

Computer Aided Process Engineering For Process Integration And Design

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Abstract

By definition Computer Aided Process Engineering (CAPE) refers to computer aided methods, algorithms, and techniques related to process and product engineering. This contribution aims at describing some achievements of the research conducted in this area by the Computer Aided Process Engineering Center (CAPEC) at the Department of Chemical Engineering, Technical University of Denmark. The emphasis will be on describing some of the methods and tools developed in the areas of property prediction, computer aided molecular design, process synthesis/design and process integration. The application of some of the presented tools are demonstrated on an industrial case study.

Introduction

The research in CAPEC is divided into seven research programs according to Figure 1, where fundamental research is located at the inner most level and applied research is located at the outer most level. In the intermediate levels, methods and tools for applied research are developed, based on the results from the inner level.

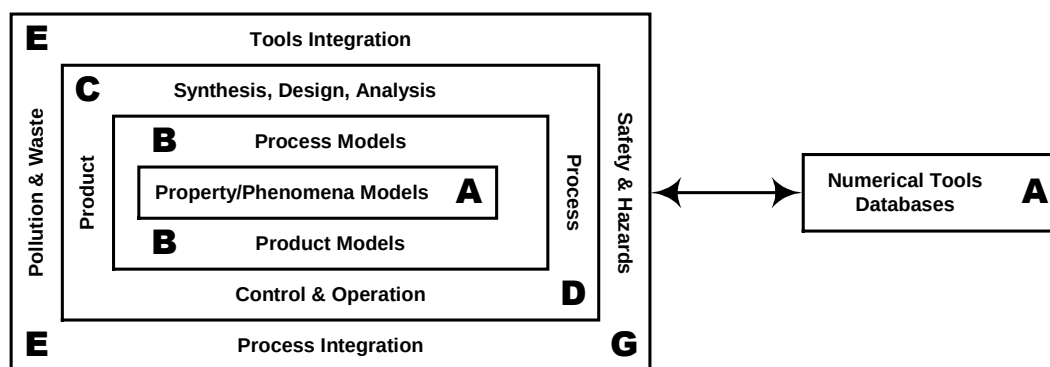


Figure 1: Research structure of CAPEC

Research program A deals with modeling of properties (phenomena), while program B deals with modeling and identification of processes, operations and phenomena not covered in research program A. Based on the models from research programs A and B; algorithms, methods and computer-aided tools for synthesis, design and analysis of

processes, products and operations (research program C) are developed. Simultaneously, the developed models provide the basis for research in process operation and control (research program D). The results from research programs A-D provide the foundation for research programs E (process and tools integration) and G (safety and hazards). Since all research programs need numerical tools and databases, research program F supplies this need to all levels. Based on the above outlined description, the research objectives of CAPEC can be summarized as:

Develop computer-aided systems for process simulation, process/product design and analysis, control/operation principally suitable for chemical, petrochemical, pharmaceutical and biochemical industries. The computer aided systems are to be developed based on fundamental modeling studies that incorporate correlation and estimation of thermo-physical and phase equilibrium properties as well as modeling the underlying principles/behavior of the process.

The emphasis of this paper will be upon property prediction, computer aided molecular design, process synthesis/design and process integration, while Andersen and Eden (2000) cover the areas of computer aided modeling, control structure design, and operability analysis.

Property Prediction

The backbone of CAPEC's process synthesis, design and simulation methodologies is the ability to accurately predict properties for which no or limited experimental data is available. Primarily the methods used are group contribution based, i.e. the property value is determined from structural information. As an alternative to the purely group contribution based approach, methods based on combined group contribution and interaction have been investigated. Based on the work by Constantinou & Gani (1994), a new combined method for estimation of pure component properties has been developed. In addition to the conventional first and second order terms, this new method utilizes a group interaction term and a third order term. With this method, the following properties can now be estimated, normal boiling points, critical constants, standard enthalpy of formation, standard enthalpy of vaporization, standard Gibbs energy and the standard enthalpy of fusion with significant improvement in prediction accuracy and application range.

