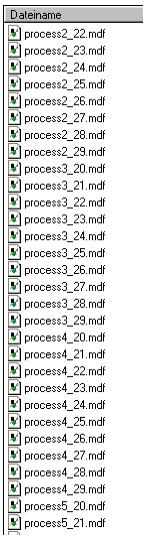
Considering ODEs for the reaction of species, the complex interactions of reaction and species transport can be illustrated.



Dr. M. Wulkow Computing in Technology GmbH

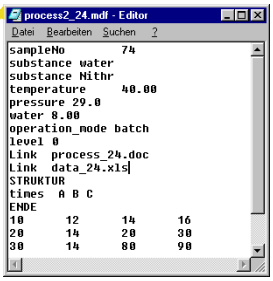
Data Hologram

- free label and group definition
- object oriented data classification
- application bounded links for files
- export file selection to PREDICI



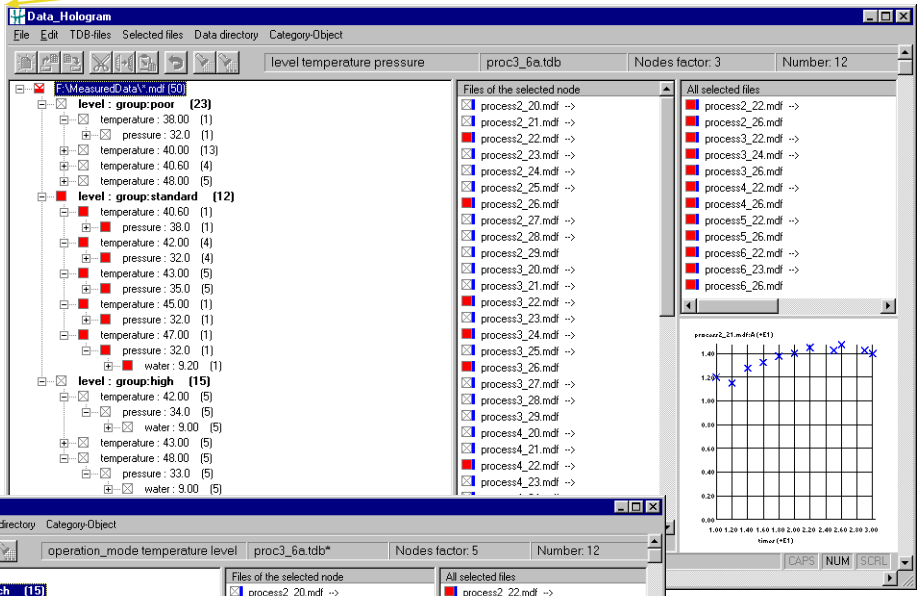
Initial situation:

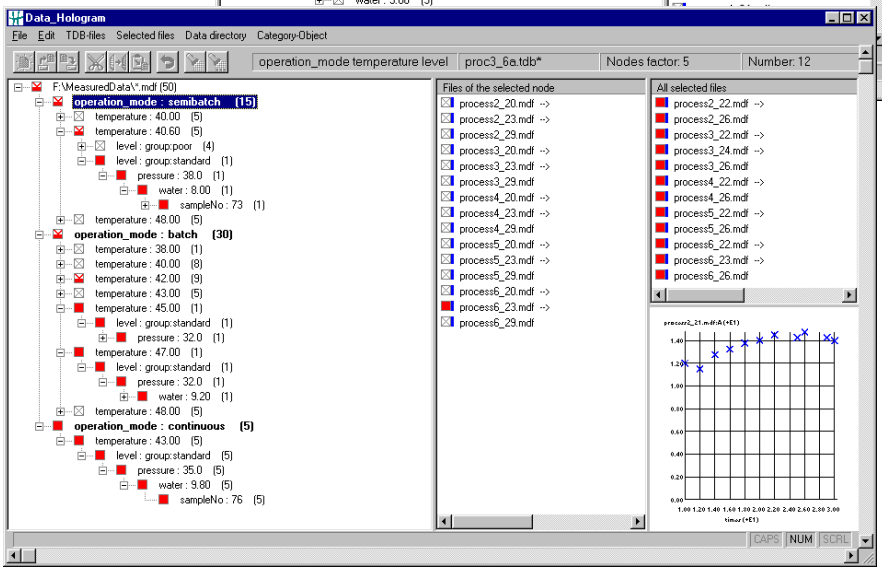
Unstructured collection consisting of individual data files with inhomogeneous content ...



Organization using the hologram:

User defined labels in arbitrary order describe the content of the data file and build the basic structure that has to be followed ...





... collect labels and data ranges to groups of your own choice and parse them hierarchically to find the data sets of your interest ...

- multi-dimensional overview of extended file collections for experimental data
- hierarchical structurization follows flexible differing aspects of interest
- labels for structurization are based on the individual files content
- user-defined labels that describe numerical data, abstract meanings, ranges of subjects
- user defined filters
- summarizing labels or numerical data in self-defined groups
- (easy) automatic scanning of labels
- export file selection to PREDICI for parameter estimation procedures

PREDICI

simulation program

Further Tools

Of course, any kinetic system (also given as pure equation system) can be simulated using PREDICI. And there are more products of CiT that feature the same outstanding mathematical methods, focusing on other specialized aspects.

Presto: reaction step patterns for general kinetics, phase transfer, feed, exit, flow
treatment of partial differential equations, convection, diffusion, kinetic reaction, boundary conditions
project management integrating different reaction conditions and kinetic approaches
parameter estimation designed for a large number of experiments
data administration: handling of experimental data by an easy-to-use tree structure

Parsival: rigorous treatment of particle size distributions in heterogeneous process units (e.g. crystallization)
reaction step patterns for particle growth, nucleation, agglomeration, breakage, fine's dissolution, convection, diffusion, boundary conditions, kinetic reactions
flow sheets with classified flow and exit
parameter estimation

Rioval: management tool for water quality modeling in streams
interface for the description of rivers and input from treatment plants
simulation based on a comprehensive and well-tested biofilm model

References

The products of CiT are used worldwide in academia and industry.
On your request it will be a pleasure for us providing a comprehensive list of reference customers and projects.

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Version 5.03.05