These methods and algorithms form the basis for a series of computer aided tools, which have been integrated in a program package called ICAS (Integrated Computer Aided System). Equilibrium data for binary and ternary mixtures have been collected in a database, which can be used for developing new models or verifying the prediction accuracy for existing models using the Group Contribution Method Development (GCMetDev) tool. Furthermore, a library of thermodynamic models (TML), which also serves as a parameter estimation tool, has been developed. Since a large number of property estimation methods are available, it can be difficult to identify the most appropriate method for a specific problem, thus a Thermodynamic Model Selection (TMS) tool has been developed. If necessary the properties of new compounds can be generated and stored in the property database using the Property Prediction (ProPred) tool, which includes a wide range of methods and properties. It utilizes a graphical representation approach, where the user simply draws the

compound structure and then the properties are calculated. A screenshot from ProPred is presented in Figure 2.

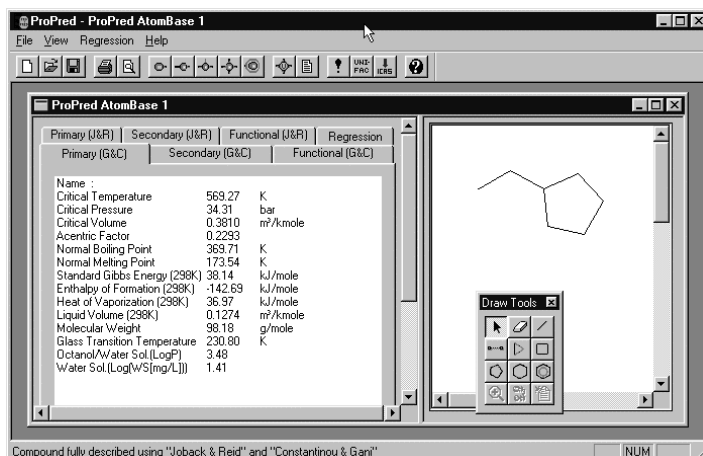


Figure 2: Property Prediction Tool (ProPred.)

When synthesizing a separation process flowsheet the ability to predict the mixture properties accurately is of great importance. Especially when investigating solvent based separations or electrolyte systems. Mixture properties are traditionally calculated using group contribution methods, equations of state, G^E -models or some combination of these. The UNIFAC method (Fredenslund *et al.*, 1977) has proven to be a fast and reasonably reliable method for prediction of liquid-phase activity coefficients. Further development of this approach in order to overcome its limitations is of great interest. The applicability and robustness of UNIFAC relies primarily on the availability and accuracy of group volume parameters, group surface areas, and the group interaction parameters. Thus a lot of effort is devoted to updating and extending existing parameter tables, while simultaneously developing a novel group contribution method, which hopefully will replace the current approaches. Based on the particular problem characteristics, the appropriate mixing rule expression will be derived and the necessary parameters estimated. In this way, given the problem description, the most suitable property model can be generated and implemented for the solution of a specified process simulation and/or design problem. Once the appropriate models have been identified for a given mixture, the Process Design Studio (PDS) can calculate the phase diagrams, azeotropic points, residue curves and distillation boundaries (see Figure 3).

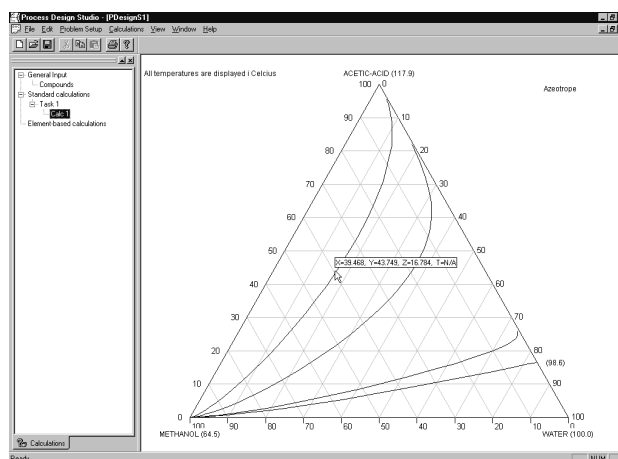


Figure 3: Process Design Studio (PDS)

Computer Aided Molecular Design

The use of Computer Aided Molecular Design (CAMD) for the identification of compounds having specific physical and chemical properties has received substantial attention from the scientific and industrial communities in recent years. CAMD can be described as “Inverse Property Prediction”, since the concept is to find component structures, which results in a desired set of property values. The CAMD methodology developed (Harper 2000) is a three-step procedure consisting of computer aided steps for problem formulation (pre-design step), compound identification (design step) and result analysis (post-design step). The methodology outlined below has been incorporated in a computer aided tool for solvent design/substitution called ProCAMD.

Pre-design Step

The goal of using CAMD techniques is to identify compounds capable of performing a specific task or a series of tasks. This is achieved by generating compounds matching a set of specifications with respect to compound type, physical and chemical properties. In order to identify compounds that are able to perform the needed tasks it is important that the desired properties match the types important for the intended use. The formulation of the design specifications is performed in a computer aided pre-design step, where the problem is *identified* and the design goals (desired compound types and properties) are *formulated* in order to provide input to the applied method of solution for compound identification.

CAMD Design Step

The employed CAMD solution method is a hybrid of generate and test type, where all feasible molecules are generated from a set of building blocks and subsequently tested against the design specifications. In order to avoid the so-called combinatorial explosion problem, the multi-level approach of Harper (2000) is employed, where successive steps of generation and screening against the design criteria ensures that the level of molecular detail is increased only for the most promising candidates.

Post-Design Step

In the post-design step, the answers from the solution procedure are *analyzed* with respect to properties and behavior that could not be part of the design considerations. Examples of such properties are price, availability, legislative restrictions and process wide performance. This step involves using other prediction methods, database sources, engineering insights and if possible simulation in order to obtain an overview of the suitability and capability of the designed compound(s) for the particular purpose.

Process Synthesis and Design

A three-stage algorithm has been developed for determining the optimal process flow-sheet. In the first stage (problem formulation stage), the different process alternatives are identified together with selection/design of solvents and materials. Driving force based separation efficiency curves (Bek-Pedersen, Gani and Levaux (2000)), together with an algorithm for integration of synthesis and design (Hostrup *et al.* 1999) are used in this stage. If any process alternative requires the use of solvents, they are designed (determined) through Computer Aided Molecular Design (Harper 2000). In the second stage (superstructure generation and initial feasible flowsheet), the identified process

alternatives are screened through the use of driving force based separation efficiency curves (where applicable) and analysis of mixture properties. The reduced set of feasible process alternatives is represented through a superstructure and an initial feasible flowsheet is generated. The results from the second stage form the basis for the mathematical formulation and solution of the structural optimization problem. For solving the structural optimization problem an interactive MINLP solver is employed. In the interactive MINLP, the ICAS (CAPEC 2000) simulation engine is used to solve the inner-loop NLP sub-problem and a MILP solver is employed to solve the outer-loop master problem. The user, therefore, does not need to supply the process model equations and rigorous process models may be used for any problem. The problem formulation step also helps to eliminate alternatives and thereby reduce the size of the final MINLP problem. In this way, large and complex process synthesis problems can be solved since the number of alternatives is not too large and the process models are available through the process simulator. The developed three-stage algorithm has been tested through a case study involving the production of cyclohexane, (Bek-Pedersen, Hostrup and Gani (2000)).

Process Integration

As the trend within process design leans more and more towards the use of process integration in order to minimize utility usage and environmental impacts the need for systematic tools is apparent. In many process plants large amounts of energy is consumed for removal of small impurities in the terminal streams. Mass integration (El-Halwagi 1997) has proven to be a valuable tool when designing new processes or optimizing existing processes. To introduce the principles of mass integration, a case study is presented which also demonstrates the use of most of the computer aided tools presented in the previous sections.

Case Study: Removal of Aniline from Water

During the production of a pharmaceutical product aniline is produced in relatively high quantities. The task for downstream processing is to reduce the aniline content in the aqueous product phase from 28000 ppm to 2 ppm. The primary objective of this investigation is to identify a more efficient separation method than the conventional approach of single stage distillation, which actually only can reduce the aniline content to approximately 500 ppm. It was decided to investigate the possible usage of liquid-liquid extraction as an alternative unit operation. The primary requirement for using liquid-liquid extraction is that a suitable solvent can be identified. First a simple database search is conducted to identify possible solvents based on collections of experimental data, e.g. DIPPR, followed by the formulation and solution of a CAMD problem. To be able to conduct an efficient solvent search it is important to identify the desired properties of the solvent. Using the CAPEC database the following results were obtained for aniline and water respectively:

Property	Aniline	Water
CAS No.	62-53-3	7732-18-5
Boiling Point (K)	457.15	373.15
Solubility Parameter (MPa ^{1/2})	24.12	47.81

Table 1: Pure component data for aniline and water.

The following primary requirements for a suitable solvent can be stated:

- 1) Immiscible with water.
- 2) No azeotropes between the solvent and aniline and/or water.
- 3) Solubility parameter has to be less than or equal to $24 \text{ MPa}^{1/2}$.
- 4) High selectivity with respect to aniline.
- 5) Minimal solvent loss to the water.
- 6) Reasonable difference in boiling points for the solvent and aniline to ensure regeneration of the solvent.

To ensure that the identified compounds are relatively simple and safe, the following groups are omitted from the search space:

- Phenols, amines and amides.
- Compounds containing double and triple bonds.
- Compounds containing silicon, fluorine, chlorine, bromine, iodine and sulfur.
- Polyfunctional compounds.

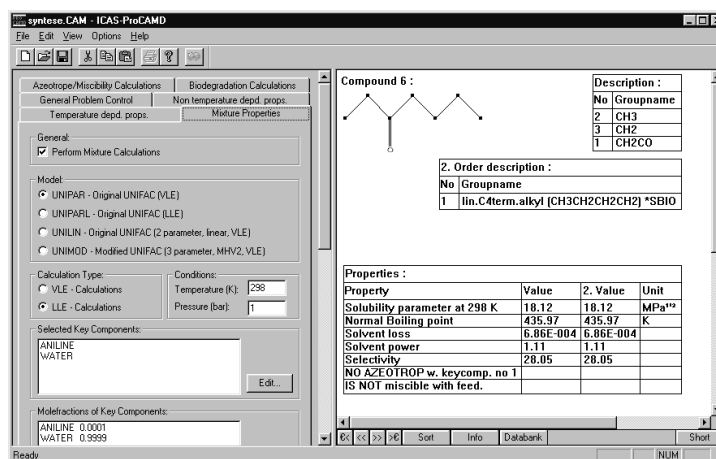


Figure 4: Screenshot from ProCAMD.

Using these criteria no suitable solvent, which is heavier than aniline, could be identified. It would be preferable that aniline was the lightest component, perhaps along with water, since very small amounts of aniline is present in the solution. However this was not possible, hence a similar search was conducted for solvents with a boiling point lower than the boiling point of aniline. In the search for solvents with a lower boiling point than aniline a series of candidates were identified. The most promising candidates are presented in the table below.

Solvent	CAS No.
n-Octane	111-65-9
2-Heptanone	110-43-0
4-Heptanone	123-19-3

Table 2: Suitable solvents.

For those compounds it was found that any isomers as well as side chains also might be used. However in the following investigation only the three compounds listed in Table 2

are considered. A screenshot from ProCAMD is presented in Figure 4 illustrating the results of this investigation.

Process Simulation

For validation of the designed solvents a commercially available process simulator, Pro/2 5.01 (Simulation Sciences 1996) is used. It is determined, that it is not possible to do the liquid-liquid extraction on a single stage without using excessively large amounts of solvent. Thus the liquid-liquid extraction is conducted in a multistage countercurrent column after which the solvent is recovered using simple distillation.

The results of the rigorous simulations are presented in Table 3. In all simulations the following specifications have been given:

1. The amount of solvent to use is determined by specifying a final concentration of aniline in the water phase of maximum 2 ppm.
2. Highest possible purity of aniline during solvent recovery.
3. In the extraction column 15 stages are used, while the distillation column is fitted with 25 stages.

Design Parameter	n-Octane	2-Heptanone	4-Heptanone
Solvent amount (mole)	2488.8	1874.0	1873.5
Solvent in water phase (ppm)	1	429	429
Aniline product purity (weight%)	100.00	100.00	100.00
Recovery of aniline (%)	100.00	99.95	99.99
Solvent loss (% on a mole basis)	0.00098	8.60	8.60
Energy usage for solvent recovery	2.223	2.245	2.009

Table 3: Simulation results.

From this table it is apparent that all three solvents are very suitable for extraction of aniline from water and can all meet the requirement of maximum 2 ppm aniline in the water phase. However some differences have to be discussed. There are large differences between the solvents with respect to solvents loss to the water phase, which needs to be taken into account in an environmental assessment. Based on the criteria under which the solvent search and validation was performed, n-Octane seems to be the best solvent. Furthermore the question of cost needs to be addressed, which is presented in the following section.

Cost Estimation

Using the URL <http://www.chemfinder.com> a rough estimate on the prices of chemicals can be determined.

Solvent	Amount	Bulk amount	Cost of bulk amount	Number	Total cost
n-Octane	402.6 l	2.50 l	\$123.12	162	\$19945.44
2-Heptanone	214.0 kg	14.5 kg	\$323.25	15	\$4848.75
4-Heptanone	213.9 kg	15.0 kg	\$614.47	15	\$9217.05

Table 4: Estimated solvent cost.

All the prices given in Table 4 are based on 99% purity of the solvent. It is obvious that the excellent performance of n-Octane comes at a cost. Furthermore it is clear that the additional cost of 4-Heptanone compared to 2-Heptanone is not justified since the difference in performance is negligible.

Process Integration Tool

The above outlined problem is in fact a very simple mass integration problem. It was solved using qualitative process knowledge in an integrated framework, ICAS (CAPEC 2000). Since the problem was a single unit operation running isothermally the complexity was very limited. For larger problems involving multiple units, streams and components heat integration must also be taken into account to ensure an economically optimal design. To meet these ends a combined mass and energy integration tool, ProInt (Eden 2000), within the ICAS program package is under development. Such a tool will provide a methodology for solving mass and energy integration problems in an integrated computer aided environment.

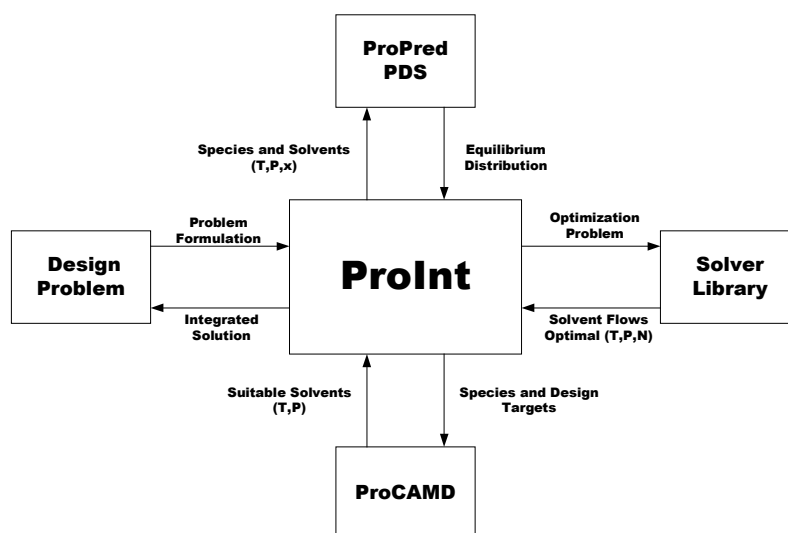


Figure 5: Structure of process integration tool.

Identifying suitable solvents is at the heart of any mass integration problem. There is a need for an integrated approach for the screening and selection of the solvents or Mass Separating Agents (MSA's), which can be accomplished by close integration with a computer aided molecular design tool, ProCAMD (Harper 2000). For the mathematical modeling of the mass exchange processes, knowledge of the equilibrium distributions of the species and the MSA's is imperative, especially when synthesizing mass and energy integration networks, accurate and wider ranging relationships are called for. This can be achieved by integration with a pure component property prediction tool, ProPred, as well as process design and analysis tools, PDS (CAPEC 2000). When synthesizing a combined mass and energy integration problem the solution often has to be found using mathematical programming (MINLP). This is even more true when allowing the use of reactive MSA's. Hence the wide range of solvers available in the ICAS library will be of great assistance.

Finally, the integrated designs should subsequently be validated using rigorous simulation, which can be accomplished using the ICAS simulation or other commercially available software.

Conclusions

An overview of the research efforts of the Computer Aided Process Engineering Center (CAPEC) has been presented. Emphasis has been upon property prediction, computer aided molecular design and process synthesis/design with purpose of describing how these methods and tools can be used for solving process integration problems. A simple mass integration problem was presented as a case study and solved in an integrated framework illustrating the need for a systematic process integration tool. Systematic tools for energy integration have been available for some time and to some small extent also for mass integration. However, no tools are available for synthesizing combined mass and energy integration networks. An integrated tool is needed to provide a systematic solution without relying on “rules of thumb” or qualitative process knowledge. To meet these ends a combined mass and energy integration tool (ProInt) is under development. The structure of this tool and the integration with existing tools within the ICAS program package has been presented.

Acknowledgements

